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EFFECTS OF AN OCEANIC ANOXIC EVENT ON THE STABLE CARBON ISOTOPIC COMPOSITION OF EARLY TOARCICAN CARBON

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ABSTRACT. The Early Toarcian transgression is marked by the occurrence of organic carbon-rich shales in large parts of western Europe and in other parts of the world as well. Based on the positive carbon isotope excursion of pelagic limestones in the middle to upper part of the *falciferum* Zone in several of the Tethyan sections, the widespread occurrence of the Early Toarcian shales was explained by an Oceanic Anoxic Event (OAE) (Jenkyns, 1988; Jenkyns and Clayton, 1997). The rapid burial of large amounts of organic carbon, which is rich in ^{12}C , would have led to a relative enrichment in ^{13}C of the global carbon reservoir and hence to an increase in $\delta^{13}\text{C}$ of the limestones. In Southwest Germany (and a number of other locations) both organic and inorganic carbon display a negative isotope excursion in the upper part of the *tenuicostatum* Zone and the lower part of the *falciferum* Zone synchronous to black shale deposition and predating the positive isotopic excursion (Küspert, 1982, 1983). It is presently unclear what the exact cause for this widespread negative isotopic excursion is (Jenkyns and Clayton, 1997).

The objective of our study was to examine if the negative carbon isotope excursion of organic matter (OM) in the Southwest German Toarcian shales can be attributed to compositional changes of the OM, or if the excursion is related to variations in $\delta^{13}\text{C}_{[\text{CO}_2]_{\text{aq}}}$ in the photic zone. To this end, we analyzed the molecular and stable carbon isotope composition of OM in ten samples spanning the Early Toarcian (TOC 2.5-10.5 percent; HI 350-700). Biomarker distributions and kerogen pyrolysates differ only slightly among the samples, and $\delta^{13}\text{C}$ values of primary production markers follow closely those of associated carbonate and kerogen ($\delta^{13}\text{C}_{\text{CARB/TOC}}$). This strongly suggests that differences in $\delta^{13}\text{C}_{\text{TOC}}$ are related to differences in $\delta^{13}\text{C}$ of $[\text{CO}_2]_{\text{aq}}$ in the photic zone supporting Küspert's model of advection of isotopically light, organic matter-derived CO_2 from anoxic bottom waters. Evidence for euxinic conditions extending into the photic zone was found by the presence of derivatives of carotenoids, such as isorenieratane, from anoxygenic phototrophic sulfur bacteria. Their concentrations are extremely low in black shales from the *tenuicostatum* Zone but are significant in the *falciferum* and *bifrons* zone with a maximum in the *exaratum* Subzone suggesting that photic zone euxinia (PZE) was a common feature of the Early Toarcian sea in Southwest Germany. Our data, therefore, support the Küspert model of advection of isotopically light, organic matter-derived CO_2 from anoxic bottom waters to the upper part of the photic zone resulting in a negative isotope spike. The enrichment in ^{13}C in the middle of the *falciferum* Zone, which followed the negative spike, may be attributed to the burial of isotopically light organic matter through worldwide black shale deposition.

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INTRODUCTION

The Liassic epicontinental basins of Central Europe, that is Yorkshire, Northwest German, Southwest German, Paris, and Chalhac Basins, were intermittently open to the Arctic and Tethys oceans, depending on sealevel fluctuations and changes in the connecting water-routes (Katz, 1995). During the Lower Toarcian, coincident with the peak of the Lower Jurassic transgression (Hallam, 1981), highly bituminous shales were deposited in extensive parts of the European epicontinental seas and in parts of the Tethyan continental margins (Loh and others, 1986; Jenkyns and others, 1991; Farrimond and others, 1994; Jenkyns and Clayton, 1997). In addition, contemporaneous black shales occur in western Canada, Japan, Madagascar, Argentina, and on the Arctic Slope. This global occurrence of the synchronous black shale facies led to the hypothesis that organic matter deposition in the Lower Jurassic was due to an Oceanic Anoxic Event, OAE (Jenkyns, 1988), analogous to the Cenomanian/Turonian boundary event (Schlanger and others, 1987; Arthur and others, 1988). The most organic carbon-rich facies of the Lower Toarcian in Germany, the Posidonienschiefer (Posidonia Shale), has long been known for its excellently preserved vertebrate and invertebrate skeletons (for a historical overview, see Oschmann, 1995). Equivalents in England and France are the equally renowned Jet Rock and Schistes Carton, respectively. Generally, the Lower Toarcian shales of northern Europe have a good to excellent oil-generation potential, but oil production is limited due to their relatively low level of thermal maturity (Tissot and others, 1971; Barnard and Cooper, 1981; Espitalié and others, 1988).

The most organic carbon-rich Toarcian shales occur in the upper part of the *tenuicostatum* Zone and the lower part of the *falciferum* Zone (Jenkyns, 1988; Jenkyns and Clayton, 1997). This assumption applies likely to all Europe because Jenkyns (1988), Jimenez and others (1996), and Jenkyns and Clayton (1997) demonstrated that the OM-rich shales in the Tethyan outcrops in Italy, Spain, and England are of identical age to those in Central Europe. Pelagic limestones in the middle to upper part of the *falciferum* Zone, that is after the start of black shale deposition, are in several sections of the European continental margin of the Tethys enriched in ^{13}C (Jenkyns and Clayton, 1986, 1997; Jimenez and others, 1996). In analogy to the Cenomanian-Turonian OAE (Schlanger and others, 1987; Arthur and others, 1988), this positive carbon isotope excursion was explained by Jenkyns and Clayton (1986) by the massive removal of ^{12}C -enriched organic carbon from the global carbon reservoir, through the rapid burial of organic carbon in black shales. Originally, the Toarcian OAE was explained by an oxygen-minimum layer model (Jenkyns, 1985, 1988), but organic geochemical data indicate that, depending on the geographical position, the causes of black shale formation are variable (Farrimond and others, 1989; Hollander and others, 1991). A further complication stems from the fact that in the Italian Monte Brughetto section, in Southwest Germany, and in the Paris Basins, both organic and inorganic carbon exhibit a sharp extensive negative isotope excursion (in many cases significantly larger than the observed positive excursion) at the end of the *tenuicostatum* Zone up to the lower part of the *falciferum* Zone (Küspert, 1982; Moldowan and others, 1986; Jenkyns and Clayton, 1986; Hollander and others, 1991). The same negative excursion has also been recently documented by Jenkyns and Clayton (1997) in sections from Great Britain where they co-occur with black shale deposition and are thought to predate the positive isotope excursion. In the case of the carbonates these negative isotope excursions may be partly explained by diagenetic overprinting, that is the incorporation of isotopically light CO_2 derived from the post-depositional bacterial oxidation of OM (Jenkyns and Clayton, 1986). In the case of the organic carbon, however, a diagenetic cause is unlikely and changes in water column stratification (Küspert, 1982; Hollander and others, 1991; Saelen and others, 1998) or changes in the planktonic community (Jenkyns and Clayton, 1986; Prauss and Riegel, 1989) have been invoked.

The objective of this study was to test if the negative carbon isotope excursion of the organic carbon of the Southwest German Posidonia Shale can be attributed to compositional changes of the nanoflora (Jenkyns and Clayton, 1986; Prauss and Riegel, 1989), or if isotopically light CO_2 was recycled into the photic zone from stagnant waters below (Küspert, 1982, 1983; Saelen and others, 1998). The first model simply assumes that successions of isotopically distinct phytoplanktonic communities were the cause of the negative isotope excursion. The second model (in the following referred to as the Küspert model) is based on the idea that in stagnant bottom waters, CO_2 , derived from the bacterial decomposition of OM, will rise significantly in concentration due to the lack of transport of inorganic carbon. At the same time due to the lack of transport of O_2 and the consumption of O_2 due to bacterial processes, oxygen concentrations are diminished as well, possibly leading to anoxic conditions. The formed CO_2 is isotopically lighter than CO_2 derived from atmospheric CO_2 . If the water column is relatively shallow then, after a seasonal overturn of the water column, isotopically light CO_2 can be mixed with atmospheric CO_2 in the photic zone. Alternatively, the chemocline may be so close to the depth of phytoplankton production that some of the CO_2 is advected or diffused from the stagnant bottom waters to the site of phytoplankton carbon fixation. This recycled CO_2 is then fixed again by phytoplankton, thereby causing a negative shift in the isotopic composition of the primary organic matter and carbonate. Increasingly more stagnant bottom waters will thus lead to a higher build up of isotopically light CO_2 and more negative isotope values for the primary production once part of the water column is seasonally overturned.

To test these two opposing explanations, ten samples spanning the Lower Toarcian were selected for detailed organic geochemical and compound-specific stable carbon isotope analysis. Assuming that to a certain extent the carbon isotopic fractionation between dissolved CO_2 and primary photosynthate was constant, the scenario of CO_2 -recycling leading to a decrease in $\delta^{13}\text{C}$ of dissolved CO_2 ($\delta^{13}\text{C}_{[\text{CO}_2]_{\text{aq}}}$) should result in a ^{13}C -depletion of photoautotrophic biomass. This was tested by measuring the stable carbon isotopic composition of primary production markers. The hypothesis that changes in $\delta^{13}\text{C}$ of the kerogen ($\delta^{13}\text{C}_{\text{TOC}}$) resulted from changes in the planktonic community was verified by examining the molecular composition of bitumen and kerogen pyrolysate. Finally, particular attention was paid to the occurrence of isorenieratene derivatives. These are highly specific markers for photic zone anoxia (Repeta, 1993; Sinninghe Damsté and others, 1993; Koopmans and others, 1996a), and depth profiles of these compounds can potentially provide important insights into the palaeoenvironmental and palaeoceanographic conditions during sediment deposition.

METHODS

Extraction and fractionation.—The powdered samples (approx 70 g) were Soxhlet extracted with methanol (MeOH)/dichloromethane (DCM) (1:7.5 v/v) for 24 hrs. Asphaltenes were removed from the extracts by precipitation in *n*-heptane. Aliquots of the maltene fractions (approx 200 mg), to which a mixture of four standards was added for quantitative analysis (Kohnen and others, 1990), were separated over a column (20 × 2 cm; column volume (V_0) = 35 ml) packed with alumina (activated for 2.5 hrs at 150°C) by elution with hexane/DCM (9:1 v/v; 150 ml; “apolar fraction”) and DCM/MeOH (1:1 v/v; 150 ml; “polar fraction”). Aliquots (approx 10 mg) of the apolar fractions were further separated using a small column (5 × 0.5 cm; V_0 = 1 ml) packed with AgNO_3 impregnated (20 percent w/w; activated for 16 hrs at 120°C) silicagel (Merck, Silicagel 60, 70-230 mesh ASTM) by elution with hexane (saturated hydrocarbons) and ethyl acetate (aromatic hydrocarbons). Saturated hydrocarbon fractions were analyzed by GC, GC-MS, and GC-MSMS. Aromatic hydrocarbon fractions were analyzed by GC and GC-MS.

n-Alkanes were removed from the saturated hydrocarbon fractions by elution over a small column (5 × 0.5 cm; V_0 = 1 ml) packed with a molecular sieve (silicalite) using

cyclohexane as the eluents. In the case of samples T11, T18, T23, and T27, *n*-alkanes were retrieved from the molecular sieve by dissolving the sieve in HF, subsequently neutralizing the solution with Na₂CO₃, and extraction with hexane (×3). Both adducts and non-adducts were analysed using GC-IRMS.

