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Late Quaternary environmental and climatic changes in central Europe as inferred from the composition of organic matter in annually laminated maar lake sediments

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[1] Geochemical (elemental analysis, bulk $\delta^{13}\text{C}_{\text{TOC}}$, thermal degradation techniques, molecular analysis of *n*-alkanes) and microscopic investigations (maceral analysis, vitrinite reflectance) were performed (1) to characterize the organic matter (OM) in sediments from two maar lakes in the Westeifel volcanic field, Germany, and (2) to discuss paleoenvironmental processes which have controlled the accumulation and preservation of OM. The annually laminated sediments show a wide range of organic carbon contents between 0.3 and 21.4% TOC and Hydrogen Index values between 80 and 501 mg HC/g TOC. Well-developed laminations mirror suboxic to anoxic bottom waters. Diagnostic compounds in the pyrolysates and microscopic analysis permit discrimination between the principal OM sources, and their variations over time provide important evidence for the reconstruction of the environmental histories of the lakes and their watershed. The significance of terrigenous OM is reflected by the occurrence of methoxyphenols in the insoluble as well as mid- and long-chain *n*-alkanes in the soluble OM which are indicative of land plant or macrophyte input to the lakes. The relative abundance of certain homologues together with the amount of terrigenous macerals can be used to show differences in higher plant input and vegetation changes through time. During the Pleniglacial and Younger Dryas period, high-reflecting reworked OM was introduced by soil erosion in an environment with relatively open vegetation. The alkylphenols in the pyrolysates originate partly from the microbial reworking of proteinaceous tyrosine moieties and/or reflect a direct contribution from cyanobacteria. We assume that variations in the carbon isotopic composition of OM are mainly due to changes in the lake's primary productivity with the exception of the Pleniglacial. Various forms of land use are reflected by increasing amounts of terrigenous particles as well as chemical plant markers from 500 varve years B.P. until present. The organic geochemical and microscopic data

correlate well with other proxy information about climate-dependent fluctuations in the ecosystem of the studied sites.

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1. Introduction

[2] The transition from the last glacial period to the Holocene in central Europe is characterized by a series of pronounced climatic fluctuations. These variations have been recorded in several studies of ice cores, marine and lacustrine records [Dansgaard *et al.*, 1993; Björck *et al.*, 1996; Ammann *et al.*, 2000; Austin and Kroon, 2001]. Temperature reconstructions indicate two major increases of the mean annual temperature at (1) the transition from the Pleniglacial to the Bølling-Allerød and (2) at the Younger Dryas/Preboreal boundary. The period of approximately 3000 years in between, commonly referred to as the Lateglacial, is characterized by several decadal to millennial-scale climatic fluctuations that occurred extremely rapidly [von Grafenstein *et al.*, 1999; Brauer *et al.*, 2000]. The longest and most prominent of these fluctuations is the Younger Dryas which marks the end of the Lateglacial. The driving forces for these events are still unclear and a matter of debate. The Younger Dryas cold event was explained by the input of low-density glacial meltwater with a consequent decrease of surface water salinities and pronounced weakening of the Atlantic thermohaline circulation and associated poleward heat fluxes [Broecker, 1994; Sarnthein *et al.*, 1994; Rahmstorf, 2002]. In addition, changes in solar radiation might have played a role since model studies revealed that the rise in atmospheric ¹⁴C concentrations at the onset of the Younger Dryas could not be explained by changes in thermohaline circulation alone [Goslar *et al.*, 2000].

[3] Lake Meerfelder Maar (MFM) and Lake Holzmaar (HZM) are located in the Westeifel volcanic field 95 km south of the city of Cologne, Germany

(Figure 1) and show striking differences in their hydrology and morphometry (Table 1). A calendar year timescale based on varve counts is available for both sediment records which enables a precise knowledge of the absolute sample ages [Brauer *et al.*, 1999b; Zolitschka *et al.*, 2000]. The sediments of both maar lakes have been intensively studied in the recent past and yielded valuable paleoclimatic data. For instance, varve thickness, micro-facies analysis and palynological data have been used to assess past environmental conditions [Brauer *et al.*, 1999a; Litt *et al.*, 2001, 2003]. Anthropogenic influences and trophic status of the Eifel maar lakes have been monitored by studying variations of several chemical elements as well as diatom records [Schettler and Romer, 1998; Schettler *et al.*, 1999; Baier *et al.*, 2004].

[4] With the increasing number of investigations on lacustrine sediment profiles, it has become evident that one other important approach to obtain reliable information about environmental and climatic changes, including anthropogenic perturbations, is the use of the organic matter (OM) composition as reviewed by Meyers and Lallier-Vergès [1999] and Meyers [2003]. The present study mainly focuses on the characterization of the kerogen which is defined as the part of the OM that is insoluble in organic solvents and non-oxidizing acids and bases [Tissot and Welte, 1984]. It represents the main form of OM in young lacustrine sediments, and is a product of the diagenetic alteration of biogenic OM combined with selectively preserved resistant biomacromolecules. Naturally occurring macromolecules such as polysaccharides, proteins, and lignins are important constituents of living organisms [de Leeuw and Largeau, 1993]. Although a very limited number



Figure 1. Location of Lake Meerfelder Maar and Lake Holzmaar, Germany.

of studies is available so far, they indicate that the geochemical composition of this quantitatively most important OM fraction provides valuable information about sources and degradation processes in lake environments [e.g., Bourdon *et al.*, 2000; Fuhrmann *et al.*, 2003].

[5] It is the aim of this research to identify climatic induced processes in the Pleniglacial, Lateglacial and Holocene using different proxy parameters derived from bulk OM, organic petrology, carbon isotopes and molecular kerogen analysis. We also present lipid distribution patterns of epicuticular plant wax derived *n*-alkanes

which are thought to remain in close association with buried plant species and thus can be used to reconstruct the paleovegetation [Rieley *et al.*, 1991; Lockheart *et al.*, 2000; Schwark *et al.*, 2002]. These data were used (1) to determine the principal OM sources of lacustrine sediments; (2) to discuss the evolution of the ecosystem; and (3) to show the association with changing climatic conditions during the last approximately 15,000 years. Maar lakes from the Eifel were selected for these studies because their seasonally anoxic bottom waters favor preservation of biogenic macromolecules and lipids within the sediments. This paper provides the first detailed analysis of the macromolecular OM in lake sediments from the Eifel, Germany and demonstrates the sensitivity of the data set for future high-resolution paleoenvironmental and paleoclimatic investigations.

2. Study Area, Limnology, and Stratigraphy

[6] The lakes of MFM and HZM occur in craters formed by phreatomagmatic eruptions. The age of HZM is estimated as 50,000 to 70,000 years ago [Büchel, 1993]. Meerfelder Maar erupted >35,360 radiocarbon years BP [Zolitschka *et al.*, 1995]. Modern MFM is holomictic and eutrophic (Table 1). More than 40 sediment cores have been taken from all parts of the lake basin [Negendank and Zolitschka, 1993]. The MFM sedimentary history provides an annually laminated varve chronology for the last 14,450 years BP [Brauer *et al.*, 1999b]. The varve chronology dates the Allerød/Younger Dryas transition at 12,680 and the transition to the Holocene at approximately 11,590 varve years B.P. The top of the sequence is not continuously varved and is composed of organic rich deposits with clastic

Table 1. Morphometric and Limnological Data of Holzmaar and Meerfelder Maar^a

Parameter	Lake Holzmaar (HZM)	Lake Meerfelder Maar (MFM)
Location	50°07'N; 6°53'E	50°06'N; 6°45'E
Elevation, m a.s.l.	425.1	336.5
Maximum depth, m	19	17
Average depth, m	8.8	2.31
Diameter, m	325	700
Volume, 10 ⁶ m ³	0.51	2.31
Lake surface area, m ²	58,000	256,000
Catchment area, km ²	2.06	5.76 (1.53 since 1950)
Trophic state (present)	mesotrophic to eutrophic	eutrophic

^a Scharf and Menn [1992]; Oehms [1995]; Brauer *et al.* [2000]. Change in MFM catchment is due to water regulations. The course of the stream (Meerbach) was changed so that it does not enter the lake to diminish eutrophication. Present catchment: Only the area inside the crater.

