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Unusual distributions of long-chain alkenones and tetrahymanol from the highly alkaline Lake Van, Turkey

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Abstract—Long-chain C_{37} to C_{40} alkenones with di-, tri-, and tetra-unsaturation are very abundant in sediment trap material and Holocene to Late Pleistocene core samples from the Earth's largest soda lake, Lake Van (Turkey). Thus, the known distribution range of these typical biomarkers for haptophyte microalgae is extended to highly alkaline environments. The observed unsaturation patterns differ strikingly from those found in open marine haptophytes and sediments by an enhanced relative abundance of the tetra-unsaturated compounds, especially the $C_{37:4}$ methyl ketone. Their preponderance is suggested to be a facies marker pattern for lacustrine and marginal marine areas of sedimentation. Using published U^K_{37} calibrations, no reliable absolute temperatures were obtained for the Lake Van samples. Accordingly, marine sea surface temperature determinations based on long-chain alkenones should be applied with caution when a contribution of these compounds from coastal or nonmarine sources can not be excluded. The presence of tetrahymanol and gammacer-3-one in the Lake Van materials is attributed to organic matter contributions of ciliates. The relative abundance of long-chain alkenones and of tetrahymanol/gammacer-3-one is considered to reflect changes in the environmental conditions, in particular in the hydrological setting. We suggest that times of pronounced stagnation are recognised by very high tetrahymanol/gammacer-3-one concentrations together with drastically increased stanol/stenol ratios, and intervals of enhanced convection or of high freshwater input are characterised by high alkenone contributions.

1. INTRODUCTION

Since their discovery in marine samples (Boon et al., 1978; de Leeuw et al., 1980; Volkman et al., 1980b), long-chain multiple unsaturated methyl and ethyl ketones (long-chain alkenones) have been widely observed in marine sediments (e.g., Brassell et al., 1986a,b; Prahl et al., 1989; Sikes et al., 1991; Conte et al., 1992; Freeman and Wakeham, 1992; Jasper and Gagosian, 1993; Rosell-Melé et al., 1995). Their detection in the ubiquitous unicellular marine coccolithophorid *Emiliania huxleyi* (Haptophyta, formerly termed Prymnesiophyta) allowed them to be used as molecular markers for inputs of organic matter to recent sediments from this widespread marine alga (Volkman et al., 1980a,b; Rechka and Maxwell, 1988). Alkenone derivatives are present as sulphur-bound compounds in fossil macromolecular organic matter (e.g., Sinninghe Damsté et al., 1988; Richnow et al., 1992; Hefter et al., 1995), and free long-chain alkenones were detected in ancient sediments as old as the Cretaceous (Farrimond et al., 1986; Ficken et al., 1995). Hence, some as-yet-unknown ancestors, probably members of the family *Gephyrocapsaceae*, must have preceded the occurrence of the nowadays important *E. huxleyi* (Volkman et al., 1980b; Marlowe et al., 1984). Recently, a member of this group, the marine coccolithophorid *Gephyrocapsa oceanica*, was found to produce long-chain alkenones and may thus contribute these compounds to marine sediments (Volkman et al., 1995).

Long-chain alkenones are not only present in haptophytes from open marine waters, but also in species from coastal waters or even from terrestrial habitats (Marlowe et al., 1984; Conte et al., 1994). Accordingly, these components have been found in freshwater sediments (Cranwell, 1985), in a saline Antarctic lake (Volkman et al., 1988), in freshwater and saline lakes of the Tibet Plateau (Li et al., 1996), and in the low-salinity waters of the Black Sea (Freeman and Wakeham, 1992). Furthermore, a single C_{38} alkenone was detected in material from a hypereutrophic, dilute alkaline lagoon in southwestern Spain (Grimalt et al., 1991).

The observation that the variation in synthesis of di- and tri-unsaturated alkenones in cultures of *E. huxleyi* is directly linked to the growth temperature allows one to use the alkenone unsaturation index (U^K_{37}) for palaeotemperature determinations (Brassell et al., 1986b). Alkenone-based temperature calculations were calibrated using haptophyte cultures (e.g., Prahl and Wakeham, 1987; Volkman et al., 1995) and field samples (Prahl and Wakeham, 1987; Conte and Eglinton, 1993; Sikes and Volkman, 1993; Rosell-Melé et al., 1995), proving a linear relationship between the alkenone unsaturation index and the sea surface water temperature (SST). However, detailed studies showed considerable variation in calibration curves which depended upon the region of the world investigated (e.g., Conte et al., 1992; Sikes and Volkman, 1993; Rosell-Melé et al., 1995). The U^K_{37} index has often been used to study annual and interannual SST variations and to understand the frequencies and cyclicities of glacial-interglacial changes (e.g., Brassell et al., 1986a; Bradshaw et al., 1991; Jasper and Gagosian, 1993; Kennedy and Brassell, 1993; Kheradyar et al., 1993; Madureira et al., 1993).

Tetrahymanol is commonly observed in samples from marine, hypersaline, and freshwater environments (ten Haven et

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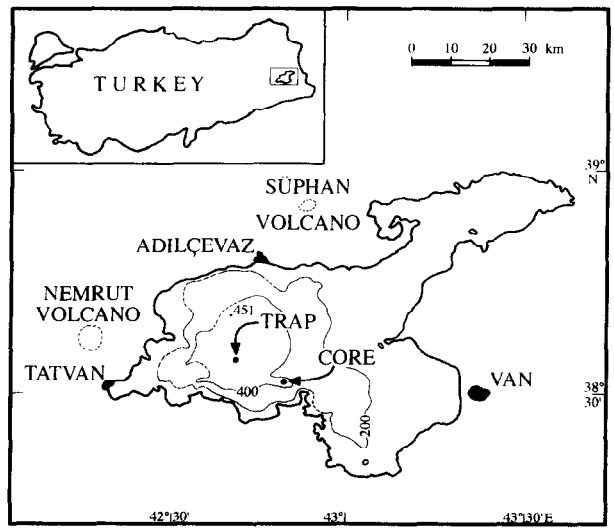

Fig. 1. Map of the Lake Van area showing the position of the sediment trap and the coring site within the Tatvan Basin.

al., 1989; Venkatesan, 1989). It is the only known biological precursor for gammacerane, the corresponding hydrocarbon, which is often found in the free and sulphur-bound fractions of fossil samples from marine and lacustrine settings (e.g., Summons et al., 1988; Michaelis et al., 1990; Peters and Moldowan, 1993; Richnow et al., 1992, 1993; Sinninghe Damsté et al., 1995). Tetrahymanol has been shown to be a principal lipid in marine and freshwater ciliates (Mallory et al., 1963; Harvey and McManus, 1991). These ubiquitous protozoa can be expected to be a major source of tetrahymanol in aquatic environments. However, tetrahymanol has also been found in an anaerobic phototrophic purple bacterium, *Rhodopseudomonas palustris* (Kleemann et al., 1990), in a fern (Zander et al., 1969), and in an anaerobic fungus (Kemp et al., 1984). Up to now, the occurrence of gammacer-3-one is rarely reported for natural samples. It is found in oxidative degradation products of the Green River Shale kerogen, probably due to ether-bound tetrahymanol (Simoneit and Burlingame, 1974; Barakat and Yen, 1990). Moreover, indications for its presence are described for sediments from the San Miguel Gap (cf. ten Haven et al., 1989).