Gas chromatography (GC).—GC was performed using a Carlo Erba 5300 or a Hewlett-Packard 5890 instrument, both equipped with an on-column injector. A fused silica capillary column (25 m × 0.32 mm) coated with CP-Sil 5 (film thickness 0.12 μm) was used with helium as carrier gas. The effluent was monitored by a flame ionisation detector (FID). Samples were injected at 70°C and subsequently the oven was programmed to 130°C at 20°C/min and then at 4°C/min to 320°C, at which it was held for 15 min.

Gas chromatography-mass spectrometry (GC-MS).—GC-MS was carried out on a Hewlett-Packard 5890 gas chromatograph interfaced to a VG Autospec Ultima Q mass spectrometer operated at 70 eV with a mass range *m/z* 50 to 800 and a cycle time of 1.8 s (resolution 1000). The gas chromatograph was equipped with a fused silica capillary column (25 m × 0.32 mm) coated with CP-Sil 5 (film thickness 0.12 μm). Helium was used as carrier gas. The samples were injected at 60°C and subsequently the oven was programmed to 130°C at 20°C/min and then at 4°C/min to 320°C, at which it was held for 15 min.

Gas chromatography-mass spectrometry-mass spectrometry (GC-MSMS).—GC-MSMS was performed on a Hewlett-Packard 5890 gas chromatograph interfaced to a VG Autospec Ultima Q mass spectrometer. The gas chromatograph was equipped with a fused silica capillary column (60 m × 0.25 mm) coated with CP-Sil 5CB-MS (film thickness 0.25 μm). The carrier gas was helium. The gas chromatograph was programmed from 60° to 200°C at a rate of 15°C/min and then at 1.5°C/min to 310°C (10 min). The mass spectrometer was operated at 70 eV with a source temperature of 250°C. Dissociation of the parent ions was induced by collision with argon (collision energy 18–20 eV). The parent ion to daughter ion transitions were analyzed with 20 ms settling and 80 to 100 ms sampling periods. Total cycle time was 1020 ms.

Gas chromatography-isotope ratio mass spectrometry (GC-IRMS).—The DELTA-C GC-IRMS-system used is in principle similar to the DELTA-S system described by Hayes and others (1990). For analysis of the isoprenoid alkanes the gas chromatograph (Hewlett-Packard 5890) was equipped with a fused silica capillary column (25 m × 0.32 mm) coated with CP-Sil 5 (film thickness 0.12 μm). Analyses of diacholestanes was problematic due to coelution problems on the 25m column. Therefore, diacholestanes were analyzed using a CP-Sil 5CB-MS column (60 m × 0.25 mm) with a film thickness of 0.25 μm. Coelutions were minor, but due to the low concentrations and complex mixtures, errors for the reported analyses are fairly high. The oven temperature was programmed from 70° to 130°C at 20°C/min, from 130° to 310°C at 4°C/min, and maintained at 310°C for 15 min. The δ¹³C values (versus PDB) were calculated by integrating the mass 44, 45, and 46 ion currents of the CO₂ peaks produced by combustion of the column effluent and those of CO₂ spikes with a known ¹³C content which were directly led into the mass spectrometer at regular intervals. The δ¹³C values reported are averages of at least two measurements.

Curie-point pyrolysis-gas chromatography (Py-GC).—Py-GC was performed with a Hewlett-Packard 5890 gas chromatograph using a FOM-3LX unit for pyrolysis. Decarbonated (6N HCl) and extracted sediments were applied to a ferromagnetic wire with a Curie-temperature of 610°C. The gas chromatograph, equipped with a cryogenic unit, was programmed from 0°C (5 min) to 310°C (5 min) at a rate of 3°C/min. Separation was achieved using a fused silica capillary column (25 m × 0.32 mm) coated with CP-Sil 5 (film thickness 0.4 μm). Helium was used as the carrier gas.

Curie-point pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was performed using the same equipment and conditions as described above for the Py-GC

in addition to a VG Autospec Ultima mass spectrometer operated at 70 eV with a mass range m/z 50 to 800 and a cycle time of 1.8 s (resolution 1000).

Quantification.—Relative concentrations of C_{16} and C_{18} – C_{20} regular isoprenoid alkanes and n -alkanes were determined by comparison of their peak areas in the FID-trace to that of the internal standard. Aryl- and diaryl isoprenoids were quantified by integration of their peaks in the m/z 133 + 134 mass chromatogram and comparison with the peak area of the internal standard (2-methyl-2-(4,8,12-trimethyltridecyl)chroman) in the m/z 107 + 147 mass chromatogram. Since these ions are the major fragment ions of both the (di)aryl isoprenoids and the internal standard, concentrations were not corrected for the different intensities of the fragment ions.

RESULTS

Sample description and bulk data.—The sampled section is located in the Dotternhausen-Schömberg area, near Tübingen, southwest Germany and comprises the complete Lower Toarcian (fig. 1). The section contains predominantly bituminous shales with intercalated carbonate layers. Bulk parameters determined at regular intervals over the section reveal that TOC-contents and Hydrogen Indices (HI) are generally high in the black shales (figs. 1 and 2). As observed with other sections, the negative carbon isotope excursion of the organic carbon and carbonate starts in the *tenuicostatum* Zone and ends in the middle part of the *falciferum* Zone where the ^{13}C -contents of OM and carbonate reach their maximum (positive excursion as suggested by Jenkyns, 1988) and then slightly shift to somewhat more depleted values (fig. 2).

The samples for this molecular study have been selected to cover the whole Lower Toarcian at characteristic stratigraphic positions in particular relative to the negative carbon isotope anomaly (fig. 2). Samples T6, T8, and T11 are OM-rich bituminous shales intercalated in OM-lean gray marls and were deposited prior to the onset of the main anoxic event. These shales are likely deposited during short-lived anoxic events within an otherwise well ventilated depositional environment. Hydrogen indices (HI) in the shales are around 400, and TOC ranges from 2.5 to 5.8 percent, indicating well preserved marine organic matter. Carbonate contents in these marls and bituminous shales range around 30 percent. Samples T18 and T23 characterize the highstand of the main anoxic event (Esw of Schoell and others, 1999) based on all organic and inorganic bulk properties (fig. 2). Carbon isotopes of organic matter and carbonate are significantly depleted in ^{13}C compared to all other samples, HI values are high (~ 700) and extraction yields are high. Samples T27 and T35 were deposited after the main anoxic event and are thinly breaking, poorly laminated, uniformly dark gray shales and have still relatively high HI values but lower TOC-values (approx 8 percent). T39 is the "Upper Schlacken," a homogeneous bituminous diagenetic replacement carbonate (Schoell and others, 1999). T41 and T45 are bituminous shales, the latter heavily weathered with relatively high TOC-values (9 percent) but somewhat reduced HI-values (~ 580). The OM in all samples is marginally mature with a vitrinite reflectance of approx 0.51 percent (Moldowan and others, 1986), and T_{max} values range from 429° to 435°C (table 1).

Saturated hydrocarbons.—All saturated hydrocarbon fractions are dominated by C_{16} and C_{18} – C_{20} regular isoprenoid alkanes and by series of n -alkanes maximizing at n - C_{16} and n - C_{17} (fig. 3). The n -alkanes do not show an odd-over-even carbon number predominance. Strictly, in samples T35 and T39 distributions of n -alkanes are bimodal, but the second maximum around n - C_{31} is subordinate (fig. 3). Pristane/phytane (pr/ph) ratios vary between 1.5 and 2.8 and are considerably higher in T6, T8, and T11 than in the other samples (table 1). In general, linear and isoprenoid alkanes make up a rather constant part of the apolar fraction.

Gas chromatography-mass spectrometry-mass spectrometry analyses of the steroid mixtures indicate the presence of both regular- and rearranged C_{27} – C_{30} desmethyl- and C_{28} – C_{30} 4-methyl steranes, including dinosterane, in all samples (fig. 4). Ratios of

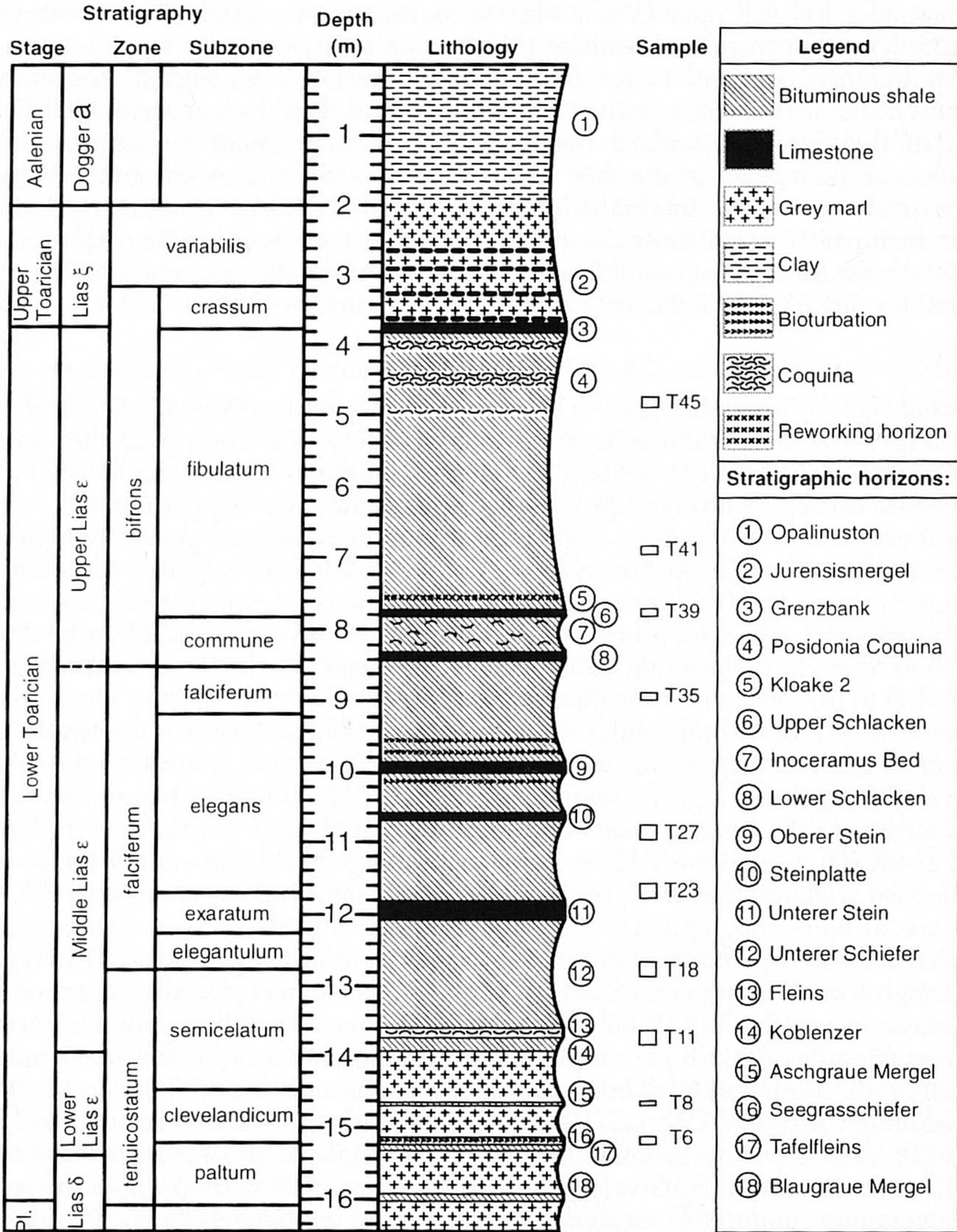


Fig. 1. Lithology and stratigraphic positions of the samples in a composite profile of sampling sites Dotternhausen (T18-T41) and Schömberg (T6-T11, T45) in Southwest Germany (Küspert, 1983).