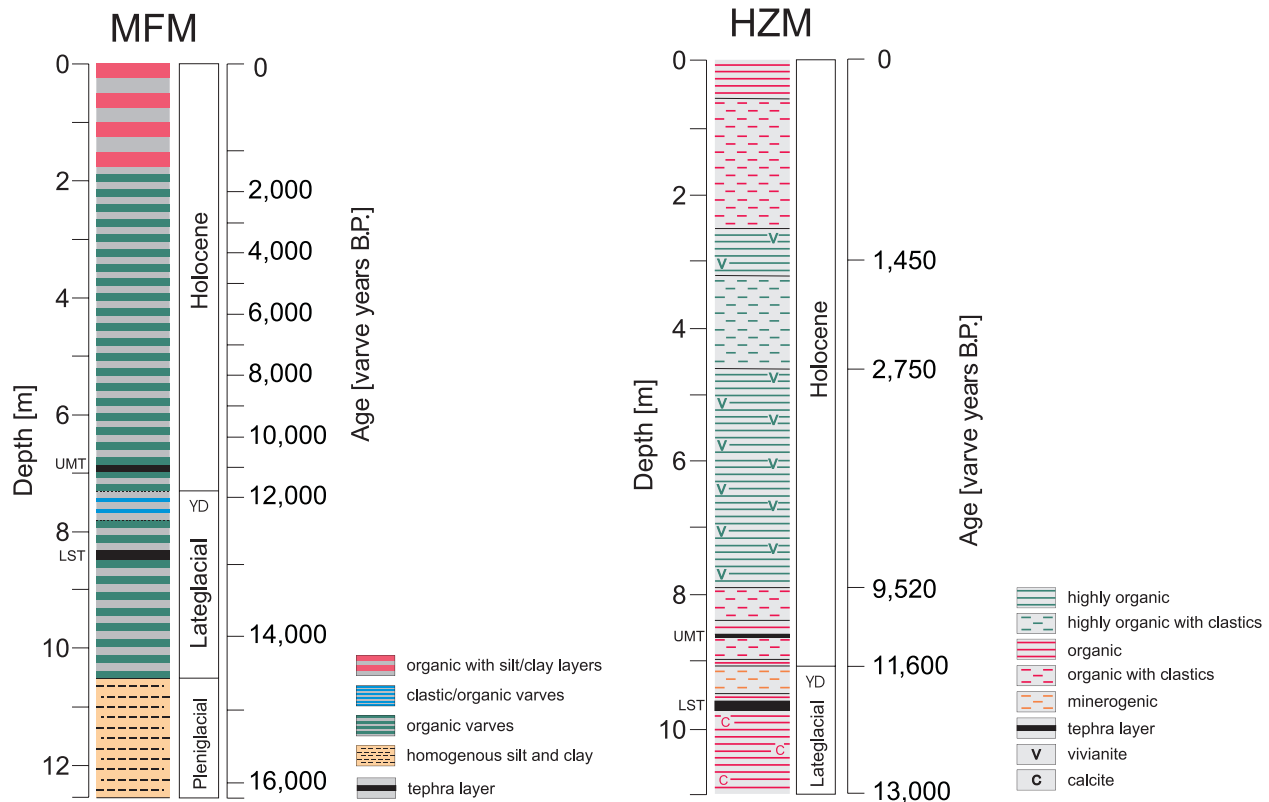


Figure 2. Lithological profiles and stratigraphy of Meerfelder Maar (MFM) and Holzmaar (HZM) [Zolitschka, 1998a; A. Brauer, unpublished data, 2001]. LST, Laacher See Tephra; UMT, Ulmener Maar Tephra; YD, Younger Dryas.

intercalations (Figure 2). The deepest part of the lithological profile below 1060 cm is predominantly clastic and non-laminated. Two tephra layers, the 7 cm thick Laacher See Tephra (LST) and the 0.3 mm thin Ulmener Maar Tephra (UMT), were recognized within the Lateglacial and Holocene sequence.

[7] Modern HZM is dimictic, holomictic, and mesotrophic to eutrophic. A small stream, the Sammetbach, discharges into the lake carrying dissolved nutrients which were mainly responsible for an increasing eutrophication since the Lateglacial [Scharf and Ehlscheid, 1992; Scharf and Oehms, 1992]. The pre-anthropogenic catchment area of the lake was smaller compared to MFM (Table 1). Seasonal anoxic conditions below a water depth of 15 m are presently observed during summer [Lücke, 1998]. A varve-based chronology was established for the past 23,220 years BP [Zolitschka et al., 2000]. The calendar-year time-scale for Lake Holzmaar dated the beginning of the Holocene at 11,600 years BP. The stratigraphic subdivision of the sediment cores is based on the varve chronology in combination with palynological studies [Zolitschka, 1998b; Litt and Stebich,

1999]. Within the Younger Dryas a hiatus occurs as derived from detailed palynostratigraphic and varve comparison between MFM and HZM [Brauer et al., 2000, 2001; Leroy et al., 2000; Zolitschka et al., 2000].

3. Materials and Methods

[8] We investigated in total 76 samples obtained from HZM core 4a and several MFM sediment cores which were recovered by high-precision piston coring (Usinger-System). The MFM and HZM sequences cover sediments dating back until the Pleniglacial and Allerød period, respectively. Samples have been taken with increments between 1 and 10 cm. Time intervals represented by these samples vary from 5 to 300 years. In addition, several field samples were taken from the lake water (particulate organic carbon; POC), the marginal lake area (emergent/floating macrophytes) and from the watershed (leaves, trees) of Lake Holzmaar. The water sample is dominated by cyanobacteria (*Oscillatoria*) which is one of the main primary producers in both maar lakes [Ehlscheid, 1992; Oehms, 1995] and was collected during a bloom period.

[9] For geochemical analysis, samples were freeze-dried and ground using pestle and mortar. Kerogen concentrates were prepared by the Houston Advanced Research Centre (HARC) - GTRI according to the patented isolation method of *Colling and Nolte* [1992] involving acid dissolution of carbonate and silicate minerals. Prior to and after kerogen concentration, the sediment was solvent extracted with a mixture of dichloromethane and methanol (99:1 vol.) using a modified flow-blending extraction [Radke *et al.*, 1978].

[10] The extracts obtained prior to kerogen concentration were used for lipid analysis. Extracts were subdivided into seven lipid classes using the separation procedure as described by *Willsch et al.* [1997] and *Radke et al.* [1980]. Prior to analysis, 5 α -androstane was added to each sample as internal standard. A Hewlett-Packard 5890 Series II gas chromatograph equipped with an HP Ultra 1 capillary column (50 m length, 0.22 mm i.d., 0.33 μ m film thickness), an on column injector and a flame ionization detector (FID) were used. The carrier gas was helium with a pressure controlled flow rate of 1 ml/min. The temperature program was initiated at 90°C (isothermal for two minutes) followed by a heating rate of 4°C/min up to 310°C (isothermal for 63 minutes).

[11] Qualitative and quantitative microscopical investigations were performed on polished blocks and kerogen concentrates in reflected white and fluorescence light (excitation at 365 nm) using a Zeiss Axiophot microscope and oil immersion objectives. The maceral composition was determined by point counting following the nomenclature as described by *Senftle et al.* [1987] and *Taylor et al.* [1998]. The unstructured amorphous OM was subdivided into fluoramorphinite and hebamorphinite. The recognizable macerals were summarized into huminite/vitrinite, terrigenous liptinite, aquatic liptinite and inertinite. Reflectance of organic particles was measured (at least 24 particles per sample) with a 40x oil immersion objective using monochromatic light (546 nm).

[12] Total organic carbon (TOC) contents were determined on decarbonated samples in duplicate using a LECO carbon-analyzer IR 112. The total nitrogen (TN) content was obtained using a Carlo Erba EA1108 CHNS-O analyzer. Known amounts of sulphanilamide were used to calibrate the instrument. Rock-Eval analyses were performed according to the standard technique as described by *Espitalié et al.* [1977] using a DELSI Rock-Eval II instrument. Bulk stable carbon isotope

measurements were made on the TOC ($\delta^{13}\text{C}_{\text{TOC}}$) with an Optima IRMS interfaced via a triple trap device to an elemental analyzer Carlo Erba NA 1500. Data are expressed in the δ notation relative to the VPDB standard in (‰).

[13] Altogether 23 kerogen concentrates and two reference samples were analyzed by open-system one-step pyrolysis-gas chromatography (Py-GC) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Up to 10 mg kerogen was heated in a flow of helium from 300 to 600°C at 50°C/min. The generated products were collected in a cryogenic trap (liquid nitrogen cooling) from which they were liberated by ballistic heating into a Hewlett Packard 5890 gas chromatograph equipped with a fused silica column of 50 m length, 0.32 mm i.d., HP-I coating of 0.5 μ m thickness. The GC oven temperature was programmed from 40°C to 300°C at 5°C/min. Helium was used as the carrier gas. Py-GC-MS was carried out using a Fisons GC 8000 coupled to a Fisons Quadrupole MD 800 mass spectrometer. GC conditions were as described for Py-GC. Full scan mass spectra were recorded over the mass range m/z 10–420 with 2.5 scans/s. Quantitative analysis of 83 compounds in the pyrolysates was performed. Compound identification is based on mass spectra and GC retention indices with reference to the literature [Horsfield, 1984, 1997; Larter, 1984; Meier and Faix, 1992; Galletti and Bocchini, 1995].

4. Results and Discussion

4.1. Bulk Geochemical Parameters

[14] Total organic carbon (TOC) contents of up to 21.4% for MFM and up to 11.3% for HZM indicate a wide range of organic richness (Figures 3 and 4). The TOC values for the Holocene MFM section are generally higher than those for the HZM. In MFM a significant TOC maximum occurs at 3,765 varve years B.P. which is followed by a continuous decrease in TOC from the Holocene to the Lateglacial. In HZM two maxima were observed, the first at 2,686 and the second at 7,390 varve years B.P. Higher overall Hydrogen Index (HI) values were found for the Holocene in MFM compared to HZM (Figures 3 and 4). This indicates that the aquatic production was enhanced in MFM, or that a more intensive oxidation of the OM in HZM has occurred due to changing bottom water oxygenation. Hydrogen-rich lake phytoplankton and bacterial remains are typically