In this paper, we present data on alkenone and tetrahymanol/gammacer-3-one contents in sediment and sediment trap samples from a large alkaline lake. Age determinations of the respective samples allowed us to investigate the compositions of these biomarkers in relation to facies variations in the depositional environments from the Late Pleistocene (including the Oldest Dryas Glacial and the Younger Dryas cooling event) to Recent times.

2. STUDY SITE AND SAMPLES

2.1. Geographical Setting and Water Chemistry

Lake Van is located in the East Anatolian Highlands of Turkey (43°E, 38.5°N, Fig. 1) at an altitude of 1650 m (Kempe, 1977; Kempe et al., 1991). It is the largest soda lake on Earth with an area of 3522 km^2, a maximum water depth of 451 m, and a water volume of 576 km^3. The geology of the Lake Van area is controlled by its position near the boundary of the Eurasian and the Afro-Arabian continental plates. Associated tectonic activity has led to extensive and still active volcanism, resulting in the formation of alkali-rich lavas (Kurtman et al., 1978). The water chemistry is strongly affected by the input of salts derived from the weathering of these volcanic rocks. Lake Van is thought to have been a closed lake for the last 200 ky (Reimer, 1996). The lack of outflows has caused the accumulation of salts in the lake and an increase in salinity to present-day 21.6‰ (Table 1). The most notable aspect of the water chemistry is the extremely high alkalinity (152 meq L^{-1}). The main cation, Na, is not only balanced by chloride but also, to a nearly equivalent extent, by carbonate and bicarbonate (Kempe et al., 1991). Accordingly, the lake water reacts like an alkaline buffer solution, giving rise to a very high pH value of 9.8. Free oxygen is present in the entire water body although the concentration drops to values below 1 mg L^{-1} in the near bottom layers (Fig. 2; Reimer, 1996).

2.2. Ecology

Few data exist about the biological community present in Lake Van. Diatoms and cyanobacteria are important members of the phytoplankton (Gessner, 1957) whereas the zooplankton appears to be dominated by copepods (Hauer, 1957) and ciliates (Gessner, 1957). The extreme water chemistry of Lake Van restricts the diversity of species to a few, mostly endemic members. There occurs, for example, only one specially adapted fish species in the lake (Danulat and Kempe, 1991). Many groups which are widespread in "normal" marine or limnic environments, such as red algae, brown algae, and molluscs, are lacking (Gessner, 1957).

Recently, Lake Van has attracted the attention of palaeontologists since a remarkable feature of its ecology is the occurrence of column-like carbonate reefs which reach up to 40 m in height from the lake bottom (Kempe et al., 1991). These structures grow in the vicinity of Ca-rich groundwater

Table 1. Hydrological parameters of the Lake Van surface water.

Parameter		
Na^+	339 meq L^{-1}	(1)
K^+	10.8 meq L^{-1}	(1)
Mg^{2+}	8.9 meq L^{-1}	(1)
Ca^{2+}	0.2 meq L^{-1}	(2)
Cl^-	161 meq L^{-1}	(1)
Alkalinity	152 meq L^{-1}	(1)
SO_4^{2-}	49.1 meq L^{-1}	(1)
PO_4^{3-}	3.7 μmol L^{-1}	(2)
Salinity	21.6 ‰	(1)
pH	9.8	(1)
O_2	7.5 mg/L	(2)
Temperature	18 to 5°C	(3)

(1) average 0–30 m, 1990; increase with depth.
(2) average 0–30 m, 1990.
(3) 1990; decrease with depth.

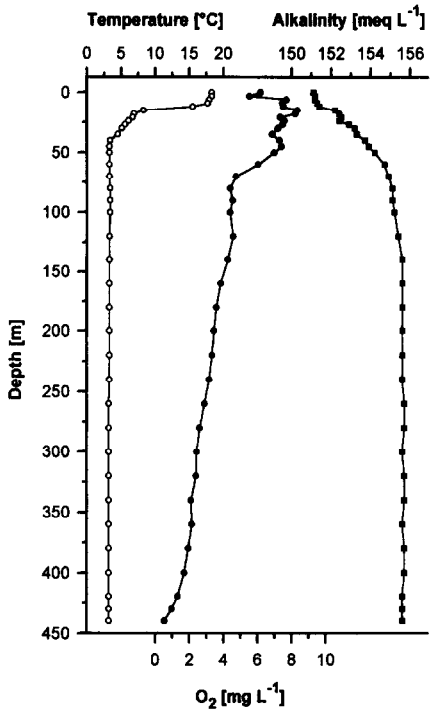

Fig. 2. Temperature (open circles), dissolved oxygen content (filled circles), and alkalinity (squares) of the water column of the central Tatvan Basin (June 1990).

springs at the lake bottom and are stabilised by actively calcifying cyanobacteria which form aragonitic crusts on the inorganic precipitate of the groundwater seepage. Because of their morphological characteristics, these structures have been considered as recent analogues of Precambrian stromatolites (Kempe et al., 1991).

2.3. Samples

The materials investigated here were collected during the Third International Lake Van Expedition in June/July 1990. The sample suite comprises one sediment trap sample and fifteen core samples (Table 2). The sediment core was obtained using a piston corer (Landmann et al., 1996). Both the coring site and the sediment trap position were located within the central Tatvan Basin (Fig. 1; sediment trap position 38°34.9′N/42°40.6′E; core position 38°32.4′N/42°48.0′E, water depth 420 m). A Mark-V sediment trap was positioned beneath the euphotic zone at a water depth of 120 m to collect the sinking particulate matter over a full year between June 1989 and June 1990. The sampling cups were poisoned with $HgCl_2$.

The sedimentary core sequence is composed mainly of dark-coloured carbonaceous silty clays. Anoxic conditions prevail within the entire sediment column (Eh −150 to −280 mV). A high preservation potential for the organic matter is reflected by a generally high organic C content (Table 2). The Lake Van deposits are characterised by a very distinct varving due to seasonal sedimentation variability and the lack of bioturbation.

The varve counting method reveals an age of 14,432 y before 1990 for the deepest core sample representing material which settled during the Oldest Dryas Glacial (Table 2; Landmann et al., 1996). Three more samples characterise the depositional setting during the last cooling event (Younger Dryas; between about 12,080–10,960 y before 1990). Special environmental conditions prevailed for about 10 y during the deposition of the Early Holocene layer (10,575 y before 1990) which differs from the other samples by a dark brown colour and a high organic C content of 4.5% (Table 2). The modern Holocene sedimentary facies is represented by the sediment trap material and the samples from a depth of 0.3–8.0 cm comprising the deposition record of the last 64 y.

3. EXPERIMENTAL METHODS

3.1. Experimental Procedure

The frozen samples were thawed, vacuum dried at 40°C, and ground. After saponification of the samples by refluxing in 6% KOH/CH_3OH for 12 h, the supernatant was decanted. The residue was extracted by ultrasonication in $CH_2Cl_2/CH_3OH/H_2O$ (60:25:4; v/v/v) until the solvent became colourless. Subsequently, the combined supernatants were three times extracted with CH_2Cl_2 vs. water (pH 2). The organic substances of the CH_2Cl_2 phases were fractionated by column chromatography (Merck silica gel 60, 70–230 mesh ASTM). The nonpolar fraction, containing alcohols, hydrocarbons, and ketones, was eluted with CH_2Cl_2, and the respective alcohols were acetylated using acetic acid anhydride and an equal volume of pyridine (14 h, RT). Subsequently, the composition of the total nonpolar fraction was analysed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

In three cases, alkenones were prepared by silica gel chromatography directly after ultrasonical extraction with CH_2Cl_2:CH_3OH. In comparison, the preceding saponification allows a slightly higher recovery rate of alkenones (by 5–10 wt% in comparison to simple CH_2Cl_2:CH_3OH extraction) whereas the relative alkenone distributions were identical for the two methods. Thus, our method allows a quick and convenient work-up procedure of samples which, furthermore, prevents problems arising from coelution of alkenones with alkenoates, wax esters, and triacylglycerols.