desmethyl/4-methyl steranes and distributions of desmethyl- ($C_{27} > C_{28} > C_{29} > C_{30}$) and 4-methyl steranes ($C_{28} \gg C_{29} \cong C_{30}$) exhibit no major differences among the samples. However, sterane distributions in T6, T8, and T11 have a less prominent 24-methylcholestane ($C_{27} \gg C_{28} \cong C_{29} \gg C_{30}$) and a slightly higher C_{27} 20S/(20S + 20R) ratio (table 1) than observed in the other samples. Assuming that the thermal history of the Southwest German Basin is similar to that of the Paris Basin, the range of 20S/(20S + 20R) values observed corresponds to a maximum burial depth of less than 1500 m, which is below the zone of hydrocarbon generation (MacKenzie and others, 1980). The ratio of dia-/(dia- + regular) steranes is positively correlated with the ratio of clay/TOC, as discussed elsewhere (van Kaam-Peters and others, 1998b).

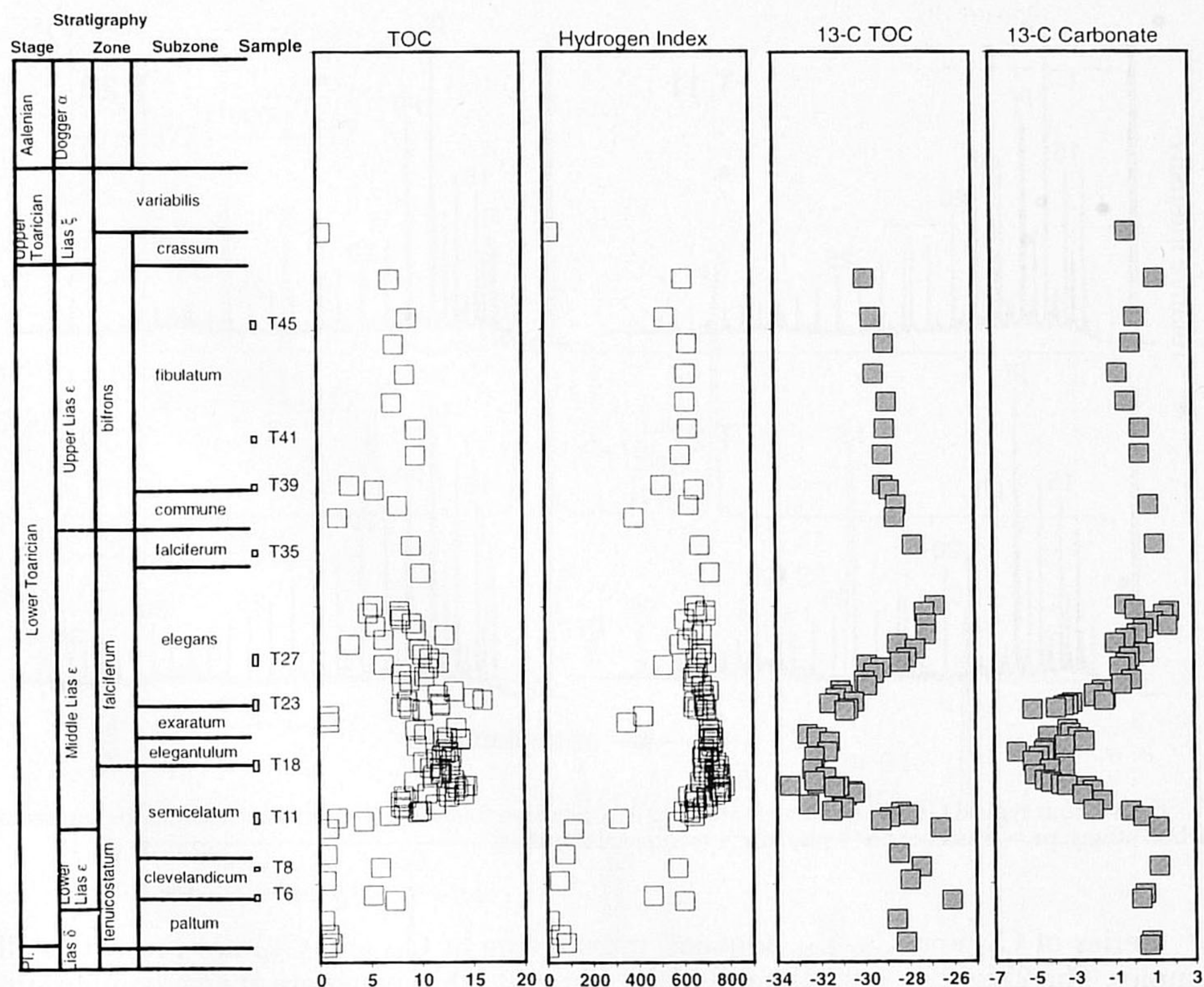


Fig. 2. Bulk data of the composite profile of sampling sites Dotternhausen and Schömberg in Southwest Germany.

TABLE 1
Bulk data, molecular parameters and yields of the different fractions

sample	TOC (%)	T _{max} (°C)	HI*	OI**	δ ¹³ C _{TOC} (‰)	Bitumen***	Asphaltenes***	Maltenes***	Polars***	Apolars***	pr/ph	C ₂₇ 20S/(S+R)
T6	5.8	433	527	12	-28.5	58	2.2	56	25	26	2.75	0.40
T8	3.6	432	424	17	-28.5	84	11	73	28	34	2.49	0.40
T11	2.5	429	364	21	-27.7	76	n.d.****	n.d.	35	8.4	2.31	0.40
T18	10.5	432	672	10	-32.0	94	2.3	92	38	42	1.68	0.35
T23	9.6	431	678	10	-31.7	110	7.6	100	48	41	1.45	0.35
T27	8.4	434	689	11	-28.5	110	10	100	45	44	1.71	0.36
T35	8.4	434	639	9	-27.8	88	13	74	32	32	1.99	0.38
T39	1.3	433	481	10	-29.6	87	n.d.	n.d.	42	34	2.14	0.38
T41	9.6	435	610	11	-29.2	77	8.0	69	29	29	1.89	0.36
T45	8.8	434	543	27	-29.5	83	16	67	30	22	1.84	0.37

*Hydrogen Index; mg HC/g TOC; **Oxygen Index; mg CO₂/g TOC; ***mg/g TOC; ****not determined

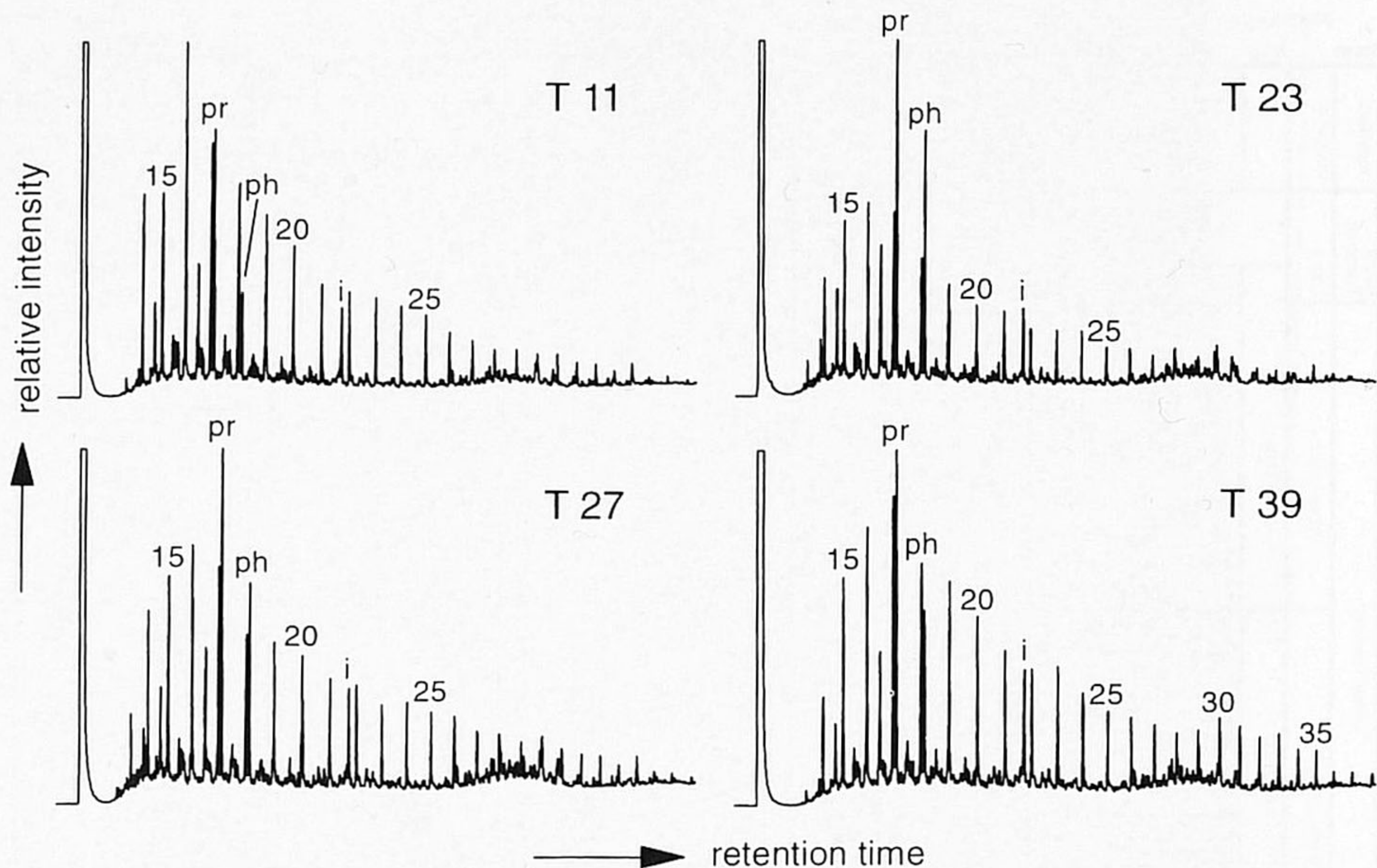


Fig. 3. Four typical GC-FID traces of saturated hydrocarbon fractions. Numbers correspond to number of carbon atoms: pr = pristane; ph = phytane; i = internal standard.