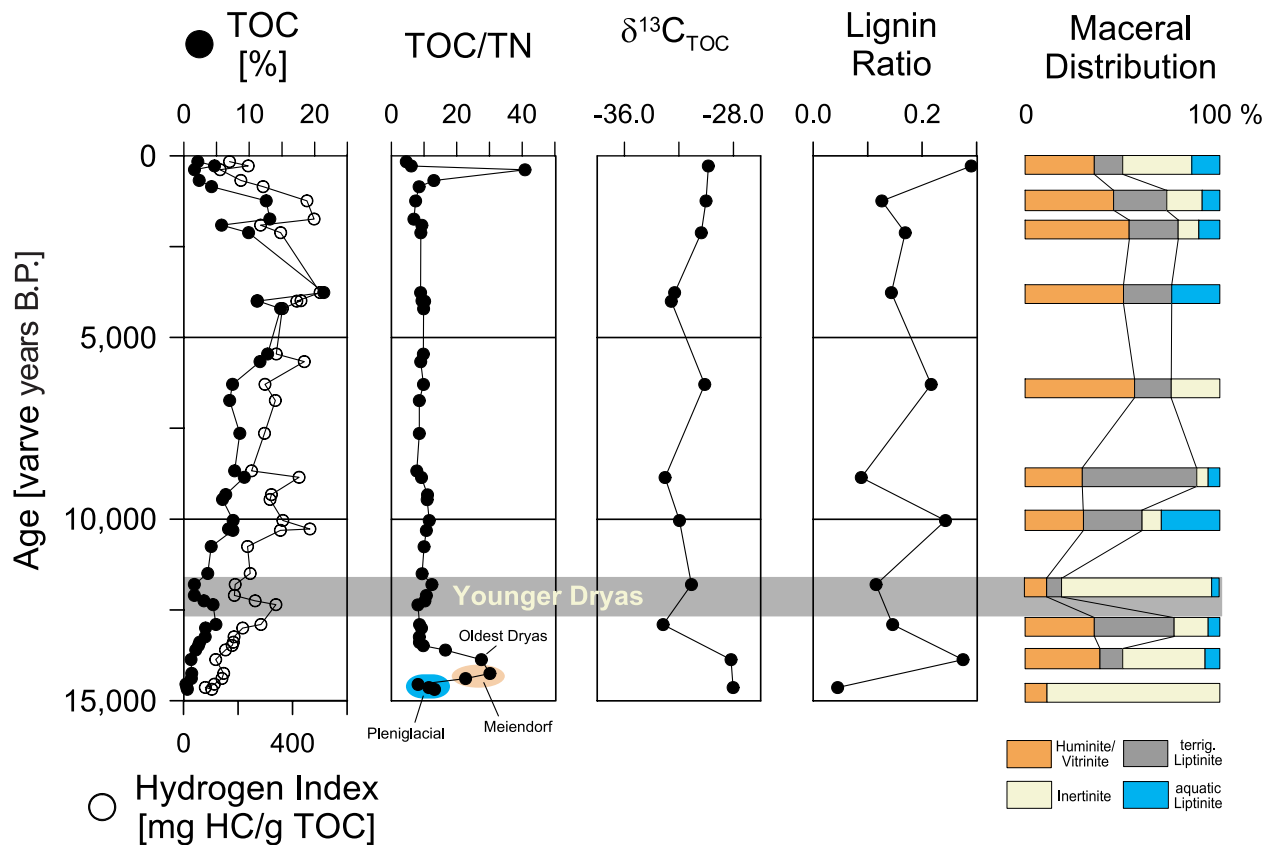


Figure 3. Total organic carbon (TOC), Hydrogen Index, TOC/TN ratio, $\delta^{13}\text{C}_{\text{TOC}}$, and organic matter composition based on maceral analysis (in vol %) for MFM. The Lignin Ratio is defined as 4-methylguaiacol/(4-methylguaiacol + 1-undecene).

characterized by high HI values [Meyers and Lallier-Vergès, 1999]. However, it is also possible that different types of major primary producers may cause different HI signatures of the lake sediments. This was particularly observed for sediments from Lago di Albano, Italy, where HI variations are related to changing contributions of cyanobacteria and diatoms and not by variations of autochthonous versus allochthonous OM sources [Ariztegui et al., 1996]. For tertiary lake sediments (Lake Enspel), a selective accumulation of fossil leaves with lipid and hydrogen-rich wax coatings and cuticles was interpreted to cause high HI values up to 600 mg HC/g TOC [Lüniger and Schwark, 2002].

[15] The TOC/TN ratio is frequently used to characterize OM sources in lacustrine environments, as reviewed by Meyers and Ishiwatari [1993]. The fundamental difference in the elemental composition is caused by the protein richness of algal OM. TOC/TN instead of TOC/ N_{org} values can be used for source interpretations because for most sedi-

ments it can be assumed that N_{inorg} is insignificant compared with TN and thus can be neglected [Müller and Mathesius, 1999; Schubert et al., 2000]. It has been reported that protein rich lake phytoplankton has TOC/TN ratios between 4 and 10, while TOC/TN ratios of terrestrial plants rich in cellulose and lignin are commonly higher than 20 and may even be higher than 200 [Hedges et al., 1986; Meyers, 1990, 1994]. An average TOC/TN ratio of 10.7 was calculated for the HZM section from 8,775 varve years B.P. upward (Figure 4), maximizing at 14.8 (143 varve years B.P.), but significantly lower values were found in the early Holocene/Lateglacial section of HZM (6.3 on average). The latter suggests, according to conventional interpretation, an autochthonous OM source. However, this disagrees particularly with the microscopic results described below which indicate a main source of land plant OM. Firstly, the contradiction may arise because the organic particles with recognizable biological structures represent on average only 30 vol % of the total OM in the lake sediments (see section 4.3). Secondly, secondary

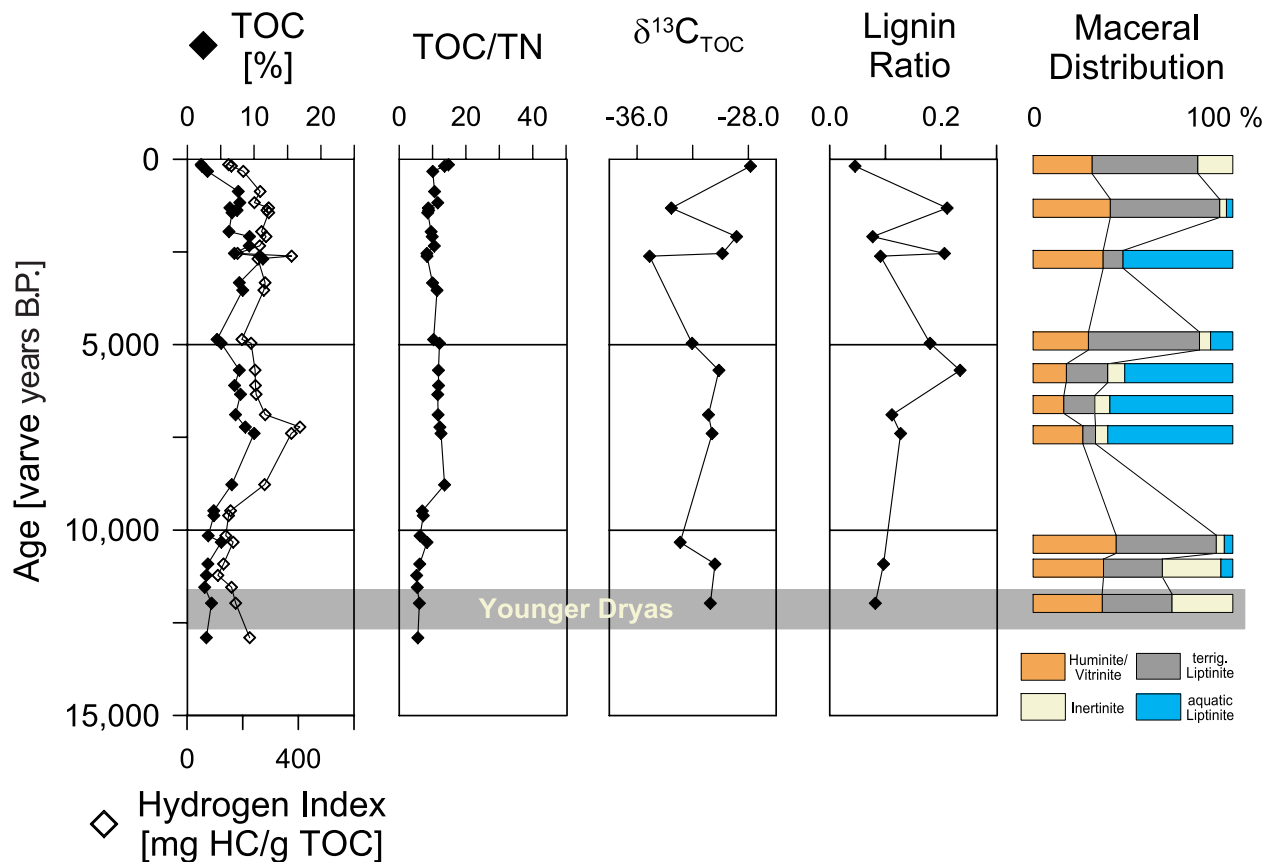


Figure 4. Total organic carbon (TOC), Hydrogen Index, TOC/TN ratio, $\delta^{13}\text{C}_{\text{TOC}}$, and organic matter composition based on maceral analysis (in vol %) for HZM. The Lignin Ratio is defined as 4-methylguaiacol/(4-methylguaiacol + 1-undecene).

processes such as the absorption and retention of N-containing compounds in the sediments might have modified the bulk geochemical parameters [Müller, 1977; Wang and Lee, 1994]. Finally, the higher TOC/TN values in the Holocene of the HZM section may record enhanced paleoproductivity, a correlation that has been previously documented in marine sediments [Twichell *et al.*, 2002]. TOC/TN ratios in MFM show two characteristic maxima of 40.9 at 380 varve years B.P. and of 30.1 at 14,245 varve years B.P. (Figure 3). Average TOC/TN ratios of 13.5 for the pre-Holocene section in MFM are significantly higher compared to HZM, whereas the Holocene ratios (10.4 on average) are in the same range.

