Advances in Organic Geochemistry 1987
Org. Geochem. Vol. 13, Nos 4–6, pp. 607–617, 1988
Printed in Great Britain.

0146-6380/88 $3.00 + 0.00

Biogeochemistry of lipids in surface sediments of the Peru Upwelling Area at 15°S

JOHN W. FARRINGTON[1,4]*, ALAN C. DAVIS[1], JACEK SULANOWSKI[2], MARK A. MCCAFFREY[1], MATT MCCARTHY[1], C. H. CLIFFORD[1], PEGGY DICKINSON[1] and JOHN K. VOLKMAN[3]

[1]Chemistry Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, U.S.A.,
[2]Earth Sciences Department, Bridgewater States College, Bridgewater, MA 02324 U.S.A.
[3]CSIRO Marine Laboratories, Division of Oceanography, GPO Box 1538, Hobart, Tasmania 7001, Australia
[4]Environmental Sciences Program, University of Massachusetts—Boston, Harbor Campus, Boston, MA 02125–3393, U.S.A.

Abstract—Organic carbon; lycopane; a monoene of 2,6,10-trimethyl-7-(3-methyl-butyl)-dodecane; C_{37} alkenones, and 20:5 and 22:6 polyunsaturated fatty acid concentrations in two box cores from the Peru continental margin area at 15°S in 90 and 268 m water depth have depth profiles that are synchronous and appear to indicate an historical record of fluctuating higher productivity–lower productivity (ENSO) periods. The U^K_{37} ratio, calculated using $C_{37:2}$ and $C_{37:3}$ alkenones, in the 268 m water depth core in the center of the upwelling zone varies with depth in the core in a manner consistent with the U^K_{37} functioning as an historical recorder of euphotic zone temperature.

Concentrations and CPI for *n*-alkanes (C_{25}–C_{31}) are reported for both cores. A C_{27} anthrasteroid has been identified and quantified in the 268 m water depth core.

Key words: surface sediments, Peru, U^K_{37}, C_{37} alkenones, organic carbon, lycopane, polyunsaturated fatty acids, ENSO, anthrasteroids, cholestatrienes, *n*-alkanes, $C_{20:1}$ branched alkene

INTRODUCTION

The importance of acquiring further knowledge of the biogeochemistry of organic matter in ecosystems of upwelling areas and their underlying sediments with respect to the high productivity–fisheries potential of these areas, paleoclimatology, and proto-depositional models for ancient sediments containing petroleum has been set forth by several authors (Suess and Thiede, 1983; Thiede and Suess, 1983; Brassell and Eglinton, 1983; Demaison and Moore, 1980; Walsh, 1981; Wakeham *et al.*, 1983a; Volkman *et al.*, 1983, 1987; Smith *et al.*, 1983a, b, among others). We, and others, have been studying a series of sediment trap and core samples from the R/V *Knorr* 73–2 (1978) cruise to 15°S off Peru (Henrichs *et al.*, 1984; Henrichs and Farrington, 1984; Wakeham *et al.*, 1983a, b, 1984; Volkman *et al.*, 1983, 1987; Staresinic *et al.*, 1983; Gagosian *et al.*, 1983a, b; Lee and Cronin, 1982; Whelan and Hunt, 1983). We report here on depth profiles in two box cores of *n*-alkanes, a $C_{20:1}$ branched alkene, lycopane, selected fatty acids and a steroidal transformation product.

We also report on depth profiles of C_{37} alkenones. Marlowe (1984) and Brassell *et al.* (1986a) have advanced compelling data and an important new hypothesis concerning the utilization of ratios of long chain unsaturated ketones, particularly C_{37} alkenones, as a tool for probing paleoclimatic temperature. We explore the possibility of applying their technique to unraveling the historical record of ENSO (El Nino Southern Oscillation) events in the Peru upwelling area sediments. Normal upwelling conditions in the Peru area are accompanied by cold surface waters. Periodically, in response to regional and global changes in climate, upwelling and phytoplankton primary productivity decline as winds change and warmer waters invade the euphotic zone, a condition designated as El Nino Southern Oscillation (Arntz, 1984; Barber and Chavez, 1983; Rasmussen and Wallace, 1983; Quinn *et al.*, 1978).

*Author to whom correspondence should be addressed at address[4].

SAMPLES AND METHODOLOGY

The two cores, SC4 (90 m water depth) and SC6 (268 m water depth), we have analyzed were obtained at 15°S off Peru (Fig. 1) utilizing a Souter Core and have been described by Henrichs and Farrington (1984) and Henrichs *et al.* (1984). Sections were sampled onboard ship and frozen until analysis.

Extraction

Frozen sediments were thawed at room temperature and then homogenized by stirring. Aliquots (5–10 g wet wt) were removed and weighed into 50 ml centrifuge tubes with known amounts of internal standards added for later determination of percent recovery. Internal standards were D_{37}*n*-C_{16}, D_{50}*n*-C_{24}, and D_{66}*n*-C_{32}, for alkanes, D_{10}-fluorene,

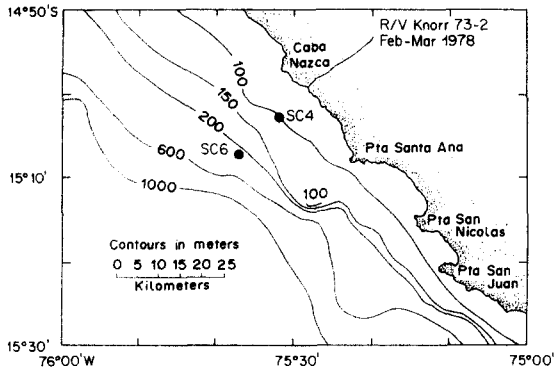

Fig. 1. Chart of sampling stations.

D_{14}-terphenyl and D_{12}-perylene for the fraction containing aromatics, sterenes and hopenes, n-C_{19}-2-one for alkenones, and 19:0 fatty acid methyl ester and 21:0 free fatty acid for the fatty acids. Unbound lipids were extracted with 40 ml isopropanol, 40 ml methanol–chloroform (1:1 v/v) and 40 ml methanol–chloroform (1:3 v/v) by sonication for approximately 10 min using a Tekmar sonic insertion probe disruptor. After each extraction the tubes were centrifuged in a Damon/IEC benchtop centrifuge at 3000 rpm for 10 min. The supernatants were decanted and combined. Neutral lipids were partitioned into isopropanol/chloroform by adding 10 ml of saturated aqueous NaCl and 100 ml of distilled H_2O and shaking in a separatory funnel followed by removal of the organic solvent layer. Two more partitioning steps were carried out using 50 ml chloroform each and the combined extracts were rotary evaporated to near dryness. Each sample was split into two aliquots with one used for column chromatography clean up and the other saved for subsequent analysis.