Series of C_{27} and C_{29} - C_{35} hopanes, maximizing at C_{30} and C_{31} , are present in all samples. The $22S/(22S + 22R)$ ratios of the $17\alpha,21\beta(H)$ -hopanes are at near equilibrium values (0.57-0.62; Peters and Moldowan, 1993; van Duin and others, 1997). Relative to the steranes, hopanes are most abundant in samples T6, T8, and T11.

Aromatic hydrocarbons.—The aromatic hydrocarbon fractions of all samples are dominated by mono- and tri-aromatic steroids, alkylbenzothiophenes, alkyl dibenzothiophenes, and alkyl naphthalenes. Distributions of these compounds have been used as molecular parameters in oil-generation studies (Tissot and others, 1971; Radke and Willsch, 1991, 1994) or in studies addressing the maturation or environmental conditions during deposition of the rocks (Moldowan and others, 1986; Lichtfouse and others, 1994). Here we describe only the diagenetic derivatives of mono- and diaromatic carotenoids.

A series of C_{13} - C_{21} aryl isoprenoids with a trimethyl substitution pattern of the aromatic ring and with the usual low abundance of the C_{17} member (Summons and Powell, 1987) is present in all samples. Their concentrations are highest in samples T18, T23, T27, and T41 (fig. 5A). Depending on the sample, up to three carotenoid derivatives with an intact carbon skeleton are present. Unlike the short-chain derivatives, these C_{40} components are extremely low in samples T6, T8, and T11 (fig. 5B). Concentrations of isorenieratane (I, see app.), identified by coinjection of an authentic standard, are variable and show a distinct optimum in T23. Chlorobactane (II), identified by coinjection of an authentic standard, is absent in T6, T8, and T11, and in the other samples its concentration is rather constant. β -Isorenieratane (III) was detected in all samples except T11, and it reaches its highest concentration in T41.

Molecular carbon isotope data.—Samples T18 and T23 are in the negative carbon isotope excursion in (figs. 2 and 6, table 1), which starts at the upper part of the *tenuicostatum* Zone and at the transition of the *exaratum* and *elegans* Subzones, respec-

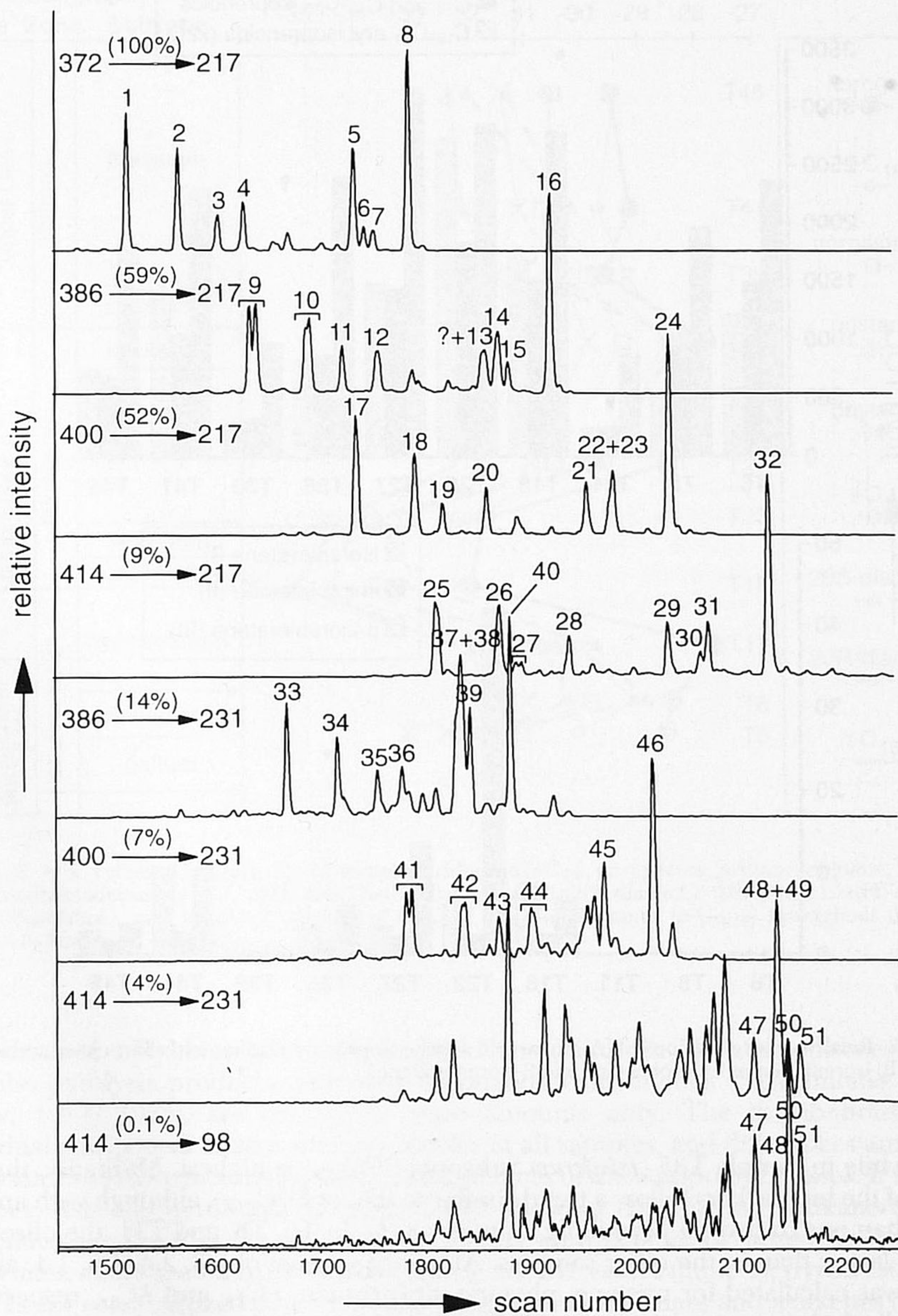


Fig. 4. Chromatograms showing desmethyl and 4-methyl sterane distributions in sample T41. The data were acquired by collisionally activated decomposition GC-MSMS. Each trace is identified with the masses of the parent and daughter ion, and the intensity of the base peak expressed as a percentage relative to the intensity of the 5α -cholestane peak. Chromatograms were smoothed at 3 points of equal weight. Numbers refer to components listed in table 6.2. The doublets of some of the diasteranes (for example compounds 9, 10, 41, and 42) are thought to represent 24S and 24R isomers.

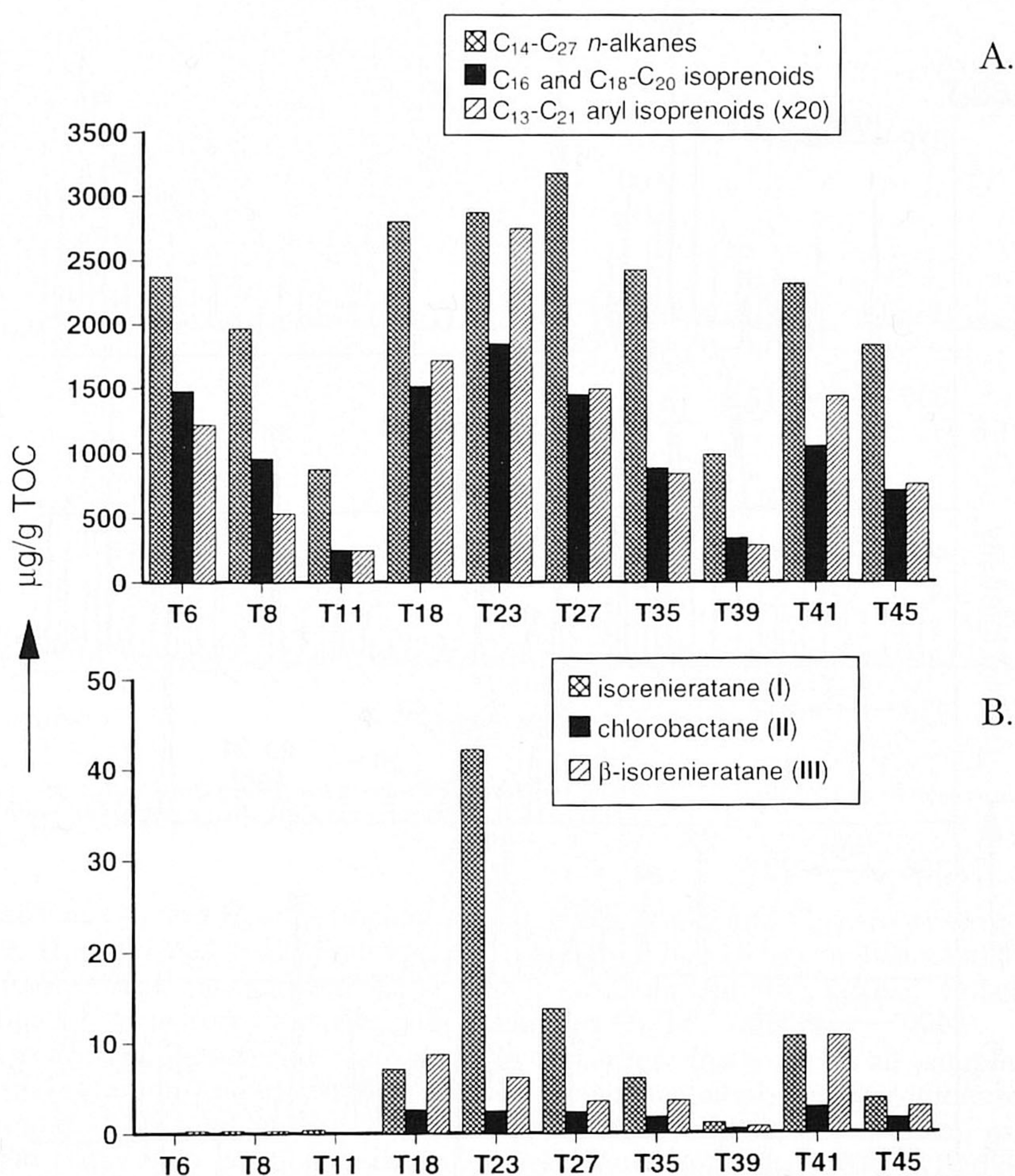


Fig. 5. Relative concentrations of (A) linear and acyclic isoprenoid alkanes and short-chain aryl isoprenoids and (B) isorenieratane, chlorobactane and β -isorenieratane.

tively, while in sample T35 (*falciferum* Subzone) $\delta^{13}\text{C}_{\text{TOC}}$ is highest. Markedly, the $\delta^{13}\text{C}$ values of the biomarkers follow a trend similar to that of $\delta^{13}\text{C}_{\text{TOC}}$, although with an offset of less than one to several permil (fig. 6; tables 3, 4). In T6, T8, and T11, the offset is on average larger than in the other samples. An average offset of 3.3, 2.4, 1.6, 1.4, and 0.7 permil was calculated for pristane, phytane, norpristane, $i\text{-C}_{21}$, and $i\text{-C}_{16}$, respectively. For the diacholestanes such an average was not determined, since they have less accurate $\delta^{13}\text{C}$ values due to the fact that they elute at the beginning of an unresolved complex mixture. The weighted average of $\delta^{13}\text{C}$ of $\text{C}_{16}\text{-C}_{19}$ n -alkanes, components abundantly present in algae (Gelpi and others, 1970), falls close to the $\delta^{13}\text{C}$ values of pristane and phytane (fig. 6).