4.2. Stable Carbon Isotopes ($\delta^{13}\text{C}_{\text{TOC}}$)

[16] Stable carbon isotopes from lake sediments have been widely used to determine paleoenvironmental and paleoclimatic excursions [e.g., Meyers, 1994; Hollander and Smith, 2001]. The $\delta^{13}\text{C}_{\text{TOC}}$ values vary between -27.9‰ in HZM at 184 varve

years B.P. and -35.1‰ in HZM at 2,608 varve years B.P. (Figures 3 and 4) [cf. Lücke *et al.*, 2003]. The $^{13}\text{C}/^{12}\text{C}$ ratio of OM in lake sediments reflects variations in the carbon isotopic signature of the inorganic carbon fixed during photosynthesis as well as variations in carbon isotope fractionation during photosynthesis in the different OM contributors (lake phytoplankton, aquatic macrophytes and terrestrial vegetation). A significant decrease in the carbon isotope values from -28.0‰ to -33.2‰ (Pleniglacial and Allerød) is observed for the sediments in MFM (Figure 3). Similar negative shifts in the $\delta^{13}\text{C}_{\text{TOC}}$ values in other late Pleistocene-Holocene lacustrine records have been interpreted as evidence of elevated lake biomass productivity [e.g., Mayer and Schwark, 1999]. Our data show that higher HI values are associated with lighter $^{13}\text{C}/^{12}\text{C}$ ratios of organic carbon (Figure 5). Although this trend is less clear for HZM compared to MFM this observation confirms the hypothesis that sequences rich in terrestrial OM (low HI) are associated with relatively heavy $\delta^{13}\text{C}_{\text{TOC}}$ values. Values of the cyanobacterial reference sam-

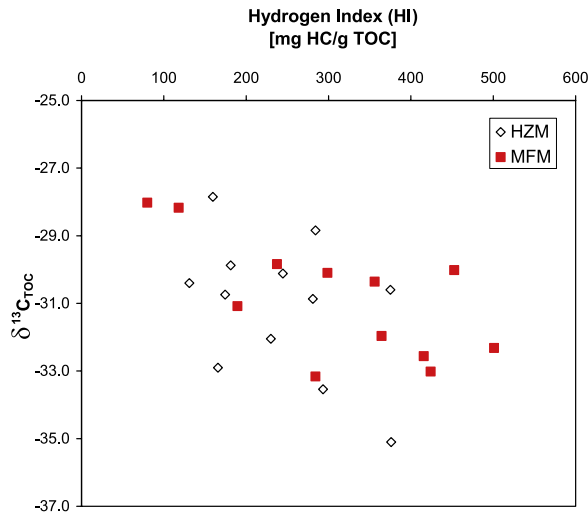


Figure 5. The $\delta^{13}\text{C}_{\text{TOC}}$ versus Hydrogen Index (HI) for MFM and HZM. The negative correlation, particularly for MFM, suggests that an increased supply of autochthonous OM leads to a lighter carbon isotopic composition of the OM.

ple (*Oscillatoria*) as well as typical plant materials (alder leaf and two macrophytes) from HZM have been also measured. The *Oscillatoria* sample has the most negative $\delta^{13}\text{C}$ value of -34.1‰ and a low TOC/TN ratio of 6.2. A wide range of isotopic values between -24.0 and -36.0‰ were previously determined for POM (cyanobacteria are part of this value and show also several per mil variations) in HZM which reflect seasonal fluctuations of the autochthonous population [Lücke *et al.*, 2003]. The submerged macrophyte *Ranunculus* has the most positive $\delta^{13}\text{C}$ value of -20.2‰ and a TOC/TN ratio of 18.0, while the emergent macrophyte *Carex gracilis* (-27.7‰ and 26.0) falls in the C₃ land plant field of Meyers and Lallier-Vergès [1999]. Finally, the alder leaf has a negative $\delta^{13}\text{C}$ value of -33.3‰ . However, the carbon isotopic composition of leaves can vary significantly due to a large number of environmental influences such as light and water availability [Ehleringer *et al.*, 1986, 1987].

4.3. Microscopic Characteristics of the Sedimentary OM

[17] OM in sediments from both maar lakes was examined by reflected white light and fluorescence-inducing blue light microscopy. Typical microphotographs which were taken during the petrographic investigation are shown in Appendix A. The samples are mainly dominated by unstructured

organic aggregates (69.9 vol % on average). The majority occurs as fluorescing amorphous OM (AOM) of irregular shape. Ultrastructural studies (TEM) on recent sediments from Lac du Bouchet, France indicate that the fluorescing AOM is composed of biological remnants verifying its mainly aquatic origin [Patience *et al.*, 1995]. Remains from higher plant sources such as huminite/vitrinite, terrigenous liptinite (mainly sporinite and cutinite) and inertinite are the major recognizable macerals in the maar lake sediments. The terrigenous OM fraction makes up between 7.7 vol % in HZM at 7,390 varve years B.P. and 44.3 vol % in HZM at 11,970 varve years B.P. Some of the woody tissues still display the original cell structure (textinite), but gelified or partly gelified particles are present as well (ulminite or telogelinite). Inertinite group macerals which include fusinite, semifusinite, funginite and inertodetrinite, are all characterized by high reflectance (i.e., above that of the associated vitrinite) [International Committee for Coal and Organic Petrology, 2001]. Increasing amounts of inertinite (up to 25.3 vol %) are detected in the most recent samples, the Lateglacial samples and the Pleniglacial samples in MFM and HZM. The great majority occurs as fine detrital fragments (inertodetrinite) which reflects redeposited debris of other inertinite macerals, while the amount of large fusinites that can be certainly related to local forest fires (pyrofusinite) is low. In combination with the high proportion of small inertinite particles, this indicates abundant fragmentation during transportation of primary oxidized and/or recycled components from allochthonous sources [Diessel and Gammidge, 1998]. It has been stressed previously that particularly inertinite particles can be widely distributed by wind due to their low apparent density and large surface area [Scott and Jones, 1994; Scott, 2000]. Samples from the Holocene, particularly those from the Holocene climatic optimum in HZM, are rich in filamentous alginite (Figures 4 and 6). They resemble structures which have been previously observed in sediments from tertiary lake sediments (Lake Enspel, Germany) and interpreted to originate from cyanobacteria [Clausing, 1998].

[18] The petrographic composition of OM in the maar lake sediments is illustrated in Figure 6, which was previously introduced by Littke and Sachsenhofer [1994] for marine sediments. The triangular diagram displays (1) a huminite/vitrinite and terrigenous liptinite class, (2) an inertinite and recycled huminite/vitrinite class, representing

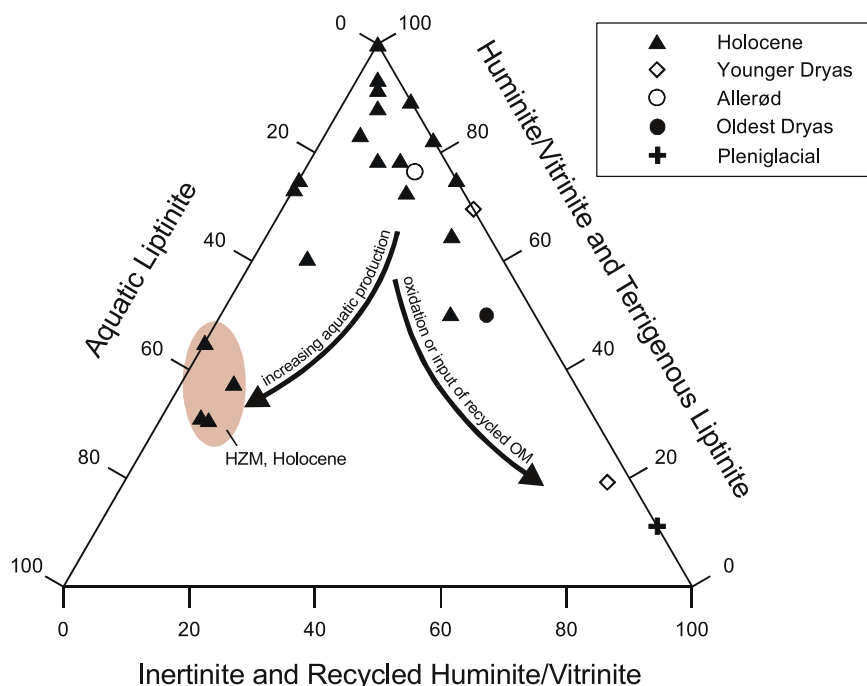


Figure 6. Petrographic composition of kerogen concentrates from Pleniglacial, Lateglacial, and Holocene sediments of H2M and MFM. The three classes were adopted from *Littke and Sachsenhofer* [1994] and determined by point counting.

material which underwent primary oxidation processes or is derived from erosion of older sediments and (3) a lacustrine aquatic liptinite class comprising alginite. In addition, reflectance measurements of all terrigenous particles were performed to distinguish fresh, huminite/vitrinite particles from higher-reflecting reworked/oxidized OM (Figure 7). Because of the small particle size in some samples, it was sometimes difficult to differentiate between fresh and recycled material. In these samples, the point counts used in Figure 6 were corrected according to the reflectance histograms. The reflectance values for terrigenous particles from H2M and MFM range between 0.16% Ro and 3.16% Ro. On the basis of microscopic observations it was decided that reflectance values >0.6% Ro are used to describe components that were oxidized or reworked (inertinite and recycled huminite/vitrinite) components, while values <0.6% Ro reflect direct input by local vegetation. This relatively high value was chosen because reflectance contrasts in the peat and lignite stage can be very large and disappear with higher levels of coalification [Taylor et al., 1998]. Significant differences in the organic petrographic composition between the Pleniglacial, Lateglacial and the Holocene sedimentary OM exist. Samples from the Plenigla-

cial, Oldest Dryas and from the Younger Dryas contain a large part of high-reflecting inertinites and recycled huminites/vitrinites (Figures 6, 7c, and 7d). In contrast, kerogens from the Holocene and Allerød consist of low-reflectance huminite/vitrinite particles with a pronounced reflectance maximum in the range between 0.0–0.3% Ro (Figures 6 and 7b). Abundant higher reflecting organic particles were also identified in the very recent samples (Figure 7a).