3.2. Identification of Gammacer-3-one

Mass spectrometric investigation revealed the presence of one pentacyclic C_{30} ketone, which was tentatively assigned as gammacer-3-one by comparison with published mass spectra (Barakat and Yen, 1990; Kleemann et al., 1990). For verification of the structural relationship between tetrahymanol and gammacer-3-one, an aliquot of the total nonpolar fraction was again hydrolysed using 6% KOH/CH_3OH (2 h, reflux) to cleave the acetates. Subsequent stirring for two h in a mixture of pyridinium dichromate (Aldrich) and dry CH_2Cl_2 converted the obtained alcohols to ketones. After filtration over silica gel 60 (Merck), the GC and GC-MS analysis confirmed the coelution of the former tetrahymanol and the already existing pentacyclic C_{30} ketone. Thus, the found component is indeed gammacer-3-one, the ketone derivative of tetrahymanol.

3.3. Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS)

GC analyses were performed on a Carlo Erba Fractovap 4160 gas chromatograph equipped with a 30 m fused silica capillary column (DB5, J&W Scientific, 0.3 mm i.d., 0.25 μm film thickness), with an "on-column" injector and a flame ionisation detector. Hydrogen was used as the carrier gas. The temperature program was 80°C isothermal for 3 min from 80°C to 210°C at 6°C min^{-1} from 210°C to 300°C at 2°C min^{-1} isothermal for 30 min. The GC-MS system was a Finnigan Mat CH7A mass spectrometer interfaced to a Carlo Erba 4160 gas chromatograph which was equipped with a 30 m fused silica capillary column (DB5, J&W Scientific, 0.3 mm i.d., 0.25 μm film thickness) and an "on-column" injector. Helium was

Table 2. Sample description.

Varve-years [before 1990 AD]	Stratigraphy	Sample [core depth]	Max. error of ages [%]	TOC [%]
0	Holocene (Recent)	Sed. trap	0.6	1.90
2	Holocene	0.3 cm	0.6	3.35
33	Holocene	4.5 cm	0.6	4.52
64	Holocene	8.0 cm	0.6	3.07
527	Holocene	46 cm	0.6	2.72
1274	Holocene	88 cm	0.6	4.84
5935	Holocene	396 cm	1.2	4.39
6611	Holocene	431 cm	1.2	4.09
9048	Holocene	547 cm	1.2	2.78
10575	Early Holocene	615 cm	1.2	4.48
10828	Younger Dryas-Holocene*	631 cm	1.2	1.50
11195	Younger Dryas	653 cm	1.2	1.30
11925	Early Younger Dryas	696 cm	1.2	1.33
12552	Allerød	722 cm	1.2	1.77
13615	Bølling	767 cm	1.2	0.77
14432	Oldest Dryas	813 cm	2.0	0.56

TOC = total organic carbon.
* = transition.

used as carrier gas. The temperature program for GC-MS analyses was 80°C isothermal for 5 min 80°C to 300°C at 3°C min^{-1} 300°C isothermal for 20 min. The identification of the compounds was based on comparison of their mass spectra and of GC retention times with those of published data or of reference compounds. Quantification was carried out by GC-peak area integration (Bruker Chromstar software) and comparison with cholestane as an internal standard.

4. RESULTS AND DISCUSSION

4.1. Long-chain Alkenones

GC-MS analyses of the total nonpolar fraction revealed the presence of a suite of long-chain di-, tri-, and tetra-unsaturated ketones (long-chain alkenones) with C chain lengths ranging from C_{37} to C_{40} (Fig. 3). Mass spectrometric investigation of the C_{37} suite revealed that all these compounds are methyl ketones showing characteristic fragment ions at $M^+ -15$, $M^+ -18$, $M^+ -33$, $M^+ -43$, and $M^+ -58$ (de Leeuw et al., 1980). The $C_{37:2}$ alkenone coeluted with synthetic heptatriaconta-15(*E*),22(*E*)-dien-2-one on DB5 and DB1 capillary columns. This indicates that the configuration of the double bonds within the Lake Van alkenones is all-E, as it was previously reported from the marine coccolithophorid *Emiliania huxleyi* and marine sediments (Rechka and Maxwell, 1988). The structures of the C_{38} members were deduced from their mass spectrometric fragmentation pattern. Enhanced fragment ions at $M^+ -18$, $M^+ -29$, and $M^+ -72$ indicated that these compounds are alken-3-ones. Long-chain alkenes were not detected in any of the investigated samples. When the organic compounds were directly extracted from the samples without saponification, alkenoates were observed in trace amounts. These compounds were tentatively assigned as $C_{36:4}$, $C_{36:3}$, and $C_{36:2}$ fatty acid methyl and ethyl esters.

Up to now, the biological sources of alkenones appear to be restricted to haptophyte nannoplankton, which is known to occupy a broad variety of terrestrial to open marine habitats. In open marine environments, the presence of these compounds is mainly attributed to inputs of the coccolithophorid species *E. huxleyi* (Volkman et al., 1980a,b). Recent studies proved the presence of long-chain alkenones in the related marine haptophyte *Gephyrocapsa oceanica* which shows a less widespread distribution than *E. huxleyi* (Volkman et al., 1995). In the alkaline waters of Lake Van, the concentration of Ca^{2+} ions is extremely low (Kempe et al., 1991), thus precluding the existence of calcifying plankton-like coccolithophorid haptophytes. Marlowe et al. (1984) reported the occurrence of long-chain alkenones in species of non-coccolithophorid haptophytes. One of them, *Chrysotyla lamellosa*, occurs in terrestrial habitats (damp, salty environments), but this species has not been described from Lake Van. Therefore, we suggest that a yet unknown, noncalcifying haptophyte species which is adapted to the lakes' extreme conditions produces the long-chain alkenones present in the samples.

Only minor differences in relative alkenone distributions were found in the Lake Van materials, indicating that the alkenone-producing organisms occurred throughout the sedimentary history. In general, the long-chain alkenones show a decrease in concentration with rising chain length ($C_{37} > C_{38} > C_{39} > C_{40}$; Table 3, Fig. 3, sediment trap). The observed preponderance of the C_{37} over homologues of higher molecular weight seems to be fairly characteristic for marine haptophytes and typically appears in samples from open marine environments (e.g., Smith et al., 1983; Brassell et al., 1986a,b; Prahl et al., 1988; Sikes and Volkman, 1993). The same feature has been described from low-salinity waters of the Black Sea (Freeman and Wakeham, 1992) and from lacustrine settings (Cranwell, 1985; Volkman et al., 1988). However, two exceptions to this rule are recognised in the Early Holocene (10575 y; Fig. 3) and the Mid Holocene (6611 y) layers in which the C_{38} alkenones predominate (Table 3). A preponderance of the C_{38} over the C_{37} alkenones has recently been reported from batch cultures of the marine haptophyte *G. oceanica* (Volkman et al., 1995). A similar pattern was also observed in a black shale sample of Cenomanian age (Farrimond et al., 1986) and in material from a recent alkaline lagoon in