Column chromatography

Sample extracts were separated into lipid classes on a Cu/silica gel column in a glass chromatographic column, 0.9 mm i.d. by 35 cm high with a 300 ml reservoir, consisting of 7 g of 5% deactivated silica gel (BioRad-BioSil, 100–200 mesh) wet packed into hexane and 2 cm activated copper (previously activated with 3N HCl). Fractionation was accomplished by loading the sample extract dissolved in hexane onto the column and elution with 20 ml each of hexane—fraction 1, hexane–toluene (3:1 v/v)—fraction 2, hexane–toluene (1:1 v/v)—fraction 3, hexane–ethyl acetate (95:5 v/v—fraction 4, and hexane–ethyl acetate (90:10 v/v)—fraction 5. More polar fractions were eluted using hexane–ethyl acetate (85:15 v/v)—fraction 6, hexane–ethyl acetate (80:20 v/v)—fraction 7 and ethyl acetate–methanol (1:1)—fraction 8. All fractions except fraction 8 were evaporated to dryness and redissolved in hexane for subsequent GC analysis. Fractions 2 and 3 were combined prior to GC injection.

Fatty acid analysis

Total saponifiable fatty acids were analyzed by evaporating one quarter of the total lipid extract to dryness in a 15 ml centrifuge tube and redissolving in 2 ml of toluene. Saponification was carried out by adding 2 ml of 0.5N KOH in methanol, and heating in boiling water for 20 min in a sealed tube flushed with nitrogen. Fatty acids were methylated by adding 2 ml of 10% BF_3-methanol and heating in boiling water for 5 min in a sealed tube flushed with nitrogen. Saturated aqueous NaCl (1 ml) and distilled water (3 ml) were added to the solution and the fatty acid methyl esters (FAME) extracted into toluene with shaking. Tubes were centrifuged and the toluene was pipetted to a flask. Partitioning was repeated twice more with 2 ml toluene and the toluene portions combined and rotary evaporated. The methyl esters were purified using the same silica gel column chromatography, as described previously, with collection of fractions 4 and 5.

Gas chromatography

All sample fractions were analyzed by high resolution glass capillary gas chromatography on a J & W Scientific Durabond DB-5 30 m fused silica capillary column, 0.32 mm i.d. and 0.25 μm film thickness mounted in a Carlo Erba 4160 gas chromatograph equipped with a flame ionization detector. Samples were injected on-column at 70°C and the GC programmed at 3°C/min to 250°C, 4°C/min to 310°C and 6°C/min to 320°C. The carrier gas was hydrogen with an inlet setting of 0.5 kg/cm^2.

Data were collected on a computer system consisting of a Digital Equipment Micro PDP-11 and processed using VG Laboratories Multichrom software. Quantitation of compounds in each fraction was through internal standard response factors based on libraries of standard mixtures injected separately and an internal quantitation standard added prior to GC injection. All values are corrected for amount of the internal recovery standards.

Gas chromatography–mass spectrometry (GC–MS)

Electron impact mass spectrometry was carried out using a Finnigan 4500 quadrupole mass spectrometer fitted with a Carlo Erba 4160 gas chromatograph. A similar DB-5 capillary column was used with helium as the carrier gas at 0.8 kg/cm^2. 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. GC–MS operating conditions were 50 eV ionization potential with the source at 100°C and electron multiplier voltage at 900–1200 V with scanning rate from 50 to 650 amu per second. Data were processed using INCOS software. Chemical ionization GC–MS was accomplished using 0.5 torr methane, 130 eV, 100°C source temperature, 100–650 amu at 1 s scans; all other conditions similar to those for EI.

Dry weights were determined by drying separate aliquots of sediment at 110°C for 24 h. Organic carbon concentrations were determined by CHN analyzer using sediment aliquots treated with HCl to remove any small amounts of carbonate present (Henrichs and Farrington, 1984).

Duplicates of lipid compound and organic carbon analyses for several core sections agreed within ±10–20% of the mean. Organic carbon data agree to ±6–10%.

RESULTS AND DISCUSSION

We cannot present all interpretations of lipid class compound data in this brief paper. We are completing analyses of lipid class compounds such as sterols, triterpanols, hopanols, ketones, fatty alcohols and aldehydes and will present other aspects of our data in future papers. Tables of data are available upon request from J. Farrington.

Organic carbon, lycopane, n-alkanes, highly branched $C_{20:1}$

Plots of organic carbon and lycopane concentrations versus depth show a reasonably good correspondence in SC4 and SC6 [Figs 2(A) and 3(A)]. Lycopane has been reported in a limited number of recent and ancient sediments (Volkman and Maxwell, 1986). The source of lycopane in surface sediments is not known, but an origin from methanogens or other bacteria has been postulated (Brassell *et al.*, 1981). If the biomass of the organisms producing lycopane is governed by the amount of organic carbon deposited or incorporated into the sediments then the correspondence of lycopane profiles to organic carbon profiles is readily explained. This is not unreasonable given the probable coupling of microbial activity to available substrate, i.e. organic carbon. The incorporation of lycopane into sediments early in the diagenetic history of organic-matter rich depositional environments may account for the occurrence of lycopane in ancient sediments deposited under conditions similar to those found today off Peru.

Lycopane coelutes with n-C_{35} under our analytical conditions. GC–MS analyses clearly indicate that less than 10% contribution of n-C_{35} to the lycopane peak was measured. It may be that lycopane has been overlooked in some earlier GC analyses of sediments due to this coelution problem. Identification of lycopane was confirmed by EI- and CI–GC–MS with comparison to published EI spectra (Philp, 1985) and M^+-1 of 561 in CI–GC–MS.

Concentrations of lycopane and TOC are generally lower in SC4 compared with SC6 over the depth intervals sampled. This is expected because SC6 is situated under an area of generally high marine productivity and is further offshore than SC4. We might expect SC4 to be more influenced by river-borne sediments that are discharged to the area under periodic pluvial/fluvial events (Krissek and Scheidegger, 1983). Terrigenous detritus would reduce the marine organic detritus concentration by dilution.

A $C_{20:1}$ branched alkene, a monounsaturated derivative of 2,6,10-trimethyl-7-(3-methyl-butyl)-dodecane, dominates over trace amounts of n-C_{17}, pristane and other compounds in the alkane–alkene fraction in the n-C_{15} to n-C_{20} molecular weight range. The exact position of the unsaturation is not known from the GC and GC–MS (EI and CI) analyses but the EI mass spectrum is identical to that published by Rowland *et al.* (1985) for the $C_{20:1}$ highly branched compound occurring in *Enteromorpha*, a green alga. This compound has been reported in trace amounts in surface sediments of Puget Sound, Washington, U.S.A., by Barrick *et al.* (1980), surface sediments of the Ebro River Estuary by Bayona *et al.* (1983), and surface sediments in hypersaline Sharks Bay, Western Australia, by Dunlop and Jeffries (1985). A review of acyclic isoprenoids as biological markers (Volkman and Maxwell, 1986) identified no other reports for surface sediment occurrence. The saturated analog has been reported in Rozel Point crude oil by Yon *et al.* (1982), who were the first to elucidate the structure.

The occurrence of this compound in Peru surface sediments has two interesting features in comparison to earlier reports. First, the concentrations are in the 10^{-6} g/g dry weight range in the surface sections of the two cores as compared to $10–100 \times 10^{-9}$ g/g dry weight in surface sediments of Puget Sound, the Ebro River Estuary, and Sharks Bay. Second, the compound dominates over trace amounts of any of its fully saturated analog 2,6,10-trimethyl-7-(3-methyl-butyl)-dodecane and n-C_{17} or n-$C_{17:1}$ in agreement with the Sharks Bay data and in contrast to reports for Puget Sound and the Ebro River Estuary where it is usually a minor component compared to these other compounds.