4.4. Molecular Distribution of *n*-Alkanes

[19] The most dominant constituents of all aliphatic hydrocarbon fractions are *n*-alkanes in the chain length range from *n*-C₁₅ to *n*-C₃₃ with a strong odd-over-even predominance. Representative gas-chromatograms for the MFM sample set are shown in Figure 8. A maximum contribution is reached from *n*-C₂₇ to *n*-C₃₁ in most of the investigated sediments like it was previously reported for various terrestrial settings [e.g., Cranwell, 1982; Wilkes et al., 1999; Schwark et al., 2002] and interpreted as land plant derived organic matter input. Absolute concentrations of individual homologues in this chain length range vary between 13–335 µg/g TOC. The C₂₇ *n*-alkane is the predominant homologue in most of

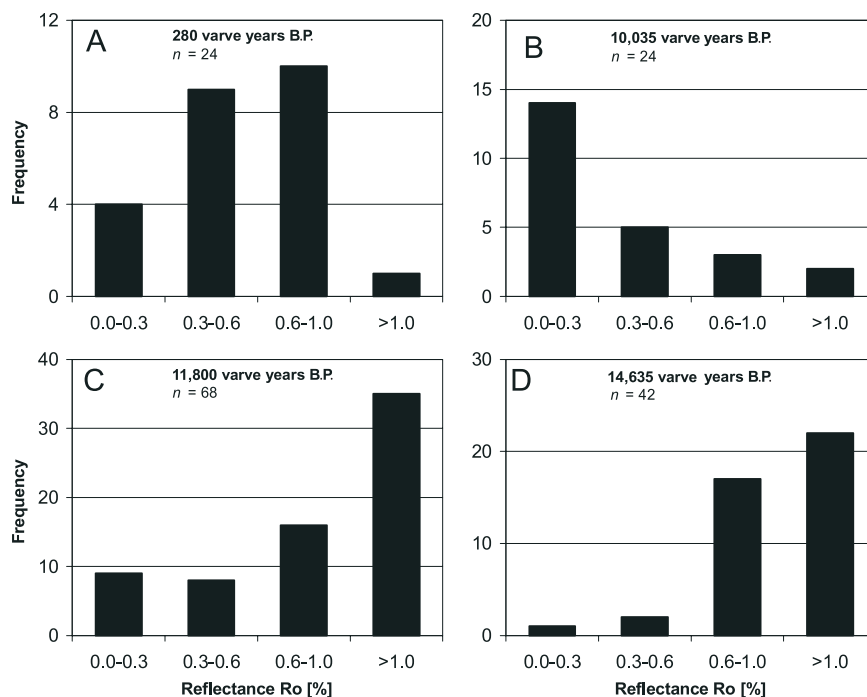


Figure 7. Histograms of reflectance measured on huminite, vitrinite, and inertinite particles in sediment samples and kerogens from MFM. The occurrence of reflecting particles above 0.6% Ro indicates enhanced sedimentation of recycled and/or oxidized terrigenous particles. (a) Holocene (280 varve years B.P.), (b) Holocene (10,035 varve years B.P.), (c) Younger Dryas (11,800 varve years B.P.), (d) Pleniglacial (14,635 varve years B.P.).

the Holocene to Oldest Dryas samples (Figure 8b), whereas samples from the Pleniglacial are enriched in n -C₃₁ and depleted in n -C₂₇ (Figure 8c). Homologues with shorter chain length between n -C₂₁ to n -C₂₅ are regarded to reflect the contribution of aquatic macrophytes to the sedimentary organic matter [Ficken *et al.*, 2000]. Concentrations of individual n -alkanes in this range are slightly lower compared to the long chain homologues, ranging between 2–198 $\mu\text{g/g}$ TOC. The C₂₃ component is particularly abundant in some samples from the early Holocene and Younger Dryas (Figure 8a). Short chain homologues, typical proxies for algal and bacterial organic matter contribution [Meyers, 2003], finally show lowest overall abundances between 0.2–26.2 $\mu\text{g/g}$ TOC for individual compounds between n -C₁₅ to n -C₁₉.

4.5. Molecular Kerogen Characterization

[20] Pyrolysis-gas chromatography is a useful tool to characterize the structure of the macromolecular OM. Because of the complexity of the pyrolysates, mass spectrometry was extensively used in this study to identify individual distribu-

tion patterns of pyrolysis compound classes. Variable proportions of n -alkane/ n -alk-1-ene doublets up to C₃₀, alkylbenzenes, alkylphenols, methoxyphenols, alkylnaphthalenes, nitrogen containing compounds (pyrroles, pyridines, indoles), fatty acids and polysaccharide derived (e.g., furans) pyrolysis products were detected in the studied samples (Figures 9, 10, and 12). Although we did not observe major compositional differences between the two maar lakes the results clearly reveal large differences in the macromolecular OM composition of the Holocene and Lateglacial samples. For instance, n -alkane/ n -alk-1-ene doublets are more abundant in pyrolysates of the Holocene samples (Figure 9a) whereas aromatic compounds are predominant in pyrolysates of the Lateglacial samples (Figure 9b). In addition we identified several specific compounds which can be used to obtain information about OM sources. Pyrolysis of the field samples was conducted in order to help allocate the different sources contributing to the OM in the sediments (Figure 10). The origin and significance of the different compound classes is discussed in the following paragraph. One important result described in this chapter is that in addition to the n -alkyl moieties a significant part of

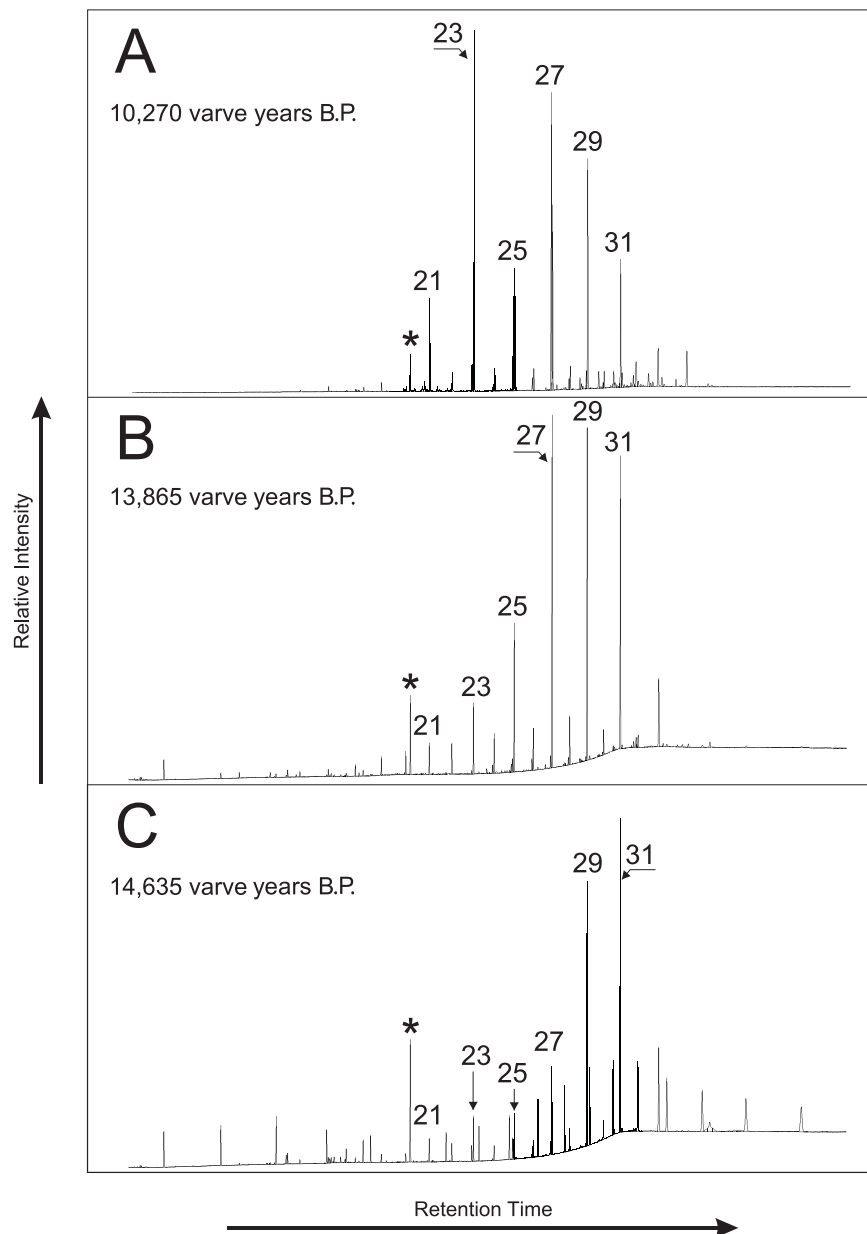


Figure 8. Chromatograms of aliphatic hydrocarbon fractions at different ages of the MFM sedimentary sequence. (a) Holocene (10,270 varve years B.P.), (b) Oldest Dryas (13,865 varve years B.P.), (c) Pleniglacial (14,635 varve years B.P.). Numbers refer to *n*-alkane chain lengths. The asterisk denotes 5 α -androstane as internal standard.

the aromatic compounds, i.e., alkylbenzenes and alkylphenols, can be traced to autochthonous OM sources.