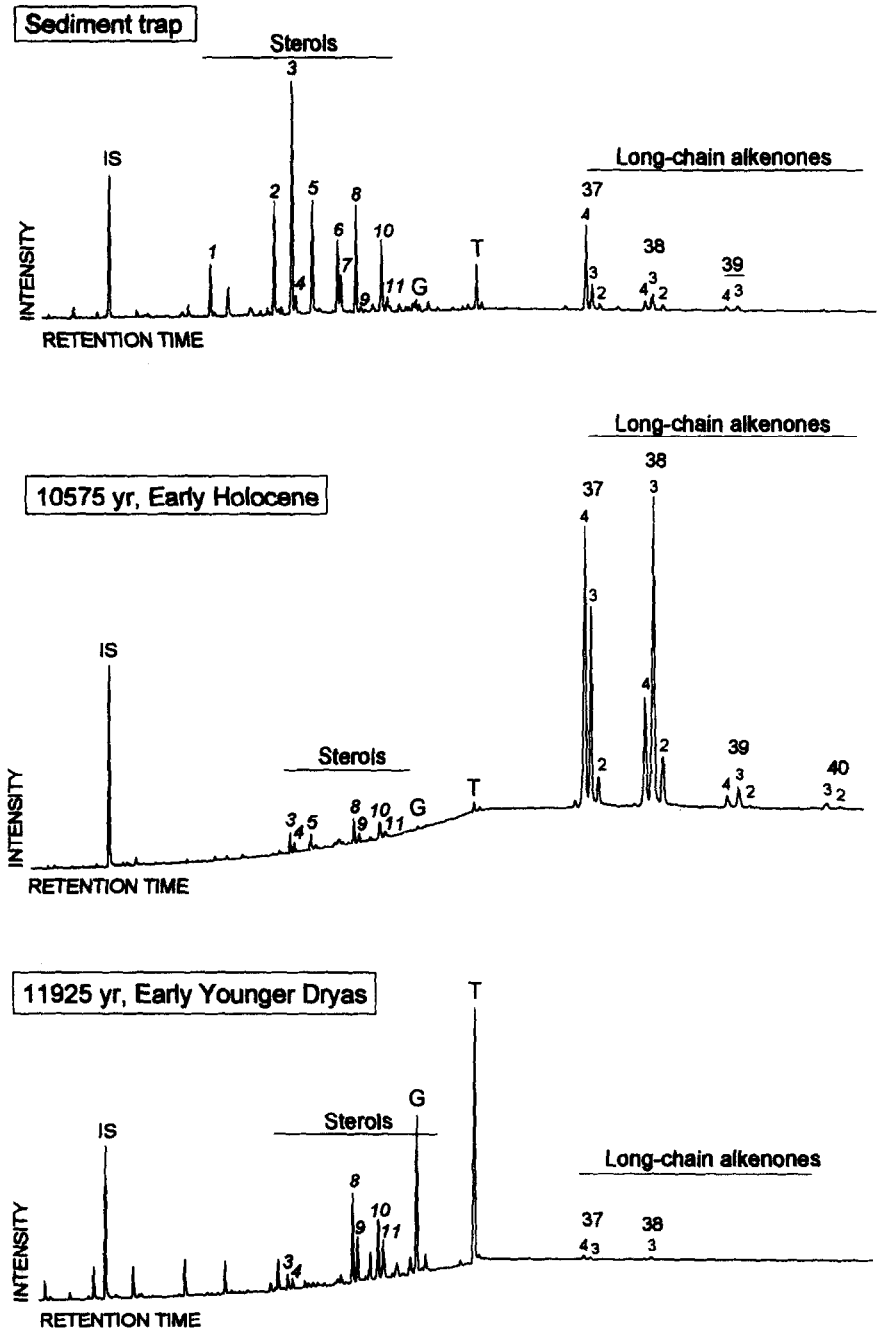

Fig. 3. Partial gas chromatograms depicting the distribution of hydrocarbons, alcohols (as acetates), and ketones isolated from the sediment trap material and samples from the deep core sequence at 10575 y (Early Holocene) and 11925 y (Early Younger Dryas). Peak labelling denotes number of C atoms (large numbers) and numbers of double bonds (small numbers) of the long-chain alkenones. T = tetrahymanol; G = gammacer-3-one; IS = internal standard. Numbers in italics below the sterol range denote major steroid alcohols (acetates): *1:* norcholesta-5,22-dien-3β-ol ($C_{26}\Delta^{5,22}$); *2:* cholesta-5,22-dien-3β-ol ($C_{27}\Delta^{5,22}$); *3:* cholest-5-en-3β-ol ($C_{27}\Delta^{5}$); *4:* 5α(H)-cholestan-3β-ol ($C_{27}\Delta^{0}$); *5:* 24-methylcholesta-5,22-dien-3β-ol ($C_{28}\Delta^{5,22}$); *6:* 24-methylcholesta-5,24-dien-3β-ol ($C_{28}\Delta^{5,24}$); *7:* 24-methylcholest-5-en-3β-ol ($C_{28}\Delta^{5}$); *8:* 24-ethylcholesta-5,22-dien-3β-ol ($C_{29}\Delta^{5,22}$); *9:* 24-ethylcholest-22-en-3β-ol ($C_{29}\Delta^{22}$); *10:* 24-ethylcholest-5-en-3β-ol ($C_{29}\Delta^{5}$); *11:* 24-ethyl-5α(H)-cholestan-3β-ol ($C_{29}\Delta^{0}$).

which only a C_{38} compound was detected (Grimalt et al., 1991). It remains an open question whether the alkenone composition of the 10575 y and the 6611 y layers is caused by inputs from different haptophyte species or by changes in environmental conditions.

The unsaturation patterns of the Lake Van long-chain alkenones reveal a notably high relative abundance of the tetraunsaturated compounds, particularly of the $C_{37:4}$ methyl ketone (Table 3; Fig. 3). This component is most prominent in all samples containing long-chain alkenones, except the

Table 3. Concentrations of long-chain alkenones, tetrahymanol, gammacer-3-one and sterols.

Varve-years [before 1990 AD]	[$\mu g\ gC_{org}^{-1}$]												[$\mu g\ gC_{org}^{-1}$]			
	$C_{37:4}$	$C_{37:3}$	$C_{37:2}$	$C_{38:4}$	$C_{38:3}$	$C_{38:2}$	$C_{39:4}$	$C_{39:3}$	$C_{39:2}$	$C_{40:4}$	$C_{40:3}$	$C_{40:2}$	Alkenones	Tetrahymanol	Gammacerone	Sterols
0	2300	768	177	334	655	212	168	204	32	n.d.	61	n.d.	4911	1507	176	20681
2	3693	1619	373	473	1184	453	283	390	51	15	114	n.d.	8648	1185	266	6134
33	4531	1958	477	526	1378	477	526	415	64	17	109	41	10519	670	226	4088
64	3351	1328	307	403	962	366	218	296	31	8	73	29	7372	688	383	9727
527	5256	2137	551	1033	1934	678	367	524	78	67	188	77	12890	1450	642	10811
1274	1853	1102	242	190	690	287	117	217	25	18	44	35	4820	3448	940	6217
5935	1010	2078	273	348	1262	473	n.d.	128	n.d.	n.d.	62	12	5646	823	421	2697
6611	300	924	294	576	3354	1590	12	138	12	n.d.	153	132	7485	123	56	10651
9048	804	2395	477	545	1469	578	48	214	26	n.d.	146	20	6722	566	226	37212
10575	5300	3234	500	2328	6068	1182	264	468	52	n.d.	168	45	19609	119	35	1651
10828	3467	1207	166	638	964	525	335	288	n.d.	n.d.	n.d.	n.d.	7590	194	185	9057
11195	2819	1110	479	461	1021	698	309	254	84	27	112	n.d.	7374	n.d.	n.d.	n.d.
11925	50	33	7	14	38	13	3	6	14	n.d.	n.d.	n.d.	178	3366	1639	3736
12552	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	11646	5730	4298
13615	3358	1438	267	755	1206	475	344	283	41	36	143	63	8409	1816	756	18790
14432	451	130	64	95	210	130	42	35	21	n.d.	22	n.d.	1200	331	239	1675

n.d. = not detected.