Concentrations of br-$C_{20:1}$ are generally lower in SC4 compared to SC6 [Figs 2(D) and 3(D)] probably because of a marine origin and there is dilution of the nearer shore SC4 by terrigenous sediments. The depth profile of br-$C_{20:1}$ for SC6 [Fig. 3(D)] is essentially exponential if smoothed. There are a few minor fluctuations of concentration with depth. The SC4 br-$C_{20:1}$ profile [Fig. 2(D)] exhibits a subbottom maximum that interrupts an otherwise fairly uniform exponential decrease of concentration with depth. This subbottom maximum for br-$C_{20:1}$ probably represents a high influx of marine organic material with appreciable concentrations of br-$C_{20:1}$. A substantial deposition of plankton detritus under the low oxygen conditions at the sediment-water interface that occurs at this location (Henrichs and Farrington, 1984) could account for the preservation of a maxima at depth in the core.

The br-$C_{20:1}$ depth profile in both SC4 and SC6 is consistent with the diagenesis model of Berner (1980) which states that there is easily remineralized or

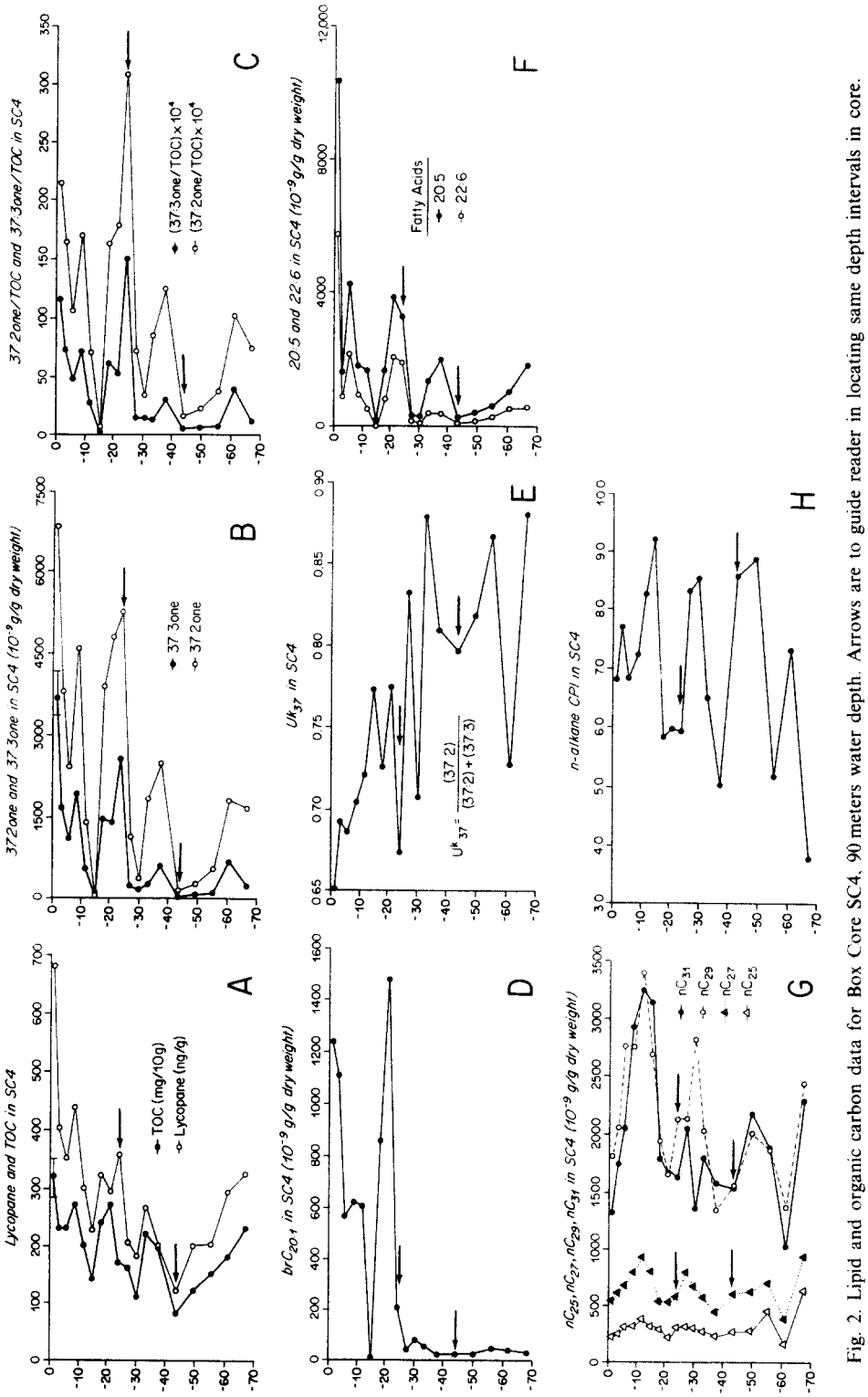

Fig. 2. Lipid and organic carbon data for Box Core SC4, 90 meters water depth. Arrows are to guide reader in locating same depth intervals in core.