4.5.1. Organic Matter Sources

[21] Chain lengths in the C₆–C₃₀ range for the *n*-alkane/*n*-alk-1-ene doublets were observed and the *n*-alkanes display a distinct odd carbon predominance in the C₁₉–C₃₀ region (Figure 9). The outer cell walls of some algae and extant plant structures

contain resistant, highly aliphatic biopolymers, which are considered the precursors for a major fraction of the *n*-alkyl moieties in lacustrine kerogens [de Leeuw and Largeau, 1993]. Interestingly, the green microalga *Pediastrum* is an important source for aliphatic hydrocarbons [Blokker *et al.*, 1998]. This alga was found in MFM with highest quantities in the early Younger Dryas [Brauer *et al.*, 1999a] where also abundant *n*-alkyl moieties were detected, suggesting that alkenes and alkanes are mainly derived from autochthonous algal sources.

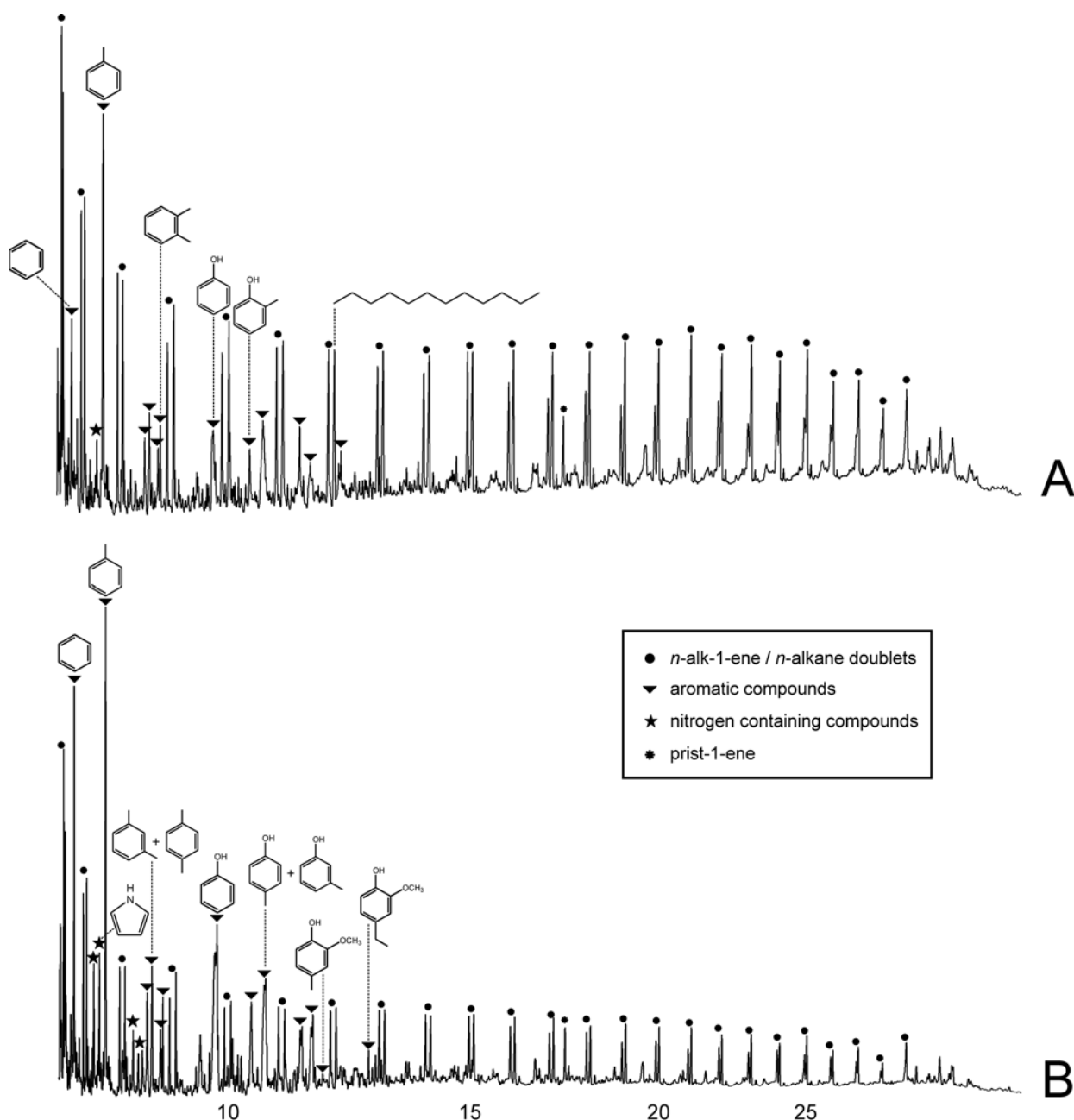


Figure 9. Pyrolysis-gas chromatograms of two selected representative maar lake kerogens from HZM: (a) 450 cm depth (2,608 varve years B.P.) and (b) 930 cm depth (11,970 varve years B.P.). Numbers refer to *n*-alkyl chain lengths. Characteristic pyrolysis products are indicated by their chemical structure.

However, homologous series of aliphatic compounds were not detected in the *Oscillatoria* field sample (Figure 10a) indicating that this important phytoplankton species is not an important contributor of *n*-alkane/*n*-alk-1-ene doublets to the OM in HZM and MFM.

[22] Alkylbenzenes (C₀–C₃) occur in a wide variety of biomacromolecules from aquatic [Derenne *et al.*, 1996; van Heemst *et al.*, 1996] to terrigenous

[van Smeerdijk and Boon, 1987]. Toluene predominates all studied programs which is also an important compound in pyrolysates of the macrophyte and *Oscillatoria* field samples. This suggests that the alkylated benzenes in the pyrolysates originate at least partly from proteins containing phenylalanine (Figure 11a) which have been, for instance, incorporated into melanoidin-type macromolecules [Tsuge and Matsubara, 1985; Stankiewicz *et al.*, 1998].

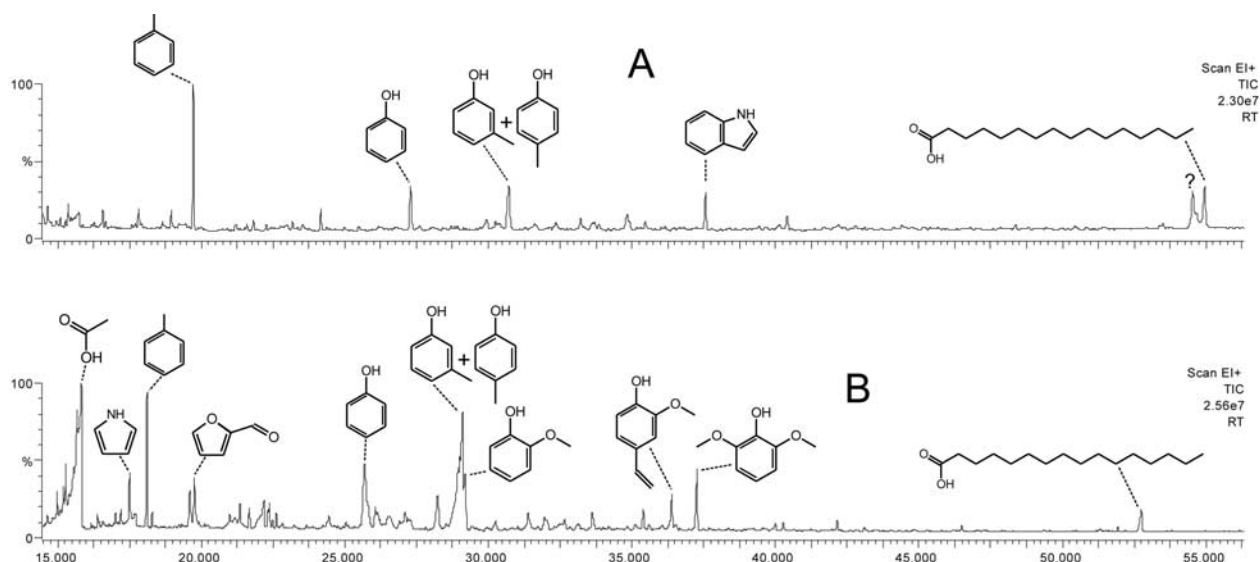


Figure 10. Pyrolysis-total ion current (TIC) traces of an (a) *Oscillatoria* and (b) *Carex gracilis* (aquatic macrophyte) reference sample. Characteristic pyrolysis products are indicated by their chemical structure.