Due to coelution and due to their relatively low abundance it was not possible to determine the ^{13}C content of any of the aryl- and diaryl isoprenoids.

Kerogen pyrolysates.—The kerogen pyrolysates of all samples are predominantly composed of homologous series of n -alkanes and n -alkenes and shorter series of

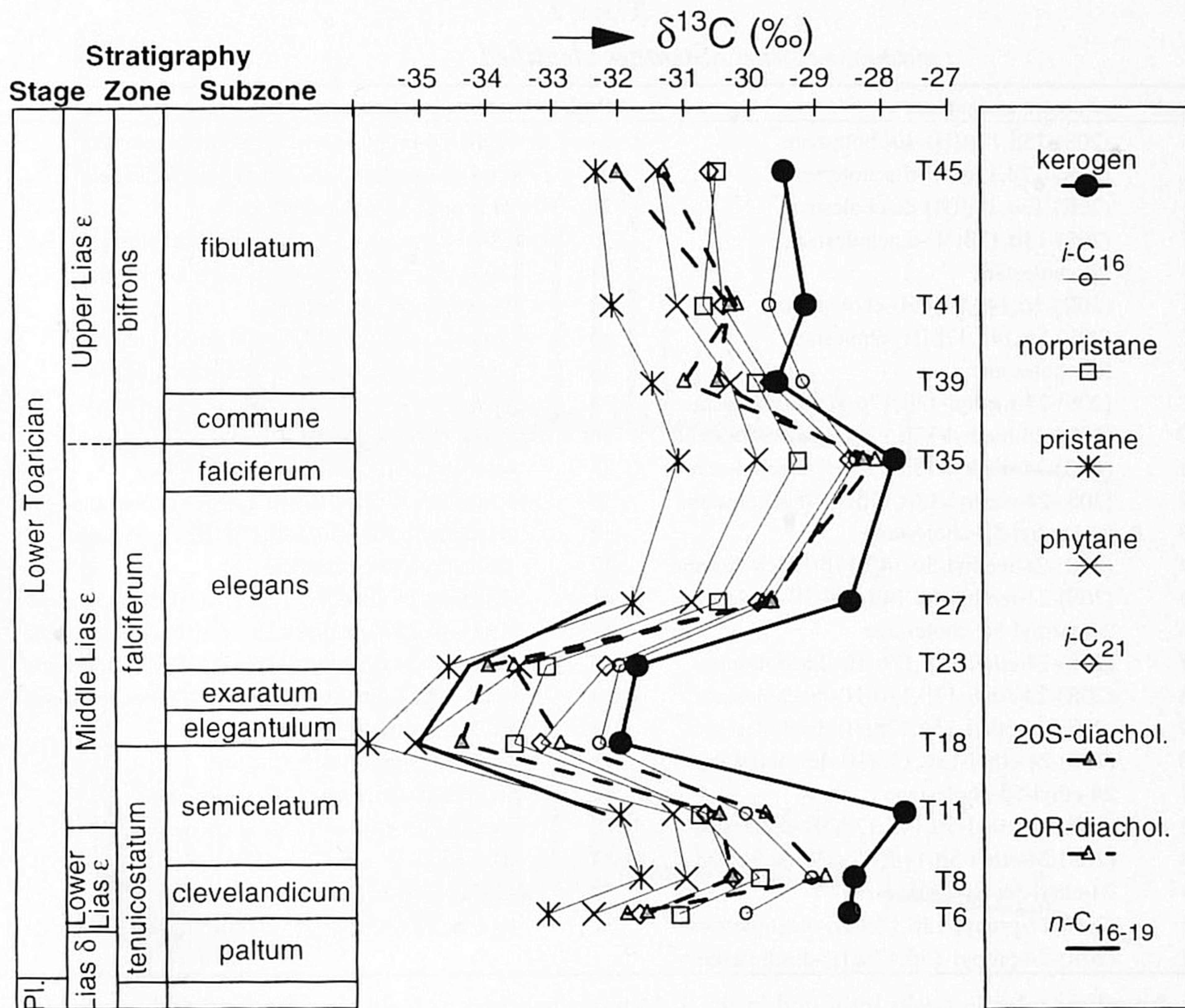


Fig. 6. $\delta^{13}\text{C}$ values of kerogen, 2,6,10-trimethyltridecane ($i\text{-C}_{16}$), norpristane, pristane, phytane, 2,6,10,14-tetramethylheptadecane ($i\text{-C}_{21}$), (20S)-13 β ,17 α (H)-diacholestane (20S-diachol.), (20R)-13 β ,17 α (H)-diacholestane (20R-diachol.), and weighted average of $\delta^{13}\text{C}$ of $\text{C}_{16}\text{-C}_{19}$ n -alkanes ($n\text{-C}_{16-19}$) throughout the Lower Toarcian in Southwest Germany.

alkylbenzenes, alkylthiophenes, alkyl-naphthalenes, and alkylbenzothiophenes (fig. 7). Phenolic pyrolysis products, probably originating from lignins (Saiz-Jimenez and de Leeuw, 1984, 1986), are present in trace amounts only. The distributions of the individual compound classes are very similar in all samples, and differences among the pyrolysates mainly concern the relative abundances of the compound classes. It is noted, however, that the pyrolysate of sample T39 shows a drop in the n -alkane/ n -alkene distribution at $\text{C}_{17}\text{-C}_{18}$ (fig. 7A), which is less conspicuous or absent in the other pyrolysates. As expected from their relatively low HI values (table 1), pyrolysates of T8 and T11 are characterized by a smaller contribution of n -alkanes and n -alkenes (fig. 7C). The other pyrolysates show a higher, more or less constant ratio of n -alkane/ n -alkene doublets over aromatic- and thiophenic pyrolysis products, but the proportions of aromatic and thiophenic compounds vary (figs. 7B-C). The contribution of organic sulfur compounds to the pyrolysate is positively correlated with HI and is greatest in the pyrolysates of T18, T23, T27, and T35. These latter pyrolysates are also virtually identical. In sediments from the Kimmeridge Clay formation an increase in ^{13}C -content was noted with increasing amounts of thiophenes in the pyrolysate due to an increasing amount of sulfurized carbohydrates (Van Kaam-Peters and others, 1998a; Sinninghe Damsté and others, 1999). In our case, however, the samples with the highest amounts of

TABLE 2
Steranes identified

Peak [*]	structure assignment	Peak [*]	structure assignment
1	(20S)-13 β ,17 α (H)-diacholestane ^{**}	27	(20R)-24-propyl-13 α ,17 β (H)-diacholestane ^{***}
2	(20R)-13 β ,17 α (H)-diacholestane ^{**}	28	(20S)-24-propyl-13 α ,17 β (H)-diacholestane ^{***}
3	(20R)-13 α ,17 β (H)-diacholestane ^{**}	29	24-propyl-5 β -cholestane
4	(20S)-13 α ,17 β (H)-diacholestane ^{**}	30	(20R)-24-propyl-5 α ,14 β ,17 β (H)-cholestane
5	5 β -cholestane	31	(20S)-24-propyl-5 α ,14 β ,17 β (H)-cholestane
6	(20R)-5 α ,14 β ,17 β (H)-cholestane	32	24-propyl-5 α -cholestane
7	(20S)-5 α ,14 β ,17 β (H)-cholestane	33	(20S)-4 α -methyl-13 β ,17 α (H)-diacholestane ^{***}
8	5 α -cholestane	34	(20R)-4 α -methyl-13 β ,17 α (H)-diacholestane ^{***}
9	(20S)-24-methyl-13 β ,17 α (H)-diacholestane ^{***}	35	(20R)-4 α -methyl-13 α ,17 β (H)-diacholestane ^{***}
10	(20R)-24-methyl-13 β ,17 α (H)-diacholestane ^{***}	36	(20S)-4 α -methyl-13 α ,17 β (H)-diacholestane ^{***}
11	(20R)-24-methyl-13 α ,17 β (H)-diacholestane ^{***}	37	4 α -methyl-5 β -cholestane
12	(20S)-24-methyl-13 α ,17 β (H)-diacholestane ^{***}	38	4 α -methyl-(20R)-5 α ,14 β ,17 β (H)-cholestane
13	24-methyl-5 β -cholestane	39	4 α -methyl-(20S)-5 α ,14 β ,17 β (H)-cholestane
14	(20R)-24-methyl-5 α ,14 β ,17 β (H)-cholestane	40	4 α -methyl-5 α -cholestane
15	(20S)-24-methyl-5 α ,14 β ,17 β (H)-cholestane	41	(20S)-4 α ,24-dimethyl-13 β ,17 α (H)-diacholestane ^{***}
16	24-methyl-5 α -cholestane	42	(20R)-4 α ,24-dimethyl-13 β ,17 α (H)-diacholestane ^{***}
17	(20S)-24-ethyl-13 β ,17 α (H)-diacholestane ^{***}	43	(20R)-4 α ,24-dimethyl-13 α ,17 β (H)-diacholestane ^{***}
18	(20R)-24-ethyl-13 β ,17 α (H)-diacholestane ^{***}	44	(20S)-4 α ,24-dimethyl-13 α ,17 β (H)-diacholestane ^{***}
19	(20R)-24-ethyl-13 α ,17 β (H)-diacholestane ^{***}	45	4 α ,24-dimethyl-5 β -cholestane
20	(20S)-24-ethyl-13 α ,17 β (H)-diacholestane ^{***}	46	4 α ,24-dimethyl-5 α -cholestane
21	24-ethyl-5 β -cholestane	47	4 α ,23S,24S-trimethyl-5 α -cholestane ^{****}
22	(20R)-24-ethyl-5 α ,14 β ,17 β (H)-cholestane	48	4 α ,23S,24R-trimethyl-5 α -cholestane ^{****}
23	(20S)-24-ethyl-5 α ,14 β ,17 β (H)-cholestane	49	4 α -methyl-24-ethyl-5 α -cholestane
24	24-ethyl-5 α -cholestane	50	4 α ,23R,24R-trimethyl-5 α -cholestane ^{****}
25	(20S)-24-propyl-13 β ,17 α (H)-diacholestane ^{***}	51	4 α ,23R,24S-trimethyl-5 α -cholestane ^{****}
26	(20R)-24-propyl-13 β ,17 α (H)-diacholestane ^{***}		

*numbers refer to peaks indicated in fig. 4; **stereochemistry at C-20 after Sieskind and others (1995); ***assuming the elution order to be similar to that of the diacholestanes; ****stereochemistries at C-23 and C-24 after Moldowan (pers. comm., 1994)

thiophenes are the ones with the most depleted ¹³C-contents suggesting that the phenomenon observed with the Kimmeridge Clay sediments are not responsible for the changes in the stable carbon isotopic composition of organic carbon.