10575 y, the 6611 y, and the 5935 y layers. The unsaturation patterns found differ sharply from those reported from open marine environments which are, in general, characterised by an abundant concentration of the di- and tri-unsaturated compounds ($C_{37:2}$ and $C_{37:3}$) and by minor relative amounts or even the absence of the $C_{37:4}$ alkenone. In marine sediments, a pronounced occurrence of the $C_{37:4}$ homologue is often restricted to very low sea surface temperatures (below about 4°C; Sikes et al., 1991; Sikes and Volkman, 1993). On the other hand, it is intriguing that increased concentrations of the tetraunsaturated compounds, especially of the $C_{37:4}$ methyl ketone, are found for all lacustrine sediments in which long-chain alkenones have so far been detected (Cranwell, 1985; Volkman et al., 1988; Li et al., 1996). The results from Lake Van illustrate that a pronounced occurrence of the tetraunsaturated alkenones is not limited to freshwater conditions, but may also be observed in alkaline waters of high salinity. Interestingly, an intermediate distribution with moderate relative amounts of the $C_{37:4}$ homologue has been reported from the Black Sea (Freeman and Wakeham, 1992). With respect to these findings, we suggest that the abundant occurrence of the tetraunsaturated ketones is restricted to lacustrine or confined marine settings, implying a possible suitability of such alkenone patterns as a facies marker for these sedimentary environments.

Long-chain alkenones are very abundant in all investigated materials (4.8–12.9 $mggC_{org}^{-1}$) except the Early Younger Dryas layer (0.15 $mggC_{org}^{-1}$; Fig. 3) and are absent in the Allerød sample (Table 3). Notably high concentrations are observed in the Early Holocene layer (19.6 $mggC_{org}^{-1}$). Total alkenones are reported to comprise about 4–5% of the organic cell carbon of coastal *E. huxleyi* strains (Conte et al., 1994). Assuming these values to resemble those of the alkenone producing haptophytes in Lake Van, these organisms could have contributed nearly half of the organic C present in the Early Holocene sample.

The variation in long-chain alkenone concentrations may arise from changes in the abundance of the alkenone-producing organisms and may thus reflect differences in environmental conditions during the deposition of the respective layers. Furthermore, the observed variability could be due to syn- or post-sedimentary processes accounting for a preferential loss or preservation of long-chain alkenones. A significant remineralisation and loss of long-chain alkenones was noted for sediments from the North Atlantic (Conte et al., 1992). This process seems to be most pronounced in the water column and the uppermost few centimeters of the sediments when free oxygen is still present. Prahl et al. (1989) reported an 85% loss of long-chain alkenones over a time span of 8 ky in the oxidised portion of an ungraded turbidite from the Madeira Abyssal Plain. Total organic C (TOC) and long-chain alkenones were remineralised to a similar extent in both the oxidised and unoxidised portions of the sedimentary sequence. A similar result was obtained from the investigation of an anoxic core sequence comprising 100 ky (Pigmy Basin, N′ Gulf of Mexico; Jasper and Gagosian, 1993). With respect to these results, we believe that differences in the postdepositional, early diagenetic regime cannot account for the observed drastic variations in the alkenone amounts relative to the TOC content. Hence, the variability in alkenone concentrations is more likely to arise from fluctuations in the abundance of the contributing primary producers due to changes in the environmental conditions, e.g., nutrient loadings, salinity, and/or climate.

4.2. Sterols

The sterol patterns of the sediment trap material and the shallow core sequence show very similar relative distributions and reflect a fairly stable assemblage of organisms present in the modern Lake Van (Fig. 3). In the sediment trap, the most prominent compound is $C_{27}\Delta^5$ (27.3% of total sterols). This compound and its $C_{27}\Delta^{5,22}$ counterpart (11%) are usually attributed to zoogenous sources in marine environments (e.g., Volkman, 1986). In Lake Van, copepods are known to occur in high individual numbers and may thus represent a likely source for the C_{27}-sterols. However, both

components are also known to be present in algae, like diatoms ($C_{27}\Delta^5$; $C_{27}\Delta^{5,22}$) or haptophytes ($C_{27}\Delta^5$, Volkman, 1986). Diatoms (Gessner, 1957) and haptophytes (this study) can indeed be regarded as important sources of sedimentary organic matter in Lake Van and may well represent an additional source for the C_{27} sterols found in the samples studied.

Sedimentary C_{26} and C_{28} sterols unambiguously reflect phytoplanktonic inputs of organic matter (Volkman, 1986). The most prominent C_{26} and C_{28} compounds observed in the young samples are $C_{26}\Delta^{5,22}$ (5.8%), as well as $C_{28}\Delta^{5,22}$ (12.6%), $C_{28}\Delta^{5,24}$ (8.1%), and $C_{28}\Delta^5$ (5.1%). These biomarkers are predominating in many diatoms ($C_{26}\Delta^{5,22}$, $C_{28}\Delta^{5,22}$, $C_{28}\Delta^{5,24}$) and haptophytes ($C_{28}\Delta^{5,22}$; Conte et al., 1994). Their presence may thus indicate a significant organic matter contribution derived from these algae.

Major C_{29} sterols found in the sediment trap and the shallow core sequence include $C_{29}\Delta^{5,22}$ (11.2%) and $C_{29}\Delta^5$ (8.6%). $C_{29}\Delta^5$ shows a scattered, fairly widespread distribution in phytoplankton, whereas $C_{29}\Delta^{5,22}$ is particularly abundant in the Chrysophyceae, the Chlorophyceae, and in many haptophytes (reviewed by Volkman, 1986; Volkman et al., 1990; Conte et al., 1994). However, both compounds are also found as characteristic land plant sterols (e.g., Karrer et al., 1977). Nevertheless, the studied samples do not show the pronounced preponderance of $C_{29}\Delta^5$ over $C_{29}\Delta^{5,22}$, which is typically observed in vascular plants (e.g., Salt et al., 1991) and in sediments receiving significant contributions of higher plant derived organic matter (Volkman, 1986). The Lake Van sediments, rather, reveal higher concentrations of the di-unsaturated compound. We therefore regard autochthonous phytoplankton as the predominant source of the C_{29} sterols in the lake.