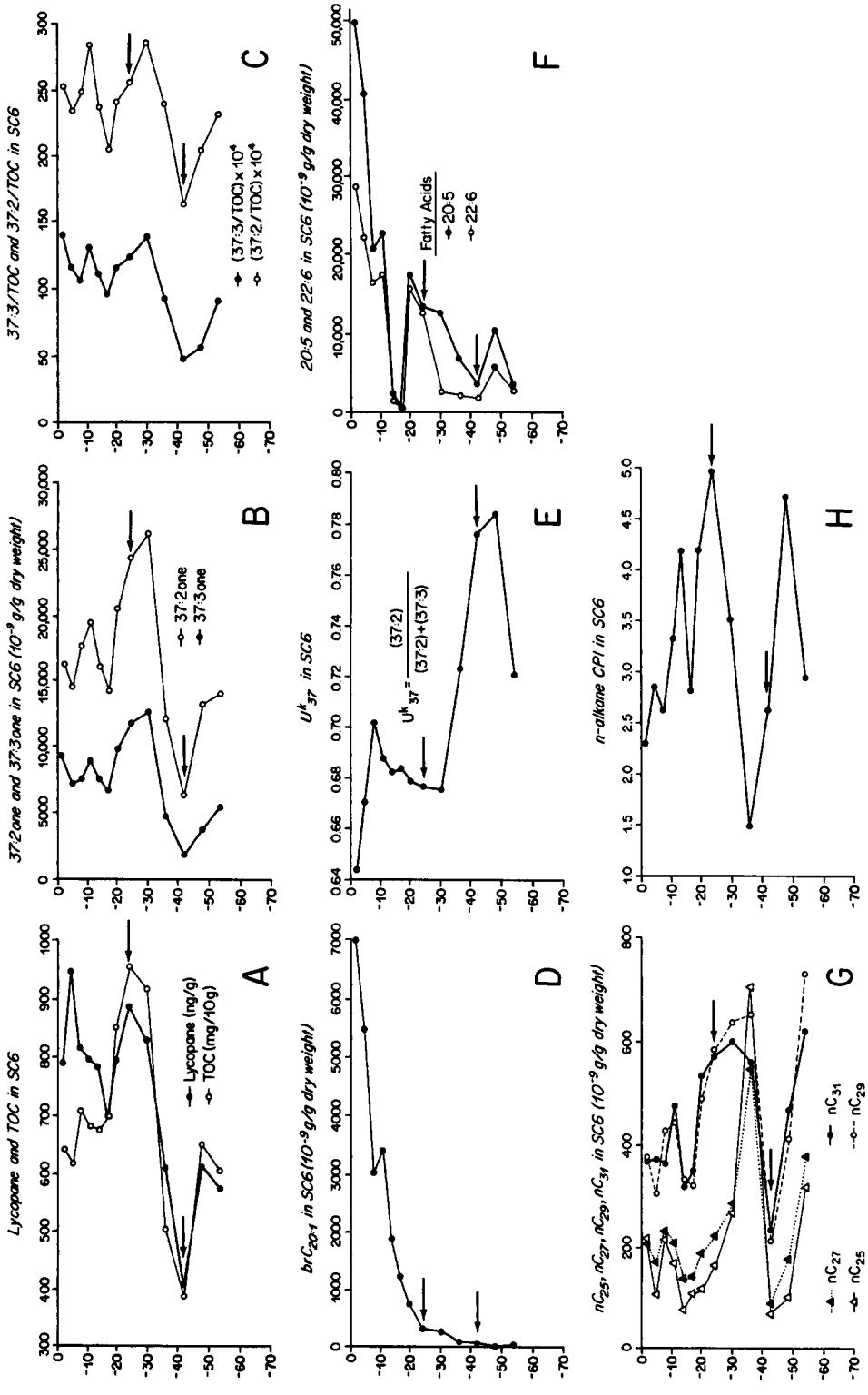

Fig. 3. Lipid and organic carbon data for Box Core SC6, 268 meters water depth. Arrows are to guide reader in locating same depth intervals in cores.

biologically transformed organic matter that is rapidly consumed at the sediment–water interface and in the upper few centimeters of sediment. This is followed by much slower rates of remineralization as deposition proceeds. The end result is an exponentially decreasing concentration of labile compounds with increasing depth under conditions of near steady state input of organic matter over time intervals sampled by the core. Deviations from this profile are reflections of non-steady state conditions as would be the case for the marked maxima in SC4.

The CPI (Carbon Preference Index) for n-C_{25} to n-C_{31} shows a clear terrigenous signal (Tissot and Welte, 1978; Hunt, 1979) for SC4 and many sections of SC6 [Figs 2(H) and 3(H)]. The CPI is greater for SC4 compared with SC6 and the differences in both concentrations and CPI are consistent with SC4 being the near-shore core and probably influenced more by terrigenous fluvial input. The n-C_{25} to n-C_{31} concentrations and CPI depth profile for SC4 have maxima and minima that are almost exactly out of phase with maxima and minima in depth profiles of organic carbon and lycopane [Figs 2(A) and 2(H)]. We interpret this phenomena as due to changes in the relative proportions of marine and terrigenous n-alkane deposited to, and incorporated into, sediments. Phytoplankton and some bacteria have low concentrations of n-C_{21} to n-C_{33} with a CPI of approximately 1.0 as we have noted in interpretation of earlier data from another core from this area (Volkman *et al.*, 1983). The lower CPI at times of presumed higher productivity indicated by maxima in organic carbon would be a function of dilution of high CPI n-alkanes by alkanes from a marine source having a CPI = 1.0. Higher concentrations of n-C_{25}, n-C_{27}. n-C_{29}, n-C_{31} alkanes and higher CPI at periods of presumed lower productivity by organic carbon minima are probably due to increased river inputs of terrigenous detritus near shore as a result of rainy conditions accompanying lower productivity ENSO events (Arntz, 1984; Barber and Chavez, 1983).

Depth profiles of CPI and n-alkanes at SC6 (Figs 3(G) and 3(H)] require a different interpretation from that advanced to explain the SC4 data. The concentrations of n-C_{25}, n-C_{27}, n-C_{29} and n-C_{31} seem to covary with organic carbon concentrations as would be expected if the main sources of these n-alkanes were marine. The higher CPI values correspond in some depth ranges to minima in the organic carbon. However, in other depth intervals maxima in CPI correspond to maxima in organic carbon. Several factors must be interacting to produce the complication in the depth profiles. Differences in ease of biotransformation and degradation of terrigenous source n-alkanes contrasted with marine source n-alkanes may be operative as has been noted elsewhere (Prahl *et al.*, 1980; Volkman *et al.*, 1987). A combination of: (i) an increase in offshore or along shore horizontal transport of resuspended near shore terrigenous sourced sediments, and (ii) increased scavenging of these particles from the water column driven by increased filter feeding and rapidly sinking large particle production at times of increased production, may also be operative.

We have reported previously on concentrations of n-C_{20} to n-C_{35} alkanes in BC7 slightly nearer to shore (Fig. 1) (Volkman *et al.*, 1983). The range of concentrations were similar to those of SC4, with n-C_{29} and n-C_{31} dominant and the other n-alkanes present in relative abundances similar to those of SC4. There were slight down core concentration fluctuations but fewer sections were analyzed and we do not have the same depth resolution as for SC4 and SC6.

C_{37} Alkenones

The depth profile concentrations of C_{37} alkenones are plotted in Figs 2(B) and 3(B) for SC4 and SC6. Concentrations for SC4 are in the same range of values reported for BC7 by Volkman *et al.* (1983). Depth profiles of C_{37} alkenones in SC4 and SC6 correspond generally to depth profiles of organic carbon and lycopane [Figs 2(A) and 2(B); 3(A) and (B)]. This is expected since it is highly probable that organic carbon concentrations are an approximate historical record of periods of high productivity in the overlying water column. The C_{37} alkenones are associated with plankton of the *Prymnesiophycae* order (Volkman *et al.*, 1980; Marlowe, 1984; Marlowe *et al.*, 1984; Brassell *et al.*, 1986). However, a strict correlation of C_{37} alkenone concentration to organic carbon as shown by the depth profile of Figs 2(C) and 3(C) might not be expected because of varying proportions of contributions of *Prymnesiophyceae* to the total primary production. Thus, it is surprising to us to have a correlation coefficient R^2 of 0.93 for combined SC4 and SC6 total C_{37} alkenone and organic carbon data. The fluctuations of C_{37} alkenone to organic carbon ratios are minor but perhaps significant. It is interesting that the ratio of C_{37} alkenones to total organic carbon is in concordance with alkenone and organic carbon depth profiles [Figs 2(A), 2(B) and 2(C); 3(A), 3(B) and 3(C)]. This may imply an increased contribution of *Prymnesiophyceae* to the biomass of phytoplankton during periods of highest productivity—mature upwelling conditions as suggested by Mitchell-Innes and Winter (1987) Less likely alternatives are differential preservation of bulk organic matter and alkenones during periods of higher and lower productivity in the chain of events leading from production to sedimentation and incorporation into the geologic record.