DISCUSSION

Environmental reconstruction based on distribution of compounds.—In all samples, the proportion of terrestrial OM is small (Schoell and others, 1999), consistent with the small amounts of long-chain odd-numbered *n*-alkanes in the extracts (Eglinton and others, 1962) and the almost absence of phenolic compounds in the kerogen pyrolysates (Saiz-Jimenez and de Leeuw, 1984, 1986). The short-chain *n*-alkanes and steranes in the saturated hydrocarbon fractions (fig. 3) are predominantly derived from algae (Gelpi and others, 1970; Volkman, 1986). Based on sterane distributions, pr/ph ratios, and relative abundance of hopanes, samples in the lower *tenuicostatum* Zone (T6, T8, and T11) differ from those higher in the sedimentary sequence. The slightly different desmethyl sterane distribution of T6, T8, and T11 as opposed to the rest of the samples may be related to the change in the assemblage of palynomorphs reported by Prauss and others (1991). These authors, in their study of the Posidonia shales near Zimmern (Southwest Germany), report an almost complete replacement of dinocysts and acritarchs by prasino-phytes at the *tenuicostatum/falciferum* transition where the anoxically deposited sediments are present. In this respect it is noteworthy that the relative abundance and distribution of 4-methyl steranes, components that are generally ascribed to dinoflagellates (de Leeuw and others, 1983; Summons and others, 1987, 1992), do not exhibit any changes

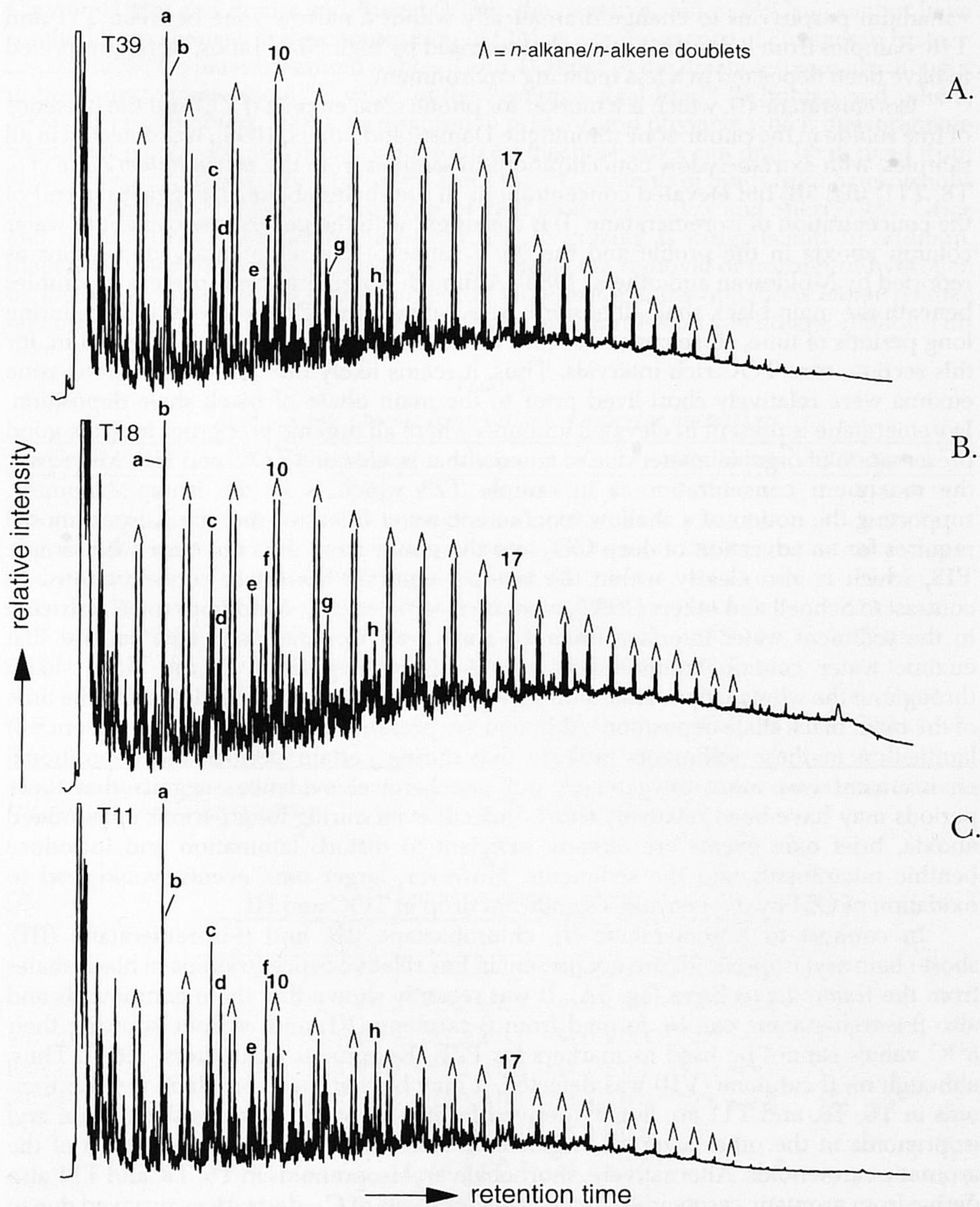


Fig. 7. Gas chromatograms of flash pyrolysates (Curie-temperature 610°C) of kerogens of samples (A) T39, (B) T18, and (C) T11. Legend: a = toluene; b = 2-methylthiophene; c = 2,5-dimethylthiophene + 1,3-dimethylbenzene + 1,4-dimethylbenzene; d = 1,2-dimethylbenzene; e = 2-ethyl-5-methylbenzene + 1-ethyl-3-methylbenzene + 1-ethyl-4-methylbenzene; f = 1,2,4-trimethylbenzene; g = 1,2,3,4-tetramethylbenzene; h = methylnaphthalene + methylbenzothiophene.

along this transition. The succession dinocysts–acritarchs–prasinophytes was attributed to a decreasing salinity of the photic zone, ultimately leading to density stratification and anoxic conditions in at least the lower part of the water column (Prauss and others, 1991). In agreement with this, Moldowan and others (1986) found the ratio of nickel to

vanadium porphyrins to change dramatically within a narrow zone between T11 and T18. Samples from below this zone, characterised by high Ni/V ratios, were interpreted to have been deposited in a less reducing environment.

Isorenieratane (I), which is a marker for photic zone euxinia (PZE) and the presence of free sulfide in the photic zone (Sinninghe Damsté and others, 1993), was detected in all samples, with extremely low concentrations in samples from the *tenuicostatum* Zone (T6, T8, T11) (fig. 5B) but elevated concentrations in the shales above. The general trend of the concentration of isorenieratane (I) is consistent with the general assessment of water column anoxia in the profile and the Ni/V ratios of the sedimentary porphyrins as reported by Moldowan and others (1986). Although isorenieratane is present in samples beneath the main black shale deposition, it is unlikely that PZE was established during long periods of time, since concentrations are low, and the markers are detected in, for this section, rare TOC-rich intervals. Thus, it seems likely that periods of photic zone euxinia were relatively short-lived prior to the main phase of black shale deposition. Isorenieratane is present in elevated amounts where all organic properties indicate good preservation of organic matter due to anoxia (that is, elevated TOC and HI). Moreover, the maximum concentration is in sample T23 which is in the isotope anomaly, supporting the notion of a shallow oxic/anoxic water interface that the Küspert model requires for an advection of deep CO₂ into the photic zone. It is not clear why sample T18, which is also clearly within the isotope anomaly has lower concentrations. In contrast to Schoell and others (1999), who inferred the anoxic conditions to be restricted to the sediment water interface (their Es zone), our isorenieratane data suggest that euxinic water column conditions prevailed during deposition of the black shales throughout the whole Upper Lias, although this occurred predominantly during the time of the main black shale deposition. Although the presence of benthos and the absence of lamination in these sediments indicate that during certain periods the depositional environment was more oxygenated, our geochemical evidence suggests that these periods may have been relatively short. Indeed, even during long periods of sustained anoxia, brief oxic events are already sufficient to disturb lamination and introduce benthic microfossils into the sediments. However, larger oxic events would lead to oxidation of OM by oxygen and a significant drop in TOC and HI.

In contrast to isorenieratane (I), chlorobactane (II), and β -isorenieratane (III), short-chain aryl isoprenoids are not present in low relative concentrations in black shales from the *tenuicostatum* Zone (fig. 5A). It was recently shown that these compounds and also β -isorenieratane can be formed from β -carotene (VI) and without knowing their $\delta^{13}\text{C}$ values cannot be used as markers for PZE (Koopmans and others, 1996). Thus, although no β -carotane (VII) was detected, it may be that the short-chain aryl isoprenoids in T6, T8, and T11 are largely derived from β -carotene, whereas short-chain aryl isoprenoids in the other samples originate, at least in part, from one or more of the aromatic carotenoids. Alternatively, short-chain aryl isoprenoids in T6, T8, and T11 also derive from aromatic carotenoids, but smaller amounts of C₄₀ derivatives survived due to differences in diagenesis. For example, if deposition of samples T6, T8, and T11 was followed by relatively longer periods in which bottom waters were oxygenated (as suggested by lower HI values), this may have led to selective degradation of the C₄₀ compounds consistent with high Ni/V ratios.

Variations in stable carbon isotopic compositions.—Apart from the minor differences discussed above, the composition of the saturated hydrocarbon fraction is very similar in all samples, and differences that do occur show no correlation with $\delta^{13}\text{C}_{\text{TOC}}$. Differences among the kerogen pyrolysates are somewhat more pronounced but do not correspond to changes in $\delta^{13}\text{C}_{\text{TOC}}$ either. Moreover, exactly the pyrolysates of samples in the *falciferum* Zone (T18, T23, T27, and T35), which have very different $\delta^{13}\text{C}_{\text{TOC}}$ values (fig. 6), are most alike. This strongly suggests that, contrary to the views of Jenkyns and

Clayton (1986) and Prauss and Riegel (1989), the negative shift in $\delta^{13}\text{C}_{\text{TOC}}$ cannot have resulted from changes in the composition of OM as a consequence of changes in biota.