Distinctly enhanced relative concentrations of C_{29} sterols are observed in the deeper core samples older than 1274 y. The relative abundance of the C_{29} sterols ranges from 26% (sediment trap) to 48% (527 y) in the young samples and between 48% (10,575 y) and 78% (Younger Dryas) in the older sediments. This observation is not simply explained by a selective enrichment of diagenetically resistant higher plant organic matter because the C_{29} sterol patterns of the deeper core sediments still resemble those of the younger samples. The older materials may rather reflect the predominance of the respective C_{29} producing biota in the lake. The abundance of long-chain alkenones does not covary with the concentration of any member of the sterol fraction. This is particularly evident for the Younger Dryas layer where significant amounts of long-chain alkenones but virtually no sterols were observed. Apparently, the alkenone producing haptophytes in Lake Van are only minor contributors of steroid alcohols.

4.3. Tetrahymanol/Gammacer-3-one

The C_{30} triterpenoid tetrahymanol is present in all Lake Van sediments except the Younger Dryas sample. It occurs in concentrations varying between 0.1 and 3.4 mg gC_{org}^{-1} for the Holocene samples, but ranges up to 11.6 mg gC_{org}^{-1} in the Allerød material (Table 3). Tetrahymanol is accompanied by the corresponding ketone, gammacer-3-one, which appears in concentrations of 0.04 to 5.7 mg gC_{org}^{-1}. No other derivatives of tetrahymanol, such as gammacerane or gammacerene, were found.

In Lake Van, tetrahymanol derives from organisms living in the well oxygenated upper portion of the water column because it is abundant in the sediment trap material from the 120 m water depth (Fig. 3). An additional origin from benthic purple bacteria or fungi can furthermore be excluded because the concentration of tetrahymanol is slightly decreased in the uppermost sediments, indicating a remineralisation/degradation of this compound during sedimentation (Table 3). Ciliates occur in Lake Van (Gessner, 1957) and can thus be regarded as the most likely source of tetrahymanol in the materials studied.

Gammacer-3-one occurs in those Lake Van sediments in which tetrahymanol was also detected and is already present in the sediment trap material (Fig. 3). Gammacer-3-one may be biosynthesised by the ciliates, but it may also be a microbial or abiotic oxidation product of tetrahymanol. Such an oxidation should be restricted to the upper water layer because no tendency to a higher gammacer-3-one abundance at the expense of tetrahymanol is observed with increasing sediment depth. The ratio of tetrahymanol over gammacer-3-one is rather fairly constant (tetrahymanol/gammacer-3-one ratio of about 2; Table 3; Fig. 4). The pronounced resemblance between the concentration profiles over the time scale indicates a very similar diagenetic stability for the two compounds.

Gammacer-3-one could directly serve for S incorporation and subsequent linkage to macromolecular structures in S-rich environments as already proposed (Sinninghe Damsté et al., 1995). Moreover, it could be converted to the corresponding hydrocarbon via reduction followed by hydrogenation and may thus contribute to the often significant gammacerane concentrations in sediments and oils (e.g., ten Haven et al., 1989).

It is known that ciliates synthesise tetrahymanol only if their supply of dietary sterols is poor or if their food source does not contain sterols at all. Otherwise, dietary sterols are utilised as cell membrane constituents instead of tetrahymanol (Harvey and McManus, 1991). The synthesis of tetrahymanol can thus be related to bacterivory and the depletion or absence of eukaryotic food sources. Accordingly, Schoell et al. (1994) suggested that tetrahymanol/gammacerane were facies markers for stratified environments where dense bacterial populations thrive at chemical interfaces and provide abundant food for bacterivorous ciliates. Similarly, Sinninghe Damsté et al. (1995) attributed the occurrence of tetrahymanol or gammacerane to the development of oxic-anoxic boundaries within the water column and proposed anaerobic phototrophs (green and purple sulfur bacteria) and sulphide-oxidising bacteria as probable food sources for the tetrahymanol producing protozoa. Thus, high amounts of tetrahymanol and its derivatives are attributed to the presence of chemoclines or oxic-anoxic boundaries in the water column.

In the modern Lake Van, a density stratification typically occurs due to freshwater runoff overlying the dense, saline water body. The lower limit of the upper mixed layer is

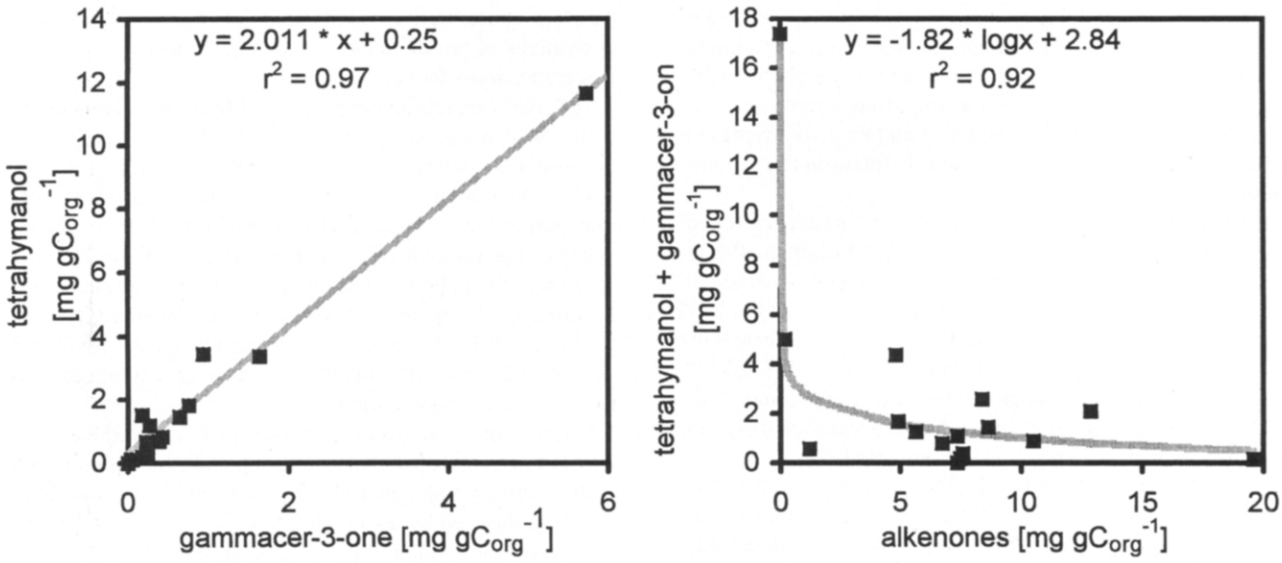

Fig. 4. The concentrations of tetrahymanol plotted against gammacer-3-one and of the sum of the two compounds against long-chain alkenones. Regression lines are indicated.

located at the 60–80 m depth, below which stable alkalinities of about 155 meq L^{-1} and temperatures of about 3°C are observed throughout the water column (Fig. 2). Moreover, a markedly decreasing O_2 concentration reflects a rapid consumption of dissolved oxygen within the 60–80 m section. This can be explained by intense bacterial activity on primary produced organic matter enriched at the thermo-/chemocline which would in turn allow pronounced ciliate grazing. However, it should be emphasised that the hydrological regime of the modern Lake Van does not give rise to the establishment of anoxic conditions within any part of the water column (Fig. 2). Moreover, sterols are present in all Lake Van samples except the Younger Dryas layer and do not show a negative correlation with tetrahymanol/gammacer-3-one. Accordingly, the mere presence of tetrahymanol/gammacer-3-one proves neither the establishment of an anoxic water body nor a poor supply with dietary sterols.