The U^K_{37} ratio fluctuates down core for SC4 and SC6 [Figs 2(E) and 3(E)]. A range of 18.2–25.3°C is calculated from the maxima and minima for U^K_{37} using the calibration curves of Prahl and Wakeham (1987) that they derived from U^K_{37} determinations for plankton cultures of *Emiliania huxleyi* (*Prymnesiophyceae*) and sediment trap collections—including sediment trap collections from 15°S off Peru. These temperature ranges are in accord with expected sea

surface temperature ranges for conditions of high productivity with lower water temperature and lower productivity with warmer water temperature ENSO (El Nino Southern Oscillation) (Barber and Chavez, 1983; Instituto del Mar del Peru data, Barber and Chavez, unpublished).

The sectioning of these box cores was governed by needs for other studies (Henrichs and Farrington, 1984; Henrichs *et al.*, 1984) and occurred prior to the availability of estimates of accumulation rates for the upper meter of sediment in the study area. Thus, the time period resolution is not optimized to provide chronologies of ENSO events. Furthermore, we must assume for the present that once deposited the C_{37} alkenones and their derived U^K_{37} value are not altered by early diagenesis in such a manner as to alter the U^K_{37} ratio.

Periods of numerous intense ENSO events during the 60–100 years prior to the time of sampling in 1978 (Quinn *et al.*, 1978, i.e. 1878–1918 AD) generally correspond to warmer water U^K_{37} ratios and lower organic carbon values (Fig. 4). The period of approximately 1918–1978 is a period of less frequent intense ENSO events and correspondingly lower temperature as indicated by the U^K_{37} ratio and higher productivity as indicated by organic carbon.

Minima for U^K_{37} and maxima for organic carbon depth profiles are not correlated for SC4 [Figs 2(A) and 2(E)]. We think that this is due to the position of SC4 being on the inshore edge of the zone of intense upwelling. The surface water–euphotic zone temperature could fluctuate markedly in the edge of the upwelling zone as a function of upwelling intensity and associated complexity of current regimes in the area. An alternative involves alteration of U^K_{37} by early diagenesis conditions at the SC4 site. Since this core is situated near the upper edge of the oxygen minimum zone its depositional environment may be more oxic on occasion in contrast to SC6 (Henrichs and Farrington, 1984). Core SC6 is located well within the zone or plume of upwelling during the periods of high productivity non-ENSO times, and well within the oxygen minimum zone and would be expected to record more faithfully the contrasting cold-higher productivity, warm-ENSO-lower productivity periods.

These interpretations are constrained by data for two cores only and must be tested by further measurements of cores sectioned on finer time intervals and with better stratigraphic control of sediment accumulation rates. The U^K_{37} ratio should be of value for reconstructing ENSO event temperatures in the Peru offshore region since some of this area is subject to intense organic matter remineralization in the surface sediments. The remineralization is accompanied by dissolution of $CaCO_3$ tests which otherwise may have preserved $^{18}O/^{16}O$ records that might have provided a measure of temperatures of the overlying water. Ideally, U^K_{37} measurements in a series of strategically located piston cores of well-characterized stratigraphy would provide a first order reconstruction of averaged hydrographic conditions in the past.

A crucial test of the validity of the U^K_{37} application in this region is the ability to detect the intense 1982–1983 ENSO event (Rasmussen and Wallace, 1983; Barber and Chavez, 1983) in recently accumulated sediments. If estimates of sediment accumulation rates for the core SC6 area are near correct at 0.6–1.0 cm/year (Henrichs and Farrington, 1984), then in 1987 the 1982–1983 ENSO event should be recorded in sediments at 2–4 cm depths. We have obtained a second set of box cores in this area during the July 1987 cruise of R/V *Moana Wave* to conduct the requisite test of the applicability of the U^K_{37} ratio in sediments as a recorder of temperature of the euphotic zone in the offshore Peru area. Analyses are at an early stage for these samples.

Fatty acids

We report here only a few depth profiles of interest for correlations with other data. More extensive discussions of the sediment fatty acids in the sediment cores and in sediment traps from the area are presented elsewhere (Farrington *et al.*, 1988).

Depth profiles of concentrations of 20:5 and 22:6 polyenoic fatty acids show a marked decrease from 0–2 and 0–3 cm surface sediments to deeper sections of cores as expected for these relatively labile polyunsaturated fatty acids [Figs 2(F) and 3(F)]. Superimposed on this trend are subsurface maxima that correspond to the subsurface maxima in organic carbon, lycopane and C_{37} alkenones for SC4 and SC6 [Figs 2(A), 2(B) and 2(F); 3(A), 3(B) and 3(F)]. Smith *et al.* (1983) have noted high concentrations of 20:5 and 22:6 in surface sediments at 12°S and 145 m water depth off Peru to the north of our sampling location, and they concluded that these high concentrations were from freshly deposited marine detritus. We cannot rule out other sources (e.g. unique bacterial biosynthesis) of elevated concentrations of these polyunsaturated fatty acids in our cores at this time as we discuss in detail elsewhere (Farrington *et al.*, 1988). The subsurface maxima of 20:5 and 22:6 in our cores are consistent with our interpretations of the organic carbon subsurface maxima reflecting an historical record of higher productivity periods of time.

Cholestatrienes

We have tentatively identified 14α(H)-1(10→6)-abeocholesta-5,7,9(10)-triene in our cores by GC–MS (Fig. 5) and comparison to the spectra reported for the authentic compound by Hussler and Albrecht (1983). This compound has been reported in Cretaceous black shales (Hussler and Albrecht, 1983), and relatively immature DSDP sample from offshore California (Rullkötter and Welte, 1983; Hussler and Albrecht, 1983; Brassell *et al.*, 1984). It also appears to be the same cholestatriene present in the surface

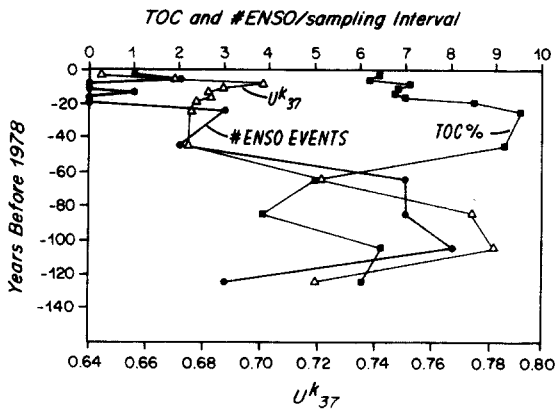

Fig. 4. Plot of organic carbon, U^{K}_{37}, and number of intense ENSO events/unit time vs time in core SC6. ENSO event data from Quinn *et al.* (1978). Chronology from Pb-210 derived estimates of Henrichs and Farrington (1984).

sediments underlying the upwelling zone off Walvis Bay as the mass spectra of that compound (Gagosian and Farrington, 1978) corresponds reasonably well with that of the authentic anthrasteroid as noted by Brassell *et al.* (1984) and Philp (1985). We have noted by mass chromatography searching for *m/z* 366 that the concentrations of cholestatrienes show an interesting fluctuation with depth in SC6 (Fig. 6). The other peaks indicated by *m/z* 366 mass chromatography are cholestatrienes of unknown structure that often coelute in several core sections with other compounds that appear to be mono- and diunsaturated early transformation products of triterpanols. We are completing the study of steroids and triterpenoids and their early diagenetic transformation products in these cores and will present the results in a later paper.