Of all $\delta^{13}\text{C}$ values measured (tables 3 and 4), those of the diacholestanes are thought to best approximate the $\delta^{13}\text{C}$ value of the "average algal lipid" (Schouten and others, 1998; Grice and others, 1998). As opposed to pristane and phytane, which may originate from both eukaryotic and prokaryotic sources, diacholestanes can only be derived from algae or heterotrophs grazing on them. Since the ^{13}C contents of lipids from heterotrophs are not significantly different from those of their food source (Fry and Sherr, 1984; Grice and others, 1998), isotopic fractionation due to grazing is insignificant. In addition, diagenetic transformations of biomarkers involving the removal or transfer of hydrogen or methyl groups, are not accompanied by large isotopic fractionations either (Hauke and others, 1992; Freeman and others, 1994a; van Kaam-Peters and others, 1998b). This

TABLE 3
Stable carbon isotopic compositions of different biomarkers

sample	$i\text{-C}_{16}^*$	norpristane	pristane	phytane	$i\text{-C}_{21}^{**}$	20S-diachol. ^{***}	20R-diachol. ^{****}
T6	-30.1 ± 0.1	-31.1 ± 0.1	-33.1 ± 0.1	-32.4 ± 0.1	-31.7 ± 0.5	-31.6 ± 0.1	-31.9 ± 0.5
T8	-29.1 ± 0.4	-29.9 ± 0.1	-31.7 ± 0.1	-31.0 ± 0.1	-30.3 ± 0.9	-30.3 ± 0.3	-28.9 ± 0.3
T11	-30.1 ± 0.2	-30.8 ± 0.2	-32.0 ± 0.2	-31.2 ± 0.2	-30.7 ± 0.5	-30.5 ± 0.2	-29.8 ± 1.3
T18	-32.3 ± 0.5	-33.6 ± 0.5	-35.8 ± 0.2	-35.1 ± 0.2	-33.2 ± 1.0	-34.4 ± 0.8	-32.9 ± 1.9
T23	-32.0 ± 0.3	-33.1 ± 0.3	-34.6 ± 0.3	-33.5 ± 0.3	-32.2 ± 0.2	-34.0 ± 0.1	-33.6 ± 1.2
T27	-29.7 ± 0.1	-30.5 ± 0.2	-31.8 ± 0.2	-30.9 ± 0.1	-29.9 ± 0.2	-29.7 ± 0.5	-29.8 ± 1.1
T35	-28.4 ± 0.2	-29.3 ± 0.9	-31.1 ± 0.3	-29.9 ± 0.1	-28.5 ± 0.9	-28.3 ± 0.4	-28.1 ± 0.3
T39	-29.2 ± 0.7	-29.9 ± 0.3	-31.5 ± 0.1	-30.3 ± 0.2	-29.7 ± 1.1	-30.5 ± 0.5	-31.0 ± 0.1
T41	-29.7 ± 0.3	-30.7 ± 0.5	-32.1 ± 0.3	-31.1 ± 0.4	-30.4 ± 0.5	-30.3 ± 0.6	-30.2 ± 0.3
T45	-29.4 ± 0.1	-30.5 ± 0.1	-32.3 ± 0.3	-31.4 ± 0.3	-30.6 ± 0.2	-32.0 ± 0.6	-31.3 ± 1.1

Note: Numbers are \pm standard deviations; *2,6,10-trimethyltridecane; **2,6,10,14-tetramethylheptadecane; ***20S-13 β ,17 α (H)-diacholestane; ****20R-13 β ,17 α (H)-diacholestane

TABLE 4
 $\delta^{13}\text{C}$ values of free n-alkanes

	T11 [*]	T18	T23	T27 [*]
$n\text{-C}_{16}$	-30.6 ± 0.5	-34.6 ± 0.5	-34.4 ± 0.3	-31.7 ± 0.6
$n\text{-C}_{17}$	-32.9 ± 0.6	-35.2 ± 0.1	-34.6 ± 0.3	-32.6 ± 0.4
$n\text{-C}_{18}$	-32.8 ± 0.9	-35.2 ± 0.1	-34.0 ± 0.3	-32.4 ± 0.1
$n\text{-C}_{19}$	-33.4 ± 0.7	-35.2 ± 0.2	-34.1 ± 0.1	-32.2 ± 0.7
$n\text{-C}_{20}$	-33.5 ± 0.3	-35.2 ± 0.1	-34.2 ± 0.4	-32.8 ± 0.3
$n\text{-C}_{21}$		-35.2 ± 0.1	-35.0 ± 0.6	
$n\text{-C}_{22}$		-34.7 ± 0.4	-34.2 ± 0.5	
$n\text{-C}_{23}$		-34.7 ± 0.1	-35.1 ± 0.7	
$n\text{-C}_{24}$		-34.9 ± 0.1	-34.8 ± 1.3	
$n\text{-C}_{25}$		-34.3 ± 0.1	-34.5 ± 1.4	
$n\text{-C}_{26}$		-33.8 ± 0.9	-34.7 ± 1.2	
$n\text{-C}_{27}$		-33.7 ± 0.1	-32.3 ± 0.3	
$n\text{-C}_{28}$		-32.8 ± 0.1	-32.3 ± 0.2	
$n\text{-C}_{29}$		-32.6 ± 0.4	-32.6 ± 0.9	
$n\text{-C}_{30}$		-32.3 ± 1.8	-32.2 ± 1.5	
$n\text{-C}_{31}$		-33.5 ± 0.1	-33.3 ± 0.8	

Note: Numbers are \pm standard deviation; * C_{20+} n-alkanes were contaminated.

implies that the ^{13}C concentration of the diacholestanes reflects the original carbon isotope signature of the algal lipids.

The $\delta^{13}\text{C}$ values of 20S and 20R 13 β ,17 α (H)-diacholestane follow a trend similar to that of $\delta^{13}\text{C}_{\text{TOC}}$ (fig. 6). Also, depending on carbon number, the $\delta^{13}\text{C}$ values of the acyclic isoprenoids have an individual, almost constant offset from $\delta^{13}\text{C}_{\text{TOC}}$ (fig. 6). It is unclear whether they are derived from different sources since large variations have been reported for ^{13}C -contents compounds of different isoprenoid structures in cultured algae (Schouten and others, 1998). In samples from the *tenuicostatum* Zone (T6, T8, T11), the difference between $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}$ of the acyclic isoprenoids is somewhat larger than in the other samples (fig. 6).

The fact that 20S and 20R 13 β ,17 α (H)-diacholestane and other, more general lipids, like pristane, phytane and short-chain *n*-alkanes (Goossens and others, 1984; Volkman, 1986; Volkman and Maxwell, 1986; Gelpi and others, 1970), all follow synchronously the isotope excursion of organic and inorganic carbon, indicates that differences in $\delta^{13}\text{C}_{\text{TOC}}$ are related to differences in $[\text{CO}_2]_{\text{aq}}$ or $\delta^{13}\text{C}_{\text{CO}_2}$ in the photic zone. The magnitude of the isotopic excursion in the primary producer molecules (approx 5 permil, fig. 4 and table 1) is the same as that observed for the carbonate (approx 5 permil, fig. 2), and thus the relative fractionation between dissolved inorganic carbon (DIC) and OM has remained constant. Since this depends amongst others on $[\text{CO}_2]_{\text{aq}}$ (Laws and others, 1995; Goericke and others, 1994), the constant fractionation suggests no significant changes in the concentration of CO_2 , and thus the changes must have been caused by changes of $\delta^{13}\text{C}_{\text{CO}_2}$ in the photic zone. This fits very well with the scenario of Küspert (1982) that during deposition of the low $\delta^{13}\text{C}_{\text{TOC}}$ samples, isotopically light CO_2 , released from the mineralization of OM in stagnant bottom waters, was recycled into the photic zone.

The effect of CO_2 -recycling on $\delta^{13}\text{C}_{\text{CO}_2}$.—If indeed recycling of CO_2 had a large effect on $\delta^{13}\text{C}_{\text{CO}_2}$ in the surface water and thus on $\delta^{13}\text{C}_{\text{TOC}}$, it must have been that waters rich in organic-derived CO_2 were at a close distance from the photic zone during the upper part of the *tenuicostatum* Zone and the lower part of the *falciferum* Zone. In cases that the oxic/anoxic interface was located in the photic zone, mixing of CO_2 present in anoxic waters with relatively high $[\text{CO}_2]_{\text{aq}}$ and low $\delta^{13}\text{C}_{\text{CO}_2}$, and CO_2 present in surface waters with relatively low $[\text{CO}_2]_{\text{aq}}$ and high $\delta^{13}\text{C}_{\text{CO}_2}$, must have been optimal during seasonal overturns of part of the water column. Since isorenieratane, indicating PZE, was detected in all samples, although to a lesser extent in the oldest samples, one could hypothesise that $\delta^{13}\text{C}_{\text{TOC}}$ is related to the frequency or duration of PZE. The highly variable concentrations of isorenieratane (fig. 5B), showing no correlation with $\delta^{13}\text{C}_{\text{TOC}}$, argue against this hypothesis. However, it is not clear if concentrations of isorenieratane properly reflect the intensity of CO_2 recycling, since in some depositional environments with PZE, recycling of CO_2 is not sufficient to have an influence on the DIC produced in the upper part of the water column.

This point can be illustrated with some recent analogues. Considering the shallow position of the chemocline in the Black Sea (that is, 80 m; Repeta and others, 1989), it may be suggested that if recycling of CO_2 has an effect on $\delta^{13}\text{C}_{\text{TOC}}$, this should currently be taking place in the Black Sea photic zone. Indeed, Goyet and others (1991) report a large increase in $[\text{CO}_2]_{\text{aq}}$ at depths below 40 m in the Black Sea. Starting from 17 to 21 $\mu\text{mol kg}^{-1}$ in the upper 40 m of the photic zone, $[\text{CO}_2]_{\text{aq}}$ reaches 39 $\mu\text{mol kg}^{-1}$ at a depth of 50 m and 71 $\mu\text{mol kg}^{-1}$ at 65 m. Below 65 m, $[\text{CO}_2]_{\text{aq}}$ gradually rises to reach a concentration of 95 $\mu\text{mol kg}^{-1}$ at 1500 m. Markedly, the large increase in $[\text{CO}_2]_{\text{aq}}$ with depth in the 40 to 65 m interval is accompanied by a decrease in $\delta^{13}\text{C}_{\text{CO}_2}$ of only 0.6 permil, and the overall decrease in $\delta^{13}\text{C}_{\text{CO}_2}$ over the first 65 m amounts to only 4 permil (Freeman and others, 1994b). Therefore, if we want to explain the 4 permil difference in $\delta^{13}\text{C}_{\text{TOC}}$ of the Early Toarcian shales by recycling of ^{13}C depleted, organic matter-

derived CO_2 , the majority of biomass must have been produced at depths near the $[\text{CO}_2]_{\text{aq}}$ maximum in the photic zone. The stable carbon isotope data of particulate organic carbon reported by Fry and others (1991) and of lipids by Freeman and others (1994b) show that in the contemporary Black Sea this is not the case. In the Black Sea, $\delta^{13}\text{C}$ of the particulate organic carbon was found generally to increase with depth (-25 to -22 permil), which suggests that most of the newly produced, isotopically light biomass decomposes rather quickly. Consequently, OM reaching the sea floor will largely bear the carbon isotopic signal of biomass produced in the upper part of the photic zone, where CO_2 is largely derived from the atmosphere. The relatively high $\delta^{13}\text{C}$ values of phytoplanktonic lipids in recent Black Sea sediments (Freeman and others, 1994b) are in agreement with this.

