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Characterisation of sedimentary organic matter by bulk and molecular geochemical proxies: an example from Oligocene maar-type Lake Enspel, Germany

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Abstract

Characterisation of organic matter composition of fossil lake sediments is important in reconstruction of fossil ecosystems and paleoclimates. High time-resolved organic matter analysis is needed to characterize sediments from small lake environments, due to their rapidly changing environmental conditions. A suitable technique for rapid analysis of organic matter in such sediments is Rock Eval pyrolysis. In small lakes, however, routine interpretation of Rock Eval data can be misleading. Lack of tributaries capable of transporting larger woody fragments into small lakes causes a bias towards the input of lipid-rich leaf waxes and cuticles. This hydrogen-rich and oxygen-depleted terrigenous organic matter (HI = 250–600 [mg HC/g TOC] and OI = 20–40 [mg CO_2/g TOC]) can easily be misinterpreted as being of algal origin. Differentiation of terrigenous plant-derived hydrogen-rich organic matter from algal organic matter is readily achieved by including C/N-elemental ratios and lipid biomarker data. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lake Enspel; Oligocene; Lacustrine organic matter; Rock Eval analysis; Hydrogen index; Oxygen index; C/N-ratios; Biomarker lipids

1. Introduction

Paleolimnology reveals a strong trend to apply high-resolution studies in order to unravel rapid environmental changes that have occurred since the last glacial maximum (von Grafenstein et al., 1999). Organic matter incorporated and preserved in (sub)-recent and fossil lake sediments contains important information on biological input (e.g. aquatic vs. terrestrial), bioproductivity or eutrophication levels, redox potential in pore and bottom waters, and other paleoenvironmental properties. Reconstruction of paleoclimatic variations based on organic matter composition requires proxies that can be measured on large, high-resolution sample sets using only small amounts of sample material. Analysis preferably should be possible without intensive sample preparation and work up procedures and the screening technique should be robust enough to accommodate for organic matter variability during earliest diagenesis.

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These demands infer that those organic matter studies cannot be performed on a molecular level although biomarker studies will provide the most detailed information on paleoenvironmental conditions. A rapid screening technique that characterises organic matter with respect to biological sources and diagenetic overprinting is the Rock Eval pyrolysis method developed for source rock assessment in fossil fuel exploration (Espitalié et al., 1977, 1985; Peters, 1986; Bordenave et al., 1993). In this technique, bulk dried samples are heated in an inert helium atmosphere, where upon thermo-vaporisation and pyrolysis, hydrocarbons are quantified by flame-ionisation detection. Compounds occurring as free gases and liquids in sediments are separated from those that occur in bound form, or as particulate organic matter by temperature control. The S_1-detector signal records free hydrocarbons, which are thermo-vaporizable at 300 °C, and the S_2-detector signal measures those compounds liberated during programmed pyrolysis from 300 to 550 °C. The amount of hydrocarbons generated during pyrolysis normalised to the amount of organic carbon comprises the hydrogen index (HI) [mg HC/g TOC]. In addition to this information about hydrogen richness of organic matter, its oxygen content is assessed by measuring the CO_2 generated from the organic matter between 300 and 390 °C. CO_2 released at higher temperatures is derived from carbonate dissociation and is ignored in the estimation of organic matter oxygen content. Pyrolytic CO_2 normalised to organic carbon yields the oxygen index (OI) [mg CO_2/g TOC].

Hydrogen richness and oxygen content of organic matter can be utilised to assess its biological origin as well as degree of microbial reworking or abiotic oxidation as routinely applied in petroleum exploration. Examples for important lacustrine source rocks include the Eocene Green River oil shales (U.S.) (Katz, 1995), the Miocene Mae Sot oil shales (Thailand) (Curiale and Gibling, 1994), tertiary saline lakes in China (e.g. Jianghan Basin and Dongpu Basin) (Fu Jiamo et al., 1988), and those deposited during early rift phases, like the Mesozoic Towaco and Feltville Fm. (Newark Basin, U.S.) (Katz et al., 1988), the Lower Cretaceous Bucomazi Fm. (Lower Congo Basin, Angola) (Burwood et al., 1995) or the Neocomian Candeias Fm. (Reconcavo Basin, Brazil) (Mello et al., 1994).