Our purpose in presenting the cholestratriene data here is to note that the marked change in the relative abundance of the cholestatrienes (Fig. 6) occurs in the sections of the core 39–45 cm and 45–51 cm and the highest concentration of the B-ring anthrasteroid occurs in the 45–51 cm core section. This corresponds with the higher-temperature less productive time periods of the core if our historical record interpretation is correct. We cannot determine from our data if the anthrasteroid is the expected product from transformation of the biological trans C/D ring juncture or the geochemically more stable cis C/D ring juncture analog (Hussler and Albrecht, 1983). The doublet peaks in Fig. 6 suggest that these compounds are isomeric at another position in addition to the 14α, 14β isomers (Brassell *et al.*, 1984). We did not detect the C_{28} and C_{29} anthrasteroid homologs using *m/z* 380 and 394 plots (Hussler and Albrecht, 1983). Since cholesterol is the dominant sterol detected in Peru surface sediments at 15°S to date (Volkman *et al.*, 1987) it may be that the C_{28} and C_{29} anthrasteroids, if present, were below our detection limits.

Our data suggest that in this depositional environment the upper 1 m of sediment may yield some interesting precursor–product transformation re-

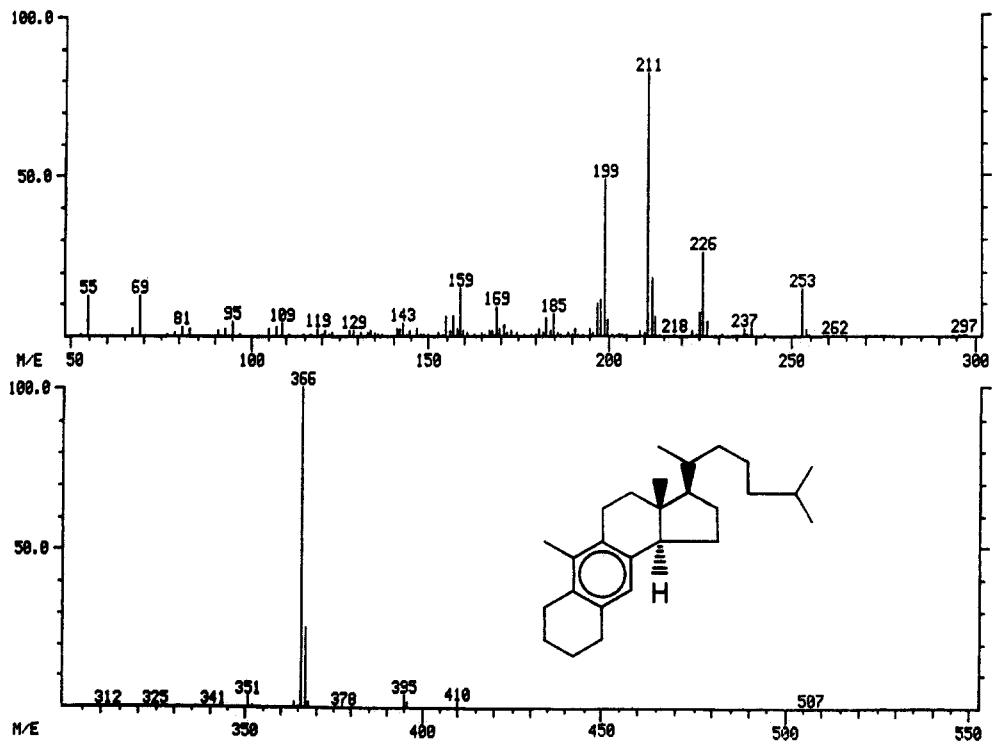

Fig. 5. Mass spectrum of 14α(H)-1(10→6)-abeocholesta-5,7,9(10)-triene. Core SC6.

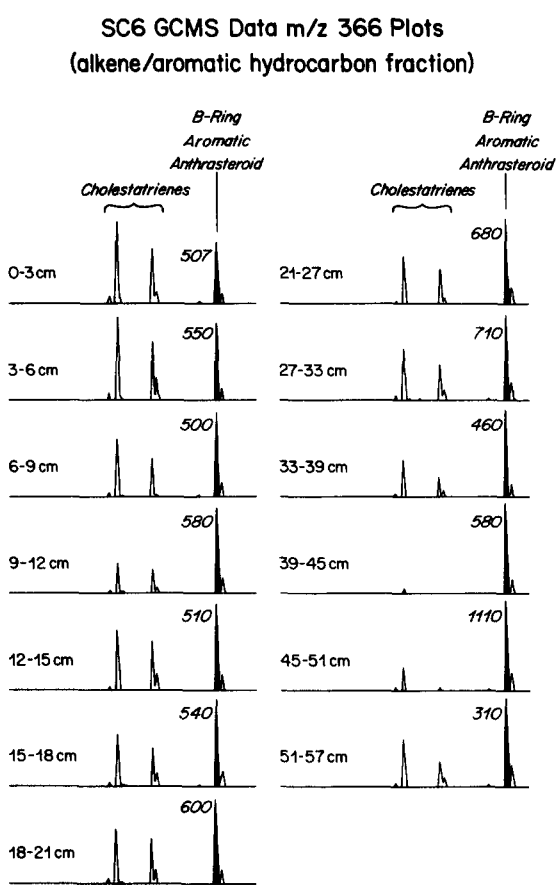

Fig. 6. Plots of m/z 366; selected portions of mass chromatograms detecting cholestatrienes and C_{27} monoaromatic anthrasteroid. Concentrations of C_{27} monoaromatic anthrasteroid given in 10^{-9} g/g dry weight.

lationships and yield further insights into interpretations of time–temperature curves in the early stages of diagenesis yielding the anthrasteroids as proposed by Rullkötter and Welte (1983) and Brassell *et al.* (1984). It appears that fluctuations in conditions at the time of deposition may play an important role in precursor–product relationships and extent of diagenesis prior to incorporation into ancient sediments.

General discussion

The two cores, SC4 and SC6, are deposited only 15 km apart on the Peru shelf at 15°S. Yet, some aspects of their depth profiles of organic compounds are markedly different as shown from this study and interstitial water depth profiles of sulfide (Henrichs and Farrington, 1984). We attribute this to the location of SC4 at the edge of the upwelling plume in this area and the location of SC6 in the main part of the upwelling plume. It is apparent that depth profiles of several compounds, viz: lycopane: C_{37} alkenones; 20:5, 22:6 fatty acids and total hydrolyzable amino acids (Henrichs and Farrington, 1984) track maxima and minima in organic carbon depth profiles. The sediments appear to contain an historical record of productivity of the overlying water column despite the remineralization of organic matter that occurs at the sediment-water interface and in the upper 50 to 70 cm of sediment as determined by interstitial water profiles of SO_4^{2-}, S^{2-}, NO_2^-, NO_3^-, NH_4^+ and total CO_2 (Henrichs and Farrington, 1984). The presence of the anthrasteroid and the depth profiles of br-$C_{20:1}$ can be interpreted as evidence of transformation of organic matter in this depositional environment.

The depth profiles of U_{37}^K ratios correlate reasonably with warmer and colder euphotic zone water temperatures expected from the known record of periodicities of ENSO events (Quinn *et al.*, 1978) and higher productivity-upwelling periods. It is not surprising that cores from selected locations of the Peru margin will record these periodic fluctuations since historical records of fisheries in the area have been deciphered from relative abundances of fish scales recorded in sediments (De Vries and Pearcy, 1982).