[23] Abundant methoxyphenols indicate the presence of intact or degraded lignin from higher plant constituents in the lake or watershed [Saiz-Jimenez and de Leeuw, 1986; van der Heijden and Boon, 1994], which is also corroborated by their occurrence in the macrophyte field sample (Figure 10b). 4-Methylguaiacol is a typical pyrolysis product from the thermal decomposition of lignin [Galletti and Bocchini, 1995] and an important compound in most of the studied samples. Thus the Lignin Ratio (Figures 3 and 4) is used to show variations of higher plant input to the maar lakes through time. Alkylphenols (C_0 – C_2) that co-occur with phenols containing methoxy groups can also partly be ascribed to the presence of lignin from plant constituents [e.g., Saiz-Jimenez and de Leeuw, 1984]. Alternatively, the generation of certain

alkylphenols can be caused by the thermal degradation of proteins containing tyrosine rich moieties [e.g., Tsuge and Matsubara, 1985] as well as algal derived polyphenolic biomacromolecules such as phlorotannins, fucols or phloroethols [Ragan and Jensen, 1978; Ragan and Glombitza, 1986; van Heemst et al., 1996]. The potential precursor can be discriminated on the basis of the alkylphenol distribution patterns in the mass chromatograms [van Heemst et al., 1999]. For the majority of our pyrolysates the distribution is characterized by a relatively low abundance of 2-methylphenol and C_2 -phenols compared with that of 3- and 4-methylphenol (Figure 12) which is typical for a proteinaceous phenol origin. It is thus thought that the majority of the alkylphenols are generated from protein units (tyrosine; Figure 11b) either resulting

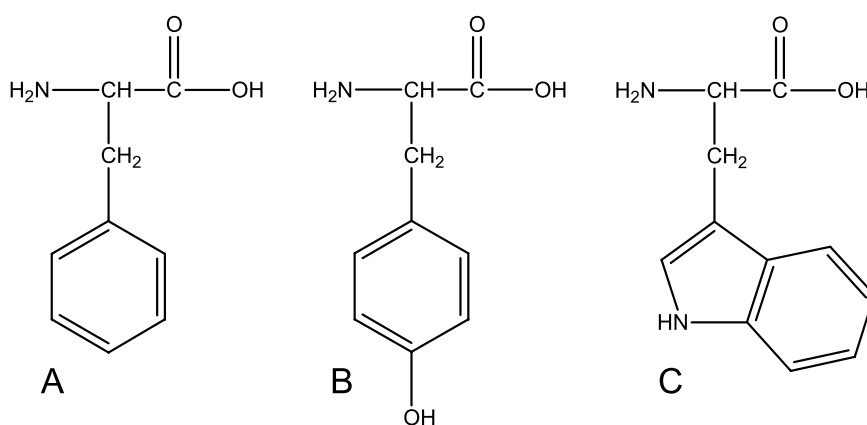


Figure 11. Chemical structures of three common amino acids: (a) phenylalanine, (b) tyrosine, and (c) tryptophan.

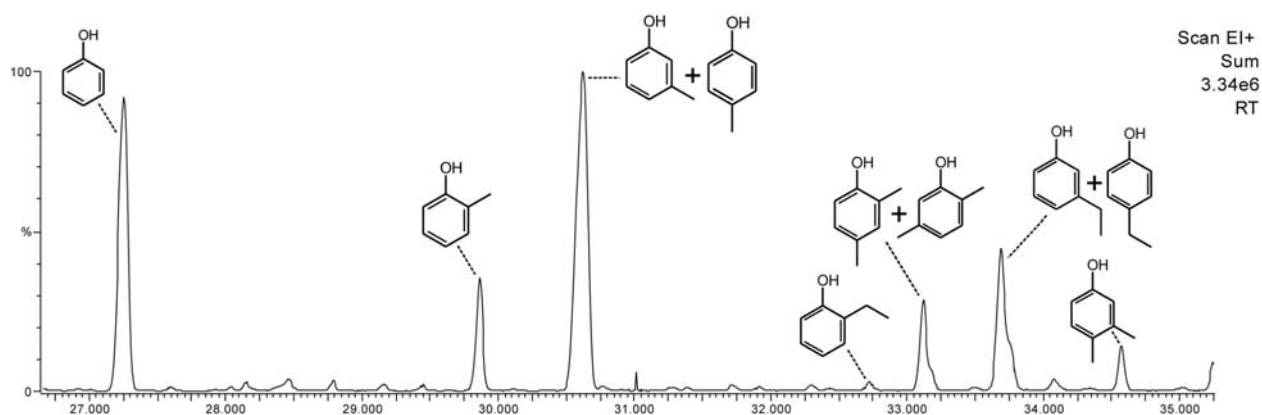


Figure 12. Partial summed mass chromatogram of m/z 94 + 107 + 108 + 121 + 122 revealing the distributions of the C_0 to C_2 alkylated phenols in a sample from MFM at 456.8 cm depth (6,290 varve years B.P.).

from the hydrolytic transformation by microorganisms in the water column/sediment [van Heemst *et al.*, 1999] or indicating a direct contribution of phytoplankton to the OM in the form of tyrosine residues from cyanobacteria [Gadel and Bruchet, 1987]. The latter assumption is confirmed by the very similar distribution pattern in the pyrolysate of the *Oscillatoria* reference sample (Figure 10a).

[24] Pyrroles, pyridines and indoles are the most important organic nitrogen compounds (ONC) in the pyrolysates (Figures 9 and 10). Similar pyrrole distributions as in the present case were previously observed in pyrolysates of dissolved OM from the North Sea [van Heemst *et al.*, 1999], suspended OM from the Rhone Delta [Sicre *et al.*, 1994] and refractory OM from the African upwelling-system [Zegouagh *et al.*, 1999]. It was interpreted that the ONC derive mainly from proteinaceous OM from autochthonous sources. For instance, indole and methylindoles are typical pyrolysis products of tryptophan moieties (Figure 11c).

5. Implications for Environmental and Climatic Change

5.1. Pleniglacial (MFM) and Lateglacial (MFM and HZM) >11,590 Varve Years B.P.

[25] Although the sample resolution is limited to detecting centennial and millennial oscillations, the major environmental evolution and climatic changes are visible. The geochemical record indicates relatively low TOC contents and HI values during the Pleniglacial (Figure 3). Because Rock-Eval indices are influenced by the OM source as well as oxidation processes (see chapter 4.1), relatively low HI values thus reflect the dominant

terrigenous and oxidized nature of the OM which is corroborated by the microscopic analyses (Figures 3, 6, and 7d). Thus a low autochthonous production can be assumed prior to 14,450 varve years B.P. This is substantiated by $^{13}C/^{12}C$ values around -28‰ which is at the lower end for C_3 plants in midlatitudes of the northern hemisphere (Figure 3) and carbon isotopic signatures of terrestrial litter from HZM [Lücke *et al.*, 2003]. Pollen data for the Pleniglacial from HZM and MFM indicate that the terrigenous OM is derived from grasses and sedges that grew in a tundra-like vegetation [Litt and Stebich, 1999; Litt *et al.*, 2001]. Lipid biomarker distributions (long chain n -alkanes) from MFM also indicate a significant contribution of land plant derived OM with a dominance of the n - C_{31} alkane over the homologues (Figure 8c). This confirms a major contribution of herbaceous plants to the sedimentary OM during the Pleniglacial [cf. Brinchat *et al.*, 2000].

[26] The climatic amelioration at the transition from the Weichselian Pleniglacial to the Lateglacial is clearly reflected by many of the organic-geochemical parameters determined in this study. An increase of HI values and lignin-derived components in the pyrolysates (methoxyphenols) in MFM (Figure 3) correlates with the major warming observed in Greenland ice cores. This is also substantiated by high TOC/TN ratios up to 30.1 at 14,385 varve years B.P. in the MFM section which coincide with the Meiendorf interstadial (Figure 3). This first warm stage after the end of the Pleniglacial is characterized by a shrub vegetation with heliophytes and birches [Litt *et al.*, 2001]. A slight reverse trend of the TOC/TN values marks the onset of the Oldest Dryas (13,865 varve years B.P.) followed by a turbidite in the Bølling (13,600 varve years B.P.). This shift in the vegeta-

tion is also obvious from the distribution of lipid biomarkers. As illustrated in Figures 8b and 8c, an increase in the abundance of *n*-C₂₇ alkane relative to *n*-C₃₁ in samples from the Lateglacial indicates a change toward dominant forest vegetation in the catchment of MFM [Brincat *et al.*, 2000; Fischer, 2004]. Increasing amounts of low reflecting huminite/vitrinite particles and terrigenous liptinite have been found in samples and kerogen concentrates from the Lateglacial compared to Pleniglacial (Figures 3 and 7) which points to a larger amount of relatively fresh plant material from shrubs and/or trees close to the investigated sites and thus corroborates the above findings. This might be indicative for a denser terrestrial vegetation in combination with decreasing erosional input from the watershed [Hammarlund, 1993].

[27] We assume that an enhanced production of lake phytoplankton is responsible for the drastic negative shift of the $\delta^{13}\text{C}_{\text{TOC}}$ values in MFM from 13,865 to 12,900 varve years B.P., leading to an increase of organic carbon contents and HI values (Figure 3). This is also confirmed by the negative correlation between $\delta^{13}\text{C}_{\text{TOC}}$ and HI in Figure 5. The characteristic HI maximum in the lower part of the Younger Dryas (12,355 varve years B.P.) in the MFM section (Figure 3) is possibly due to an increased primary production in the lake as a result of significant eutrophication caused by soil erosion and reworking of littoral sediments [Brauer *et al.*, 1999a]. The authors found thick diatom layers (*Stephanodiscus* sp.), *Pediastrum* alginite and an increase in biogenic opal. For the upper part of the Younger Dryas reduced organic carbon and HI values are observed. A decrease of the Lignin Ratio (Figure 3) toward the Younger Dryas cold event marks a reduction of the shrub and woodland vegetation. This is confirmed by increased oxidation of OM, associated with an abundance of the maceral inertinite and higher reflectance values (Figures 3, 6, and 7c) which indicates an input of eroded OM. These allochthonous components were most likely introduced by surface runoff which in turn reflects a predominantly open vegetation. Such a reduction of the forest during the Younger Dryas is in agreement with pollen results by Litt and Stebich [1999] who observed a strong increase of non-arboreal pollen (NAP) including *Graminae* and heliophilous taxa such as *Artemisia* indicative for the expansion of open habitats. Brauer *et al.* [1999a] stated that the formation of mainly clastic-organic varves during this time was controlled by spring snowmelt. The subsection of the Younger Dryas in an early stage with a high autochthonous

productivity and a later stage with a reduced activity of lake phytoplankton is also supported by sedimentological data [Brauer *et al.*, 1999a; Lücke and Brauer, 2004], and investigations of the lipid OM in MFM [Fischer, 2004]. Reduced concentrations of unsaturated C_{16:1} and C_{18:1} fatty acids are particularly evident for a relatively low algal and bacterial OM production. This evolution of the ecosystem during the Younger Dryas has been explained by pronounced hydrological changes indicating major changes in the course and discharge of the Meerbach [Brauer *et al.*, 1999a].