Comparatively few Rock Eval data sets are available from (sub)recent to postglacial sediments and for organic matter from small lakes, i.e. lakes with a surface area of less than 5 km^2. Maar-lakes, which deserve special attention because of their significance as geological archives conserving continental paleoclimatic and paleoenvironmental information, often fall into the category of small lakes. Maar-lakes generally exhibit a steep bathymetry, whereby great water depth in comparison to low surface area favours the establishment of permanently stratified deep-water bodies. Those lakes often lack tributary rivers or creeks and frequently possess very small catchment areas. For example, Lake Bouchet, located in Massif Central (France), has a surface area of 0.44 km^2 and a catchment area of 0.97 km^2. In this respect maar-lakes are thought to precisely reflect local paleoenvironmental conditions and show a dominance of autochthonous organic matter input (Patience et al., 1995).

Application of bulk organic matter composition determined by Rock Eval analysis in general is focussed on interpretation of HI-values, whereas OI-values and the temperature of maximum pyrolysis yield, the Tmax, receive less attention. HI-values in postglacial sediments vary between 10 and 600 [mg HC/g TOC] (e.g. Talbot, 1988; Talbot and Livingstone, 1989; Dean and Stuiver, 1993; Patience et al., 1995; Ariztegui et al., 1996; Beuning et al., 1997; Buillit et al., 1997). Prequaternary source rocks with type I kerogen often reach HI-values close to or even slightly above 1000 [mg HC/g TOC]. HI-values of more than 600 [mg HC/g TOC] in Quaternary strata are only reported for near-surface sediments from Lake Greifen by Hollander et al. (1990). In this sequence, the lowest HI-values vary around 400–500 [mg HC/g TOC] and correspond to organic matter contents of only 1% TOC, which indicates very special depositional settings or an analytical overestimation of the HI-values. Similarly, a data set reported by Talbot and Lærdal (2000) reveals two populations of HI values, one well within the limits observed for most Quaternary lake sediments and one population from the same core bearing HI-values around 800 [mg HC/g TOC], again probably due to analytical overestimation.

Variations in HI-values of lake sediments can be ascribed to various processes (Talbot and Livingstone, 1989; Meyers and Lallier-Vergès, 1999). Very low values of less than 150 [mg HC/g TOC] are due to predominantly terrigenous-derived woody organic matter and/or bacterial degradation and oxidation (Espitalié et al., 1977, 1985; Tissot and Welte, 1984; Hunt, 1995). For samples with HI-values ranging between 150 and 600 [mg HC/g TOC], a decrease in HI may be due to: (i) admixture of type III to type I organic matter, (ii) reworking of organic matter during transportation through the water column, i.e. low settling rates, (iii) fluctuations in the position of the chemocline within the water column, thus providing free molecular oxygen for oxidation of sedimented organic matter or allowing aerobic microbial degradation. Admixed type III organic matter may be of contemporaneous origin, including charcoal and other debris derived from forest fires, or may comprise eroded fossil material. Microscopical investigation, or other supplementary techniques like elemental or isotopic analysis and biomarker studies often achieve discrimination between such sources.

We here provide evidence that discrimination of organic matter deposited in the small maar-type Enspel lake, Germany (Fig. 1), when based on standard Rock Eval interpretation techniques may lead to erroneous conclusions. We offer an explanation for an additional important source mechanism leading to enhanced HI values and reduced OI-signatures in small lake settings. A method for identification of landplant-derived hydrogen-rich organic matter in lacustrine sediments is provided.