Nevertheless, we suggest that the abundance of tetrahymanol/gammacer-3-one is linked to the extent of stratification of the Lake Van water column. The remarkable predominance of this biomarker in the Allerød and the Early Younger Dryas samples (Fig. 5; Table 3) may thus be indicative of a prolonged stagnant phase during these times. Support for this assumption comes from twofold to threefold increased stanol/stenol ratios observed for these two layers compared to the overlying and underlying sediments (Fig. 6). The conversion of Δ^5 unsaturated sterols into their saturated 5α(H)-counterparts has been widely used as a measure for microbial steroid alteration (Gaskell and Eglinton, 1975; Gagosian et al., 1980). This process is favoured under reducing conditions, particularly near oxic-anoxic interfaces in the water column (Wakeham, 1989). The observation of strikingly increased stanol levels in combination with a pronounced tetrahymanol/gammacer-3-one abundance thus points to the establishment of a stagnant, anoxic water body during the deposition of the Allerød and the Early Younger Dryas samples.

4.4. Tetrahymanol/Gammacer-3-one vs. Long-chain Alkenones

No correlation was observed between alkenone and sterol concentrations (r^2 = <0.01), indicating that their primary producers depend on different growth conditions, e.g., nutri-

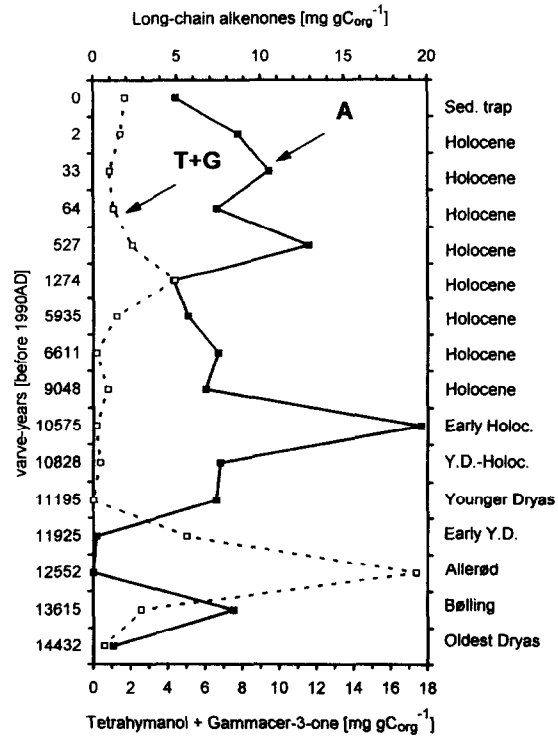

Fig. 5. Concentrations of long-chain alkenones (A; filled squares, upper scale) and tetrahymanol/gammacer-3-one (T + G; open squares, lower scale) in sediment trap and core samples.

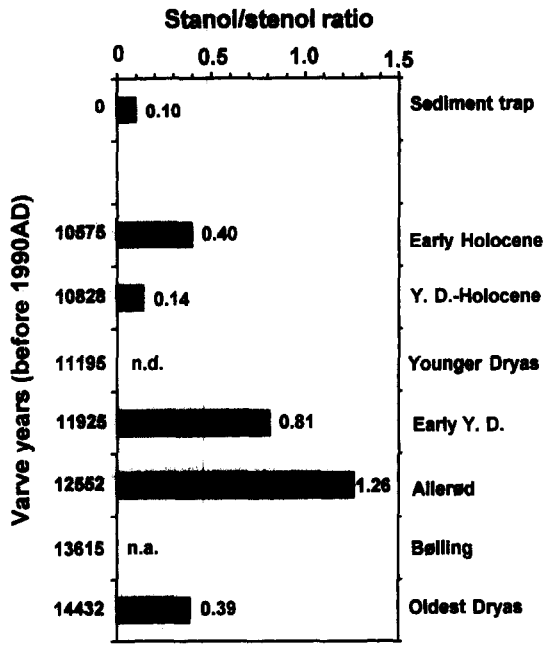

Fig. 6. Stanol/stenol ratios of the sediment trap and the deep core samples (saturated sterols/Δ^5-sterols; averaged from the C_{27}, C_{28}, and C_{29} pairs). n.d. = sterols not detected; n.a. = no value obtained (coelution).

ent levels, temperatures, and salinity. Furthermore, neither the alkenone, sterol, or tetrahymanol/gammacer-3-one abundance nor the sum of the three compound classes shows a linear or logarithmic correlation with TOC (r^2 = <0.22). Thus, the bulk of organic C has probably received variable contributions from other organic fractions (e.g., sugars, biopolymers) and is influenced by changes in the depositional environment and/or diagenetic reactions (e.g., bacterial reworking). These data point out that the pathways of organic matter input and preservation in this limnic environment are very complex.

Interestingly, the concentration of tetrahymanol/gammacer-3-one reveals a negative correlation trend with the logarithmic concentration of long-chain alkenones (Fig. 4). Obviously, very high concentrations of long-chain alkenones are coupled with very low amounts of tetrahymanol/gammacer-3-one (e.g., in the Early Holocene layer), and vice versa (Allerød and Early Younger Dryas; Fig. 5). However, the presence of one compound does not exclude the occurrence of the other and both can coexist at moderate concentration levels, as in the younger samples and in the recent sediment trap material.

If the assumption of increased tetrahymanol/gammacer-3-one inputs during more stagnant periods holds true, the distinct predominance of long-chain alkenones should in turn reflect phases of favourable ecological conditions for haptophyte primary producers due to enhanced water body circulation or freshwater inputs, for example. This interpretation is substantiated by analytical data from Lake Van water samples which indicate that winter convection is incomplete for time spans of several years. For example, a maximum mixing depth of only 70–80 m was observed in 1989 and 1990 and a complete convection occurred in the years before (Wuest, pers. commun.). Prolonged intervals of reduced convection would consequently promote the development of a stagnant water body. In connection with a limited input of freshwater, significantly diminished primary production rates can be expected due to a gradual removal of nutrients from the productive zone and their concurrent accumulation in the deeper water body. These environmental conditions should result in a low abundance of sedimentary long-chain alkenones and high relative amounts of tetrahymanol/gammacer-3-one (e.g., Allerød and Early Younger Dryas). In turn, a renewed onset of water column mixing after such periods would cause the raising of the chemocline and a marked increase of the trophic level in the upper water layer. Such events could explain mass blooms of certain phytoplankton species—like the alkenone-producing haptophytes— and may be the reason for the pronounced abundance of long-chain alkenones in the Bølling, the Early Holocene, and the 527 y samples.

4.5. U^k_{37} Index

The question arises as to whether the temperature estimations based on the U^k_{37} index reflect variations in the water temperature during the lake's history and whether climatic changes can thus be traced back, as it has been suggested, for other lacustrine settings (Li et al., 1996). We have calculated the alkenone unsaturation index using the equation originally introduced by Brassell et al. (1986; Table 4; Fig. 7). The U^K_{37} ratios derived for the Lake Van samples are dramatically lower than those so far reported from any environment. This is due to the high abundance of the $C_{37:4}$ methyl ketone which depresses the corresponding U^K_{37} values far below zero. However, this compound should probably not

Table 4. Alkenone unsaturation ratios and calculated temperatures.