Application of various statistical treatments (e.g. Brassell *et al.*, 1986b) of the entire set of data on lipids, organic carbon, amino acids and other parameters should yield further insights into the historical record preserved in these cores and early diagenesis of organic matter in these organic-matter rich sediments.

CONCLUSIONS

(1) Depth profiles of organic carbon, lycopane, $C_{37:2}$, and $C_{37:3}$ alkenones, and 20:5 and 22:6 fatty acids generally correspond in their maxima and minima for two box cores from 90 and 268 meters water depth at 15°S off Peru. The profiles appear to correspond to an historical record of fluctuations in higher and lower productivity periods in the overlying water column.

(2) The U_{37}^K ratio as determined in these cores shows promise as a paleothermometer in assessing historical records of temperature in the overlying waters.

(3) Depth profiles of n-C_{25} to n-C_{33} alkanes and CPI values in the nearer shore SC4 indicate a greater influence of terrigenous detritus input to the sediments at times of minima in organic matter and marine organic matter input as described in 1) above. This is consistent with more extensive pluvial/fluvial inputs of terrigenous materials during ENSO events. The higher molecular weight n-alkanes at SC6 further offshore are more extensively influenced by marine sources.

(4) The anthrasteroid 14α(H)-1(10→6)-abeocholesta-5,7,9(10)-triene has been tentatively identified and quantified in one core, has a fluctuating abundance relative to other cholestatrienes in the core, and its production by transformation of cholest-5-en-3β-ol appears to be related in some

manner to fluctuating conditions in early diagenesis coupled with productivity fluctuations in the overlying water column.

Acknowledgements—We thank Drs Stuart G. Wakeham, John Ertel, Daniel Repeta, Simon Brassell, and Jean Whelan for valuable discussions; Dr Nelson Frew and Mr Carl Johnson for assistance with GC–MS analyses; Ms Martha tarafa, Ms Bonnie Woodward, and officers, crew and scientific group of R/V *Knorr* 73/2 for technical assistance in the laboratory and in the field; and Ms Peggy Chandler for typing the manuscript. Financial support was provided primarily by U.S. National Science Foundation Grant OCE 85-09859; with additional support from U.S. National Science Foundation Grants OCE 79-18665, OCE 77-26184 and U.S. Office of Naval Research Contract N00014-79-C-1171 at the time of sampling. This is Contribution Number 6696 of Woods Hole Oceanographic Institution.

REFERENCES

Arntz W. E. (1984) El Nino and Peru: Positive aspects. *Oceanus* **27,** 36–39.

Barber R. T. and Chavez F. P. (1983) Biological consequences of El Nino. *Science* **222,** 1203–1210.

Barrick R. C., Hedges J. I and Peterson M. L. (1980) Hydrocarbon geochemistry of the Puget Sound region. I Sedimentary acyclic hydrocarbons. *Geochim. Cosmochim. Acta* **44,** 1349–1362.

Bayona J. M., Grimalt J., Albaiges J., Walker W. II, Lappe B. W. de and Risebrough R. W. (1983) Recent contributions of high resolution gas chromatography to the analysis of environmental hydrocarbons. *J. H.R.C. and C.C.* **6,** 605–511.

Berner R. A. (1980) *Early Diagenesis, A Theoretical Approach*, 241 pp. Princeton University Press.

Brassell S. C. and Eglinton G. (1983) The potential of organic geochemical compounds as sedimentary indicators of upwelling. In *Coastal Upwelling. Its Sediment Record, Part A: Responses of the Sedimentary Regime to Present Coastal Upwelling* (Edited by Suess E. and Thiede J.), pp. 545–571. Plenum Press, New York.

Brassell S. C., Wardroper A. M. K., Thomson I. D., Maxwell J. R. and Eglinton G (1981) Specific acyclic isoprenoids as biological markers of methanogenic bacteria in marine sediments. *Nature* **290,** 693–696.

Brassell S. C., McEvoy J., Hoffman C. F., Lamb N. A., Peakman T. M. and Maxwell J. R. (1984) Isomerization rearrangement and aromatization of steroids in distinguishing early stages of diagenesis. In *Advances in Organic Geochemistry 1983* (Edited by Schenck P. A., Leeuw J. W. de and Lijmbach G. W. M.). *Org. Geochem.* **6,** 11–24. Pergamon Press, Oxford.

Brassell S. C., Eglinton G., Marlowe I. T., Pflaumann U. and Sarntheim M. (1986a) Molecular stratigraphy: a new tool for climatic assessment. *Nature* **320,** 129–133.

Brassell, S. C., Brereton R. G., Eglinton G., Grimalt J., Liebezeit G., Marlowe I. T., Pflaumann U. and Sarnthein M. (1986b) Paleoclimatic signals recognized by chemometric treatment of molecular stratigraphic data. In *Advances in Organic Geochemistry 1985* (Edited by Leythaeuser D. and Rullkötter J.). *Org. Geochem.* **10,** 609–660. Pergamon Journals, Oxford.

Demaison G. J. and Moore G. T. (1980) Anoxic environments and oil source bed genesis. *Bull. Am. Assoc. Pet. Geol.* **64,** 1179–1209.

DeVries T. J. and Pearcy W. G. (1982) Fish debris in sediments of the upwelling zone off central Peru: a Late Quaternary record. *Deep-Sea Res.* **28,** 87–102.

Dunlop R. W. and Jeffries P. R. (1985) Hydrocarbons of the hypersaline basins of Sharks Bay, Western Australia. *Org. Geochem.* **5,** 313–320.

Farrington J. W., Sulanowski J., Wakeham S. G., Davis A., McCaffrey M. and Volkman J. K. (1988) Fatty acids in surface sediments and sediment trap material from off Peru. In preparation.

Gagosian R. B. and Farrington J. W. (1978) Sterenes in surface sediments from the southwest African shelf and slope. *Geochim. Cosmochim. Acta* **42,** 1091–1101.

Gagosian R. B., Nigrelli G. E. and Volkman J. K. (1983a) Vertical transport and transformation of biogenic organic compounds from a sediment trap experiment off the coast of Peru. In *Coastal Upwelling. Its Sediment Record, Part A: Responses of the Sedimentary Regime to Present Coastal Upwelling* (Edited by Suess E. and Thiede J.), pp. 241–272. Plenum Press, New York.

Gagosian R. B., Volkman J. K. and Nigrelli G. E. (1983b) The use of sediment traps to determine sterol sources in coastal sediments off Peru. In *Advances in Organic Geochemistry 1981* (Edited by Bjorøy M. *et al.*), pp. 369–379. Wiley, Chichester.

Henrichs S. M. and Farrington J. W. (1984) Peru upwelling region sediments near 15°S. 1. Remineralization and accumulation of organic matter. *Limnol. Oceanogr.* **29,** 1–19.

Henrichs S. M., Farrington J. W. and Lee C. (1984) Peru upwelling sediments near 15°S. 2. Dissolved free and total hydrolyzable amino acids. *Limnol. Oceanogr.* **29,** 30–34.

Hunt J. M. (1979) *Petroleum Geochemistry and Geology*. W. H. Freeman, San Francisco.