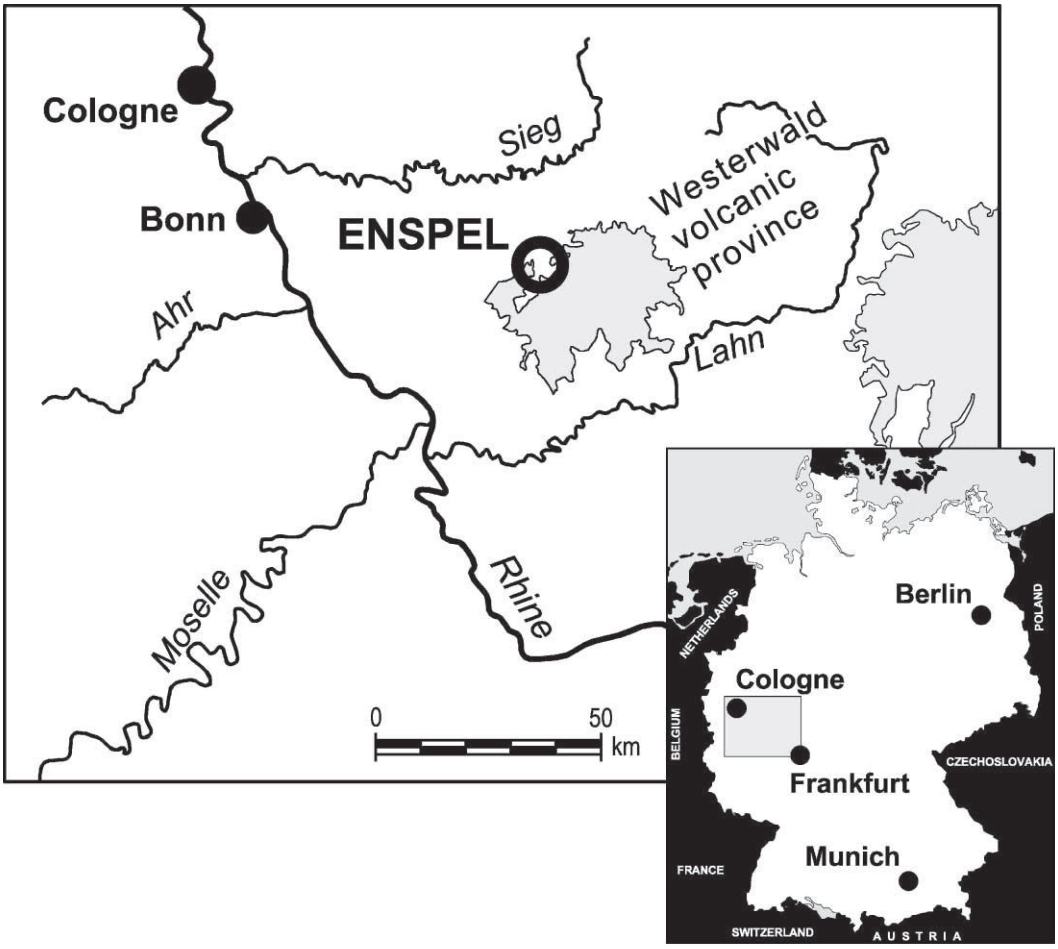


Fig. 1. Map with location of Enspel study area within the Tertiary volcanic province of the Westerwald, Rhineland-Palatinate.

2. Geological setting and methods

The lake deposit of Enspel is situated 35 km E of Koblenz and 6 km SW of Bad Marienberg at the village of Enspel in the Westerwald, Rhineland-Palatinate, Germany (Fig. 1).

During the Upper Oligocene, intensive volcanic activity in the Westerwald area leads to a vast number of basaltic flows covering the variscian deformed, siliciclastic lower Devonian basement (Meyer and Stets, 1980; Schreiber, 1994). At the western rim of this volcanic province, the Enspel oil shale deposit developed in a complex maar-like depressive structure of most probably combined caldera and tectonic graben origin (Lehmann, 1930; Pirrung, 1998). A basaltic flow, erupted by a volcano in the direct neighbourhood to the lake, catastrophically terminated the lake-succession by filling up the lake basin and preserving the sediments and included organic matter from degradation (Schreiber, 1995).

During the last decade, the uppermost part of the lake sediments was subject of intensive, mostly paleontological studies. Excavation campaigns focused on the extremely well preserved fossil content revealed numerous findings of animals including insects, fishes, mammals and amphibians as well as a high number of excellent preserved landplant-derived leafs and fruits. Köhler (1997) found an Upper Oligocene age of the floral assemblage, which matches with datings based on mammal remains by Storch et al. (1996), revealing an age of approximately 25.8 Ma. Consistent with this paleontological data is a radiometric K–Ar dating of the overlying basalt (Horn and Müller-Sohnius, 1988). Although the overall age of the oil shale deposit is well determined, it is yet unknown over which period of time the lake persisted. Preliminary sedimentological reconstructions show a small, but relatively