Varve-years [before 1990]	U^k_{37}	$U^{k'}_{37}$	[°C] a	[°C] b
0	−0.65	0.19	−13.60	−13.76
2	−0.58	0.19	−11.85	−12.00
33	−0.58	0.20	−11.80	−11.95
64	−0.61	0.19	−12.51	−12.66
527	−0.59	0.20	−12.06	−12.21
1274	−0.50	0.18	−9.85	−10.00
5935	−0.22	0.12	−2.73	−2.88
6611	−0.00	0.24	2.65	2.50
9048	−0.09	0.17	0.53	0.38
10575	−0.53	0.13	−10.53	−10.68
10828	−0.68	0.12	−14.30	−14.45
11195	−0.53	0.30	−10.52	−10.67
11925	−0.48	0.18	−9.19	−9.34
12552	n.d.	n.d.	n.d.	n.d.
13615	−0.61	0.16	−12.51	−12.66
14432	−0.60	0.33	−12.25	−12.40

n.d. = no alkenones detected
U^k_{37} = ([37:2] − [37:4])/([37:2] + [37:3] + [37:4]) (Brassell et al., 1986b)
$U^{k'}_{37}$ = [37:2]/([37:2] + [37:3]) (Brassell et al., 1986b; Prahl and Wakeham, 1987)
a U^k_{37} = 0.040T − 0.110 (Prahl and Wakeham, 1987)
b U^k_{37} = 0.040T − 0.104 (Prahl et al., 1988)

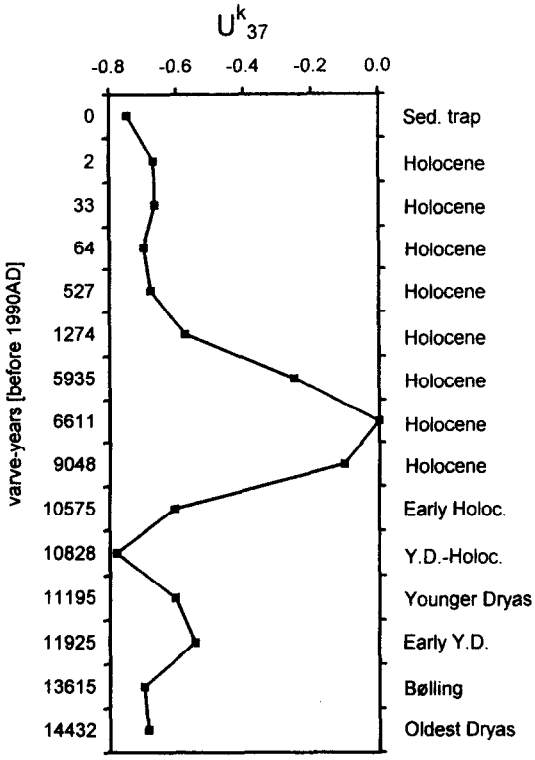

Fig. 7. Plot of U^{K}_{37} values calculated for the Lake Van materials. No long-chain alkenones were present in the Allerød layer. U^{K}_{37} = ([37:2] − [37:4])/([37:2] + [37:3] + [37:4]).

be discarded in the determination of a temperature dependent alkenone unsaturation ratio because tetraunsaturated alkenones showed strongest correlation with temperature in studies with coastal *E. huxleyi* strains (Conte et al., 1994). When using the U^{K}_{37} equations based on laboratory calibrations for *E. huxleyi*, very low values ranging from −14.5°C to 2.5°C are obtained (Table 4, columns a and b). These low values are obviously inconsistent with the aquatic temperature regime in Lake Van (0–17°C).

These results indicate that the reported calibrations are not appropriate to this particular environment and that no absolute temperatures can be determined in the absence of field calibrations.

Nevertheless, it may be supposed that the alkenone unsaturation ratios of the Lake Van sediments are positively correlated to the surface water temperature, as is reported from marine environments. If such a relationship is assumed, the found, fairly constant U^{k}_{37} indices during the deposition of the sediment trap and the shallow core samples (2 to 1274 y; Table 4; Fig. 7) are highly consistent with the expectation of relatively stable temperature conditions in the nearest past of the lake.

Highest alkenone unsaturation ratios are found in the organic material settled 9048, 6611, and 5935 y before 1990 (Fig. 7), indicating relatively higher water temperatures than present. Indeed, these samples were deposited during the rapid increase and maximum abundance of tree pollen in the Early and Mid Holocene, probably reflecting a climatic optimum in the Lake Van area during that time (van Zeist and Woldring, 1978; Landmann et al., 1996).

Comparably low U^{K}_{37} indices are found for the Late Pleistocene materials (Younger Dryas-Holocene transition and Bølling), but they show an unprecedented maximum with even higher values than present during the Younger Dryas event and a slightly elevated ratio for the Oldest Dryas (Table 4, Fig. 7). This evidence for higher temperatures is in contrast to palaeoclimate reconstructions for the Last Glacial Maximum and the Younger Dryas which indicate a dry summer and wet winter climate with temperatures substantially lower than present for the northern Mediterranean and the Lake Van area (by about 3–6°C; Prentice et al., 1992; Landmann et al., 1996).

However, the observed variation in alkenone distributions can also depend on the vertical position of the alkenone producing population within the temperature graded euphotic zone or on the seasonal time of bloom onset. In this respect, sedimentary alkenone compositions might not be characteristic for the ambient climate of nonmarine environments. It may also be argued that growth conditions like salinity, nutrient loadings, or trace metal availability control the respective alkenone mixtures rather than growth temperature. These uncertainties regarding the dependency of lacustrine alkenone unsaturation ratios clearly require further work, i.e., culture experiments and field calibrations in the respective environments. Given the relatively broad distribution of long-chain alkenones reported to date, these investigations may reveal a useful tool for palaeoenvironmental assessments in these nonmarine settings.

5. CONCLUSION

1) High concentrations of long-chain unsaturated ketones with 37 to 40 C atoms have been identified in sediment trap and core samples from the largest soda lake on Earth, Lake Van (Turkey), thus extending their known distribution range to highly alkaline environments.

2) The alkenone unsaturation patterns display notably high relative amounts of the tetraunsaturated compounds, in particular of the $C_{37:4}$ methyl ketone. Such distributions sharply differ from those observed in open marine environments, but appear to be a characteristic feature of limnic or marginal marine alkenone inventories.

3) The U^{K}_{37} ratios for the Lake Van sequence yield no reliable absolute temperatures. Accordingly, SST-determinations based on long-chain alkenones should be applied with caution when a contribution of alkenones from coastal or nonmarine sources can not be excluded. Nevertheless, relative alkenone indices suggest higher lake temperatures than present during Oldest Dryas and Younger Dryas times. Further investigations are necessary to confirm whether lacustrine U^{K}_{37} data are an applicable measure for palaeotemperature assessment or rather depend on species composition, growth conditions, or the hydrological/hydrochemical setting.

4) The presence of tetrahymanol and gammacer-3-one in the Lake Van materials is attributed to organic matter contributions of ciliates. Both compounds occur in a stable relative and absolute ratio, pointing to a very similar diagenetic stability.

5) A negative correlation trend is evident from the comparison of long-chain alkenone with tetrahymanol/gammacer-3-one concentration, which is considered to reflect changes in the environmental conditions. A very high abundance of tetrahymanol/gammacer-3-one is coupled with drastically increased stanol/stenol ratios and is suggested to be connected with a significantly stratified water body. By analogy, long-chain alkenones are thought to be most abundant during intervals of enhanced convection or high freshwater inputs, coupled with high nutrient loadings in the euphotic zone. Thus, most pronounced stagnant conditions characterise the Allerød and the Early Younger Dryas, but appear to cease towards the Holocene. In this respect, alkenone and tetrahymanol/gammacer-3-one abundance may serve as facies markers for the reconstruction of palaeoenvironmental settings in lacustrine environments.

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