The effect of CO_2 -recycling on the stable carbon isotopic composition of photoautotrophic biomass is, however, much more noticeable in systems that have a very shallow chemocline (in the upper 20 m) and a shallow water column such as meromictic lakes. For instance, Lake Cadagno (Switzerland) is a shallow meromictic lake with a chemocline located approx 8 to 12 m from the air-water interface. The $\delta^{13}\text{C}$ value of phytol derived from collected green algal cell material is approx -34 permil (Putschew and others, 1996), which corroborates with the equally light carbon isotopic values for steroids at approx -35 permil extracted from sediment cores of the lake (Schaeffer and others, 1998). These values are much lighter than those reported for compounds derived from photoautotrophic eukaryotes of, for instance, the Black Sea (Freeman and others, 1994b). This suggests an input of isotopically light CO_2 , from below the chemocline into the upper part of the water column after seasonal overturns of the water column. Indeed, Wachniew and Rozanski (1997) calculated for a shallow mid-altitude lake (approx 22 m water depth; Lake Goszcz, Poland) that about two-thirds of the DIC was supplied by remineralization of organic matter. Their data show that even during spring, when the stratification of the water column is re-established after being overturned in the winter, the $\delta^{13}\text{C}_{\text{DIC}}$ is still about 4 to 5 permil lighter than that expected on the basis of pure atmospheric CO_2 -exchange. Thus, during times when primary producers such as algae bloom the isotopic composition of the CO_2 which is fixated is isotopically lighter by several permil.

Considering this, it is interesting to note that chlorobactene, the biological precursor of chlorobactene (II), is biosynthesized only by the green-colored strains of Chlorobiacae (de Wit and others, 1995). These strains require more light for photosynthesis than the brown-colored strains (Pfennig, 1989), which biosynthesize isorenieratene, the biological precursor of III. Hence, this suggests strongly that the chemocline in the depositional environment of the Toarcian Southwest Germany must have been much more shallow than in today's Black Sea. Indeed, sediments of the Black Sea only contain isorenieratane (III) (Sinninghe Damste and others, 1993) and no trace of chlorobactane. In contrast, chlorobactane is found in shallow lake systems such as Lake Cadagno (Schaeffer and others, 1998) and Ace Lake (Kok and others, unpublished results) where intense CO_2 -recycling occurs. Thus, the shallow chemocline, combined with the assumed shallow water depth of the Lower Toarcian epicontinental sea in Southwest Germany (approx 50 m or less; Bandel and Knitter, 1986), was probably sufficient for a pronounced influence of recycled CO_2 on the stable carbon isotopic composition of upper water column DIC, that is the Küspert model.

Alternative hypothesis.—Alternatively to the Küspert's model, other external factors like volcanic eruptions, forest fires, or changes in the input of dissolved inorganic carbon (DIC) by rivers, can be suggested as causes for the negative isotope excursion, but neither provides any good explanations. With respect to the latter, stable carbon isotope analyses of the Great Lakes-St. Lawrence system have shown that $\delta^{13}\text{C}$ of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) in tributary waters may be controlled partly by bacterial respiration, but DIC in the

Great Lakes themselves is in isotopic equilibrium with atmospheric CO_2 (Yang and others, 1996). By analogy, $\delta^{13}\text{C}_{\text{DIC}}$ in the Lower Toarcian epicontinental seas is not likely to have been regulated by the inflow of river water DIC. As for eventual volcanic eruptions or forest fires, assuming that these led to enhanced concentrations of $^{12}\text{CO}_2$ in the atmosphere, it is highly improbable that their impact was so profound in the Southwest German section and absent in the nearby Toarcian of Northwest Germany.

In our view, the negative excursion of $\delta^{13}\text{C}_{\text{TOC}}$ in the Southwest German section is thus best explained by the CO_2 recycling hypothesis (Küspert, 1982). A similar hypothesis was put forward by Saelen and others (1998) for the time-equivalent Withby formation, although they did not detect any PZE-markers. However, recent data suggest that aromatic carotenoid derivatives, indicating PZE, are also present in samples from this formation (Pancost and others, unpublished data).

The oxic/anoxic interface was very shallow in the Southwest German Basin compared to today's chemocline in the Black Sea and more comparable to the shallow chemoclines observed in contemporary lakes. In that case, primary production perhaps could occur at depths where DIC is for a large part organic matter-derived. This would suggest that from the upper part of the *tenuicostatum* Zone up to the lower part of the *falciferum* Zone, during periods of water column stratification, only DIC in the very uppermost part (perhaps the upper 10–20 m) of the photic zone was in isotopic equilibrium with CO_2 in the atmosphere.

Termination of the negative isotope shift.—The question arises why the negative excursion ended in the *falciferum* Zone, while black shale deposition and PZE still occurred. Saelen and others (1998) suggested that the intensity of CO_2 -recycling was changing. However, a better explanation may be the hypothesis of Jenkyns (1988) who suggested that at that time high amounts of isotopically light organic matter (made additionally light through CO_2 -recycling) had been buried due to global black shale deposition and thus led to an ^{13}C -enriched atmospheric CO_2 . Hence, this may have reversed the carbon isotopic shift toward a positive direction. Indeed, the most positive values for $\delta^{13}\text{C}_{\text{CARB/TOC}}$ are at the end of the negative isotope spike. At a certain point, probably during a regression, PZE occurred less frequently and less organic matter (of increasing ^{13}C -content) was buried. In addition, part of the buried organic matter was exposed to air and thus was reoxidized, and isotopically light CO_2 entered the atmosphere, slowly bringing the global carbon budgets back to their initial state, that is before black shale deposition.

CONCLUSIONS

The OM in the Early Toarcian shales of the Southwest German Basin displays a negative carbon isotope excursion in upper part of the *tenuicostatum* Zone up to the lower part of the *falciferum* Zone. Since the contribution of terrestrial OM is minor in all samples, this excursion cannot have resulted from differences in the ratio of terrestrial to marine OM. Biomarker distributions and kerogen pyrolysates exhibit only minor differences among the samples, and these do not correspond to differences in $\delta^{13}\text{C}_{\text{TOC}}$. Therefore, changes in the composition of the planktonic community are not a likely cause for the excursion of $\delta^{13}\text{C}_{\text{TOC}}$ either.

The $\delta^{13}\text{C}$ values of primary production and other markers follow a trend similar to that of $\delta^{13}\text{C}_{\text{TOC}}$ (fig. 6) and of $\delta^{13}\text{C}_{\text{CAR}}$, indicating that differences in $\delta^{13}\text{C}_{\text{TOC}}$ are related to differences in $\delta^{13}\text{C}_{\text{CO}_2}$. This fits the hypothesis of Küspert (1982), that the negative carbon isotope excursion resulted from the recycling of isotopically light CO_2 , derived from the mineralization of OM in stagnant bottom waters, into the surface water.

Literature data on the ^{13}C contents of organic and inorganic carbon in water column and sediments of the present-day Black Sea show that, despite the occurrence of photic zone euxinia, suggesting good conditions for CO_2 recycling, sedimentary OM is mainly produced in the upper part of the photic zone, where CO_2 is largely derived from the

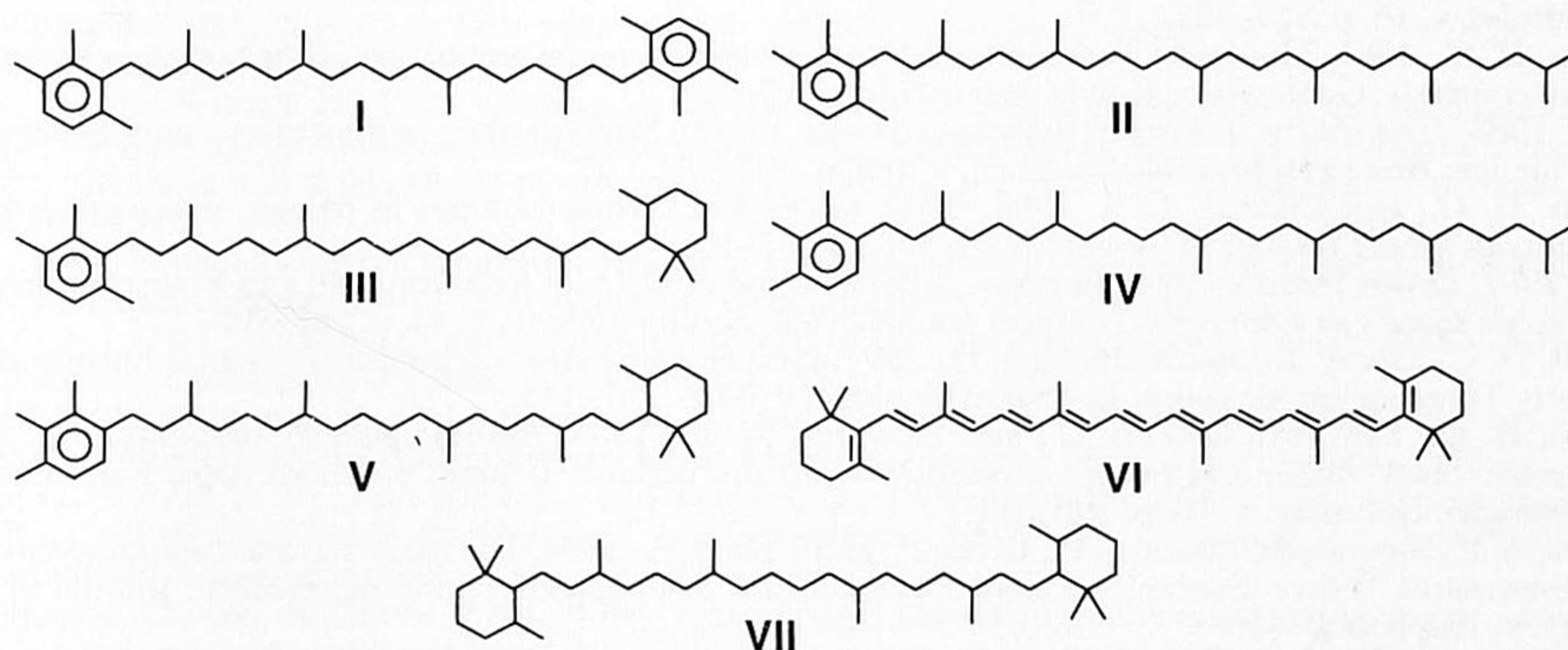
atmosphere. However, with shallower chemoclines and shallower water depths similar to present day lake systems, photic zone euxinia does enhance CO_2 -recycling and affects the ^{13}C -contents of $[\text{CO}_2]_{\text{aq}}$ in the photic zone. Based on presence of carotenoid derivatives (isorenieratane and especially chlorobactane) in TOC-rich samples, it seems likely that the chemocline in the Southwest Germany basin during the Early Toarcian has indeed been shallower than that of the Black Sea. The combination of the very shallow chemocline and the shallow water depths was enough for a marked influence of CO_2 recycling on $[\text{CO}_2]_{\text{aq}}$ and thus Küsperts model is believed to be the best explanation for the negative excursion of $\delta^{13}\text{C}_{\text{TOC}}$ in the Southwest German Toarcian shales. It is deemed unlikely that the shift in $\delta^{13}\text{C}_{\text{TOC}}$ was caused by external factors, like volcanic eruptions, forest fires, or changes in the supply of DIC by rivers.

The negative excursion may have ended by the burial of ^{13}C -depleted OM which enriched atmospheric CO_2 in ^{12}C and thus shifted $\delta^{13}\text{C}_{\text{DIC}}$ back to more positive values. At a certain point PZE was less frequent and OM was reoxidized leading to more ^{13}C -depleted atmospheric CO_2 and a return to pre-OAE conditions.

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APPENDIX



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