5.2. Holocene (MFM and HZM) < 11,590 Varve Years B.P.

[28] TOC and HI values increase relatively rapidly in both lakes during the Holocene (Figures 3 and 4). This reflects an increase of OM supply to the lake sediments in response to an intensified paleoproductivity during the Holocene. The establishment of woodland around the lake during the Preboreal and the Boreal is documented by an increasing amount of lignin derived components in MFM at 10,035 varve years B.P. With the exception of the transition from the Pleniglacial to the Lateglacial, changes in the carbon isotopic composition are reported to reflect changes in the aquatic primary productivity [Lücke *et al.*, 2003]. Thus $\delta^{13}\text{C}_{\text{TOC}}$ values mainly below -30% during the Holocene document an increasingly dominant input of organic carbon derived from autochthonous OM. This is also substantiated by many physically intact algae (filamentous and colonial) at various depths in the sediments. The isotopic composition of the *Oscillatoria* reference sample of -34.1% and the $\delta^{13}\text{C}_{\text{TOC}}$ versus HI plot in Figure 5 also indicate that autochthonous OM is generally associated with lighter $^{13}\text{C}/^{12}\text{C}$ values of organic carbon. According to the variations described above, it is assumed that the HI variations in HZM and MFM thus describe changes in the relative contributions of autochthonous *versus* allochthonous OM rather than oxidation processes.

[29] The high contribution of aquatic OM, observed in HZM (Figure 4) between 7,390 and 5,690 varve years B.P., reflect the enhanced primary productivity during the Holocene climatic optimum. Chromatograms of pyrolysates from the Holocene show a dominance of *n*-alkyl over aromatic moieties (Figure 9a). The results described above thus support the predominantly aquatic origin of the *n*-alkane/*n*-alk-1-ene doublets.

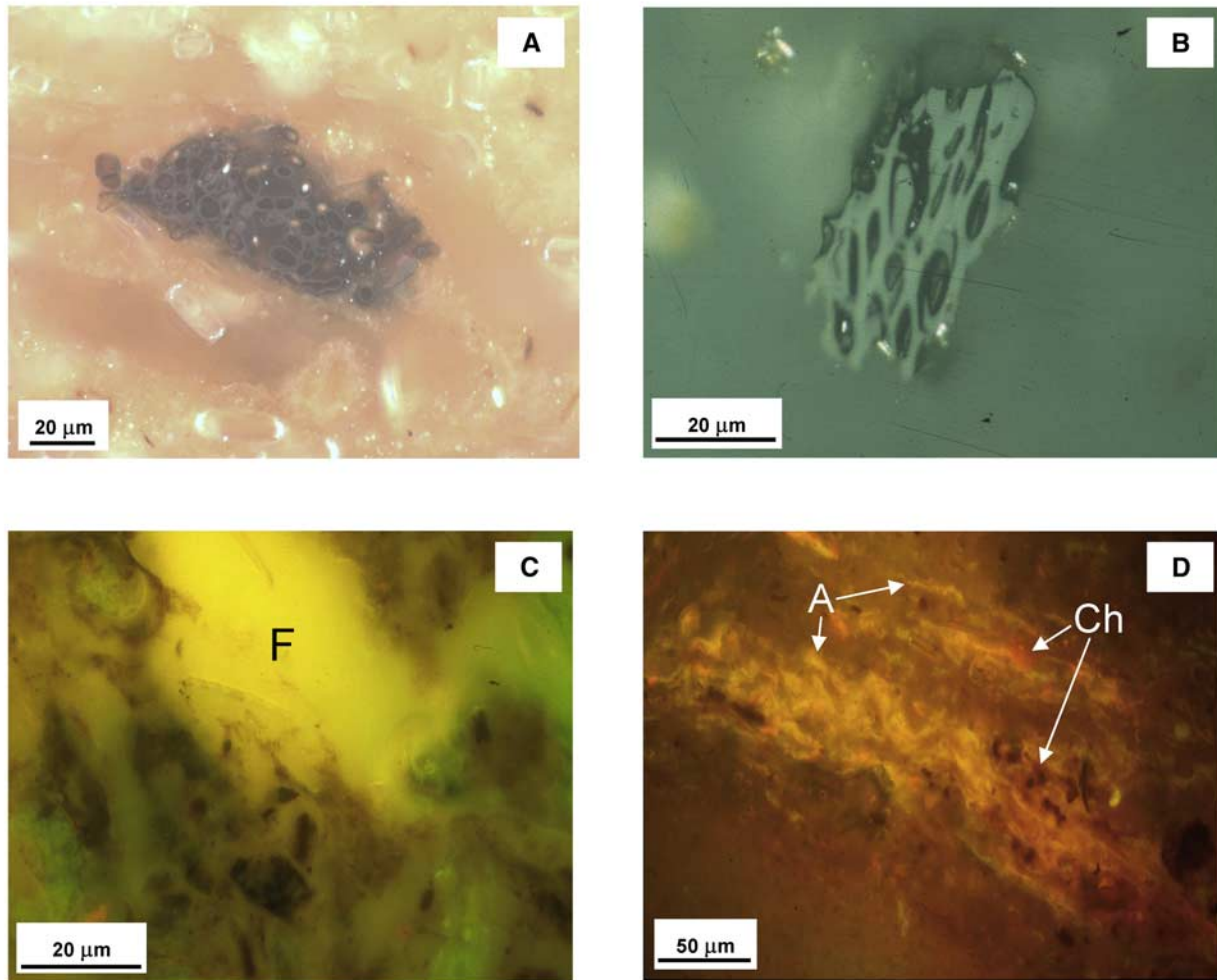


Figure A1. (a) Sample dominated by terrestrial OM with gray to dark gray huminite, reflected white light (MFM; 13,000 varve years B.P.). (b) High reflecting fusinite, reflected white light (HZM; 184 varve years B.P.). (c) Fluorescing amorphous OM (fluoramorphinite; F), blue light excitation (MFM; 280 varve years B.P.). (d) Yellow fluorescing filamentous alginite (A) and red fluorescing chlorophyllinite (Ch), blue light excitation (HZM; 4,960 varve years B.P.).

[30] The increase of lignin derived pyrolysis products around 500 varve years B.P. could be due to enhanced soil erosion and therefore input of land derived organic particles (Figure 3). This might be interpreted as the result of increased human impact due to intensive forest clearing and thus high erosion rates. Therefore both, low reflecting fresh plant OM and high reflecting reworked OM were identified in the studied sediments (Figure 7a). An enhanced higher plant delivery to the lakes is also indicated by lower HI and higher TOC/TN values in both sediment sections (Figures 3 and 4).

[31] The different TOC and HI values of the two maar lakes during the Holocene are interpreted to

reflect local differences in aquatic productivity because no major variations in the oxidation status of the terrigenous organic particles was observed. Local dynamics are very important in that the diatom productivity in HZM is often linked to an increased water column circulation and not necessarily to absolute changes in the nutrient supply [Baier *et al.*, 2004]. One other factor might be the course and nutrient load of the two streams, namely Sammetbach to HZM and Meerbach to MFM. HZM gets little input from its relatively small catchment area. In comparison, MFM received a three times larger discharge from the catchment compared to HZM [Schettler *et al.*, 1999]. Thus the Meerbach might have carried a higher amount of

dissolved nutrients that are available for uptake by biota.

6. Conclusions

[32] • The composition of bulk, macromolecular and lipid OM in maar lake sediments from the Westeifel volcanic field traces fluctuations of paleoenvironmental conditions triggered by climatic change and anthropogenic influences.

[33] • Lignin derived pyrolysis products (methoxyphenols) are used as specific biomarkers to document the input of higher plant constituents to the maar lakes, demonstrating the potential for finer sample resolution in the future.

[34] • Pyrolysis of the macromolecular OM suggests that a large fraction of the detected compounds are derived from protein-rich autochthonous sources. The phenols in the pyrolysates have a double origin. They originate from the lignocellulose of higher plants as well as from tyrosine units of the primary lake producers, particularly cyanobacteria.

[35] • High reflectance values (>0.6% Ro) determined on terrigenous particles indicate allochthonous components that were introduced to the maar lakes by erosion of soils through run-off during periods with an open vegetation. This was observed during cold periods (Pleniglacial and Younger Dryas). Fresh, low-reflecting plant material (mainly <0.3% Ro) is interpreted as a sign for abundant vegetation around the maar lakes during warm periods.

[36] • Shifts in the ¹³C/¹²C isotopic ratio of organic carbon are mainly caused by fluctuations of the aquatic primary production, disregarding the oldest investigated samples (Pleniglacial), where relatively heavy δ¹³C_{TOC} values reflect a predominant terrigenous OM origin probably introduced from poorly developed soils in the watershed.

[37] • Cuticular lipids (*n*-alkanes) extracted from the sediments show a shift in the abundance of *n*-C₃₁ relative to *n*-C₂₇ from the Pleniglacial to the Lateglacial, most likely indicative of a change from a dominant herbaceous to a forest vegetation.

Appendix A

[38] Figure A1 shows microphotographs of typical organic matter in sediments and kerogens from Holzmaar (HZM) and Meerfelder Maar (MFM).

Acknowledgments

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