Hussler G. and Albrecht P. (1983) C_{27}–C_{29} Monoaromatic anthrasteroid hydrocarbons in Cretaceous black shales. *Nature* **304,** 262–263.

Krissek L. A. and Scheidegger K. F. (1983) Environmental controls on sediment texture and composition in low oxygen zones off Peru and Oregon. In *Coastal Upwelling. Its Sediment Record, Part B: Sedimentary Records of Ancient Coastal Upwelling* (Edited by Suess E. and Thiede J.), pp. 163–180. Plenum Press, New York.

Lee C. and Cronin C. (1982) The vertical flux of particulate organic nitrogen in the sea: decomposition of amino acids in the Peru upwelling area and the equatorial Atlantic. *J. Mar. Res.* **40,** 227–251.

Marlowe I. T. (1984) Lipids as paleoclimatic indicators. Ph.D. thesis, Organic Geochemistry Unit, School of Chemistry, University of Bristol, U.K., 273 pp.

Marlowe I. T., Green J. C., Neal A. C., Brassell S. C., Eglinton G. and Course P. A. (1984) Long-chain (*n*-C_{37}–C_{39}) alkenones in the *Prymnesiophyceae:* Distribution of alkenones and other lipids and their taxonomic significance. *Br. Phycol. J.* **19,** 203–216.

Mitchell-Innes B. A. and Winter A. (1987) Coccolithophores: a major phytoplankton component in matrix upwelled waters off the Cape Pensinsula, South Africa in March 1983. *Mar. Biol.* **95,** 25–30.

Philp R. P. (1985) *Fossil Fuel Biomarkers, Applications and Spectra*, 294 pp. Elsevier, New York.

Prahl F. G. and Wakeham S. G. (1987) Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature assessments. *Nature* **330,** 367–369.

Prahl F. G., Bennett J. T. and Carpenter R. (1980) The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington, *Geochim. Cosmochim. Acta* **44,** 1967–1976.

Quinn W. H., Zopf D. O., Short K. S. and Kuo Yang R. T. (1978) Historical trends and statistics of the Southern Oscillation, El Nino, and Indonesian droughts. *Fish. Bull.* **76,** 663–678.

Rasmussen E. M. and Wallace J. M. (1983) Meteorological aspects of the El Nino/Southern Oscillation. *Science* **222,** 1195–1202.

Rowland S. J., Yon D. A., Lewis C. A. and Maxwell J. R. (1985) Occurrence of 2,6,10-trimethyl-7-(3-methyl-butyl)-

dodecane and related hydrocarbons in the green alga *Enteromorpha prolifera* and sediments. *Org. Geochem.* **8,** 207–213.

Rullkötter J. and Welte D. H. (1983) Maturation of organic matter in areas of high heat flow. A study of sediments from DSDP Leg 63, Offshore California and Leg 64, Gulf of California. In *Advances in Organic Geochemistry 1981* (Edited by Bjorøy M. *et al.*), *pp.* 438–448. Wiley, Chichester.

Smith D. J., Eglinton G. and Morris R. J. (1983a) The lipid chemistry of an interfacial sediment from the Peru continental shelf: fatty acids, alcohols, aliphatic ketones and hydrocarbons. *Geochim. Cosmochim. Acta* **47,** 2225–2232.

Smith D. J., Eglinton G., Morris R. J. and Poutanen E. L. (1983b) Aspects of the steroid geochemistry of an interfacial sediment from the Peru upwelling. *Oceanol. Acta* **6,** 211–219.

Staresinic N., Farrington J., Gagosian R. B., Clifford C. H. and Hulbert E. M. (1983) Downward transport of particulate organic matter in the Peru coastal upwelling: role of the anchoveta *Engraulis ringens*. In *Coastal Upwelling. Its Sediment Record, Part A: Responses of the Sedimentary Regime to Present Coastal Upwelling* (Edited by Suess E. and Thiede J.), pp. 225–240. Plenum Press, New York.

Suess E. and Thiede J. (Eds) (1983) *Coastal Upwelling. Its Sediment Record, Part A: Responses of the Sedimentary Regime to Present Upwelling*, 604 pp. Plenum Press, New York.

Tissot B. P. and Welte D. H. (1978) *Petroleum Formation and Occurrence*. Springer, New York.

Thiede J. and Suess E. (Eds) (1983) *Coastal Upwelling. Its Sediment Record, Part B: Sedimentary Records of Ancient Coastal Upwelling*, 604, pp. Plenum Press, New York.

Volkman J. K. and Maxwell J. R. (1986) Acyclic isoprenoids as biological markers. In *Biological Markers in the Sedimentary Record* (Edited by Johns R. B.), pp. 1–42. Elsevier, Amsterdam.

Volkman J. K., Eglinton G., Corner E. D. S. and Sargent J. R. (1980) Novel unsaturated straight-chain C_{37}–C_{39} methyl and ethyl ketones in marine sediments and a coccolithophorid *Emiliania huxleyi*. In *Advances in Organic Geochemistry 1979* (Edited by Douglas A. G. and Maxwell J. R.), pp. 219–227. Pergamon Press, Oxford.

Volkman J. K., Farrington J. W., Gagosian R. B. and Wakeham S. G. (1983) Lipid composition of coastal marine sediments from the Peru upwelling region. In *Advances in organic Geochemistry 1981* (Edited by Bjorøy M. *et al.*), pp. 228–240. Wiley, Chichester.

Volkman J. K., Farrington J. W. and Gagosian R. B. (1987) Marine and terrigenous lipids in coastal sediments from the Peru upwelling region at 15°S: Sterols and triterpene alcohols. *Org. Geochem.* **11,** 463–477.

Wakeham S. G., Farrington J. W. and Volkman J. K. (1983a) Fatty acids, wax esters, triacylglycerols and alkyldiacylglycerols associated with particles collected in sediment traps in the Peru upwelling. In *Advances in organic Geochemistry 1981* (Edited by Bjorøy M. *et al.*), pp. 185–197. Wiley, Chichester.

Wakeham S. G., Livramento J. B. and Farrington J. W. (1983b) Fatty acids and fatty acid esters of particulate matter collected in sediment traps in the Peru upwelling area. R/V *Knorr* cruise 73, February/March 1978. Woods Hole Oceanographic Institution Technical report WHOI 83-28, 49 pp.

Wakeham S. G., Farrington J. W. and Gagosian R. B. (1984) Variability in lipid flux and composition of particulate matter in the Peru upwelling region. In *Advances in Organic Geochemistry 1983* (Edited by Schenck P. A., Leeuw J. W. de and Lijmbach G. W. M.). *Org. Geochem.* **6,** 203–215. Pergamon Press, Oxford.

Walsh J. J. (1981) A carbon budget for overfishing off Peru. *Nature* **290,** 300–304.

Whelan J. K. and Hunt J. M. (1983) Volatile C_1–C_7 organic compounds in sediments from the Peru upwelling region. *Org. Geochem.* **5,** 13–28.

Yon D. A., Ryback G. and Maxwell J. R. (1982) 2,6,10-trimethyl-7-(3-methyl butyl)-dodecane, a novel sedimentary biomarker compound. *Tetrahedron Lett.* **23,** 2143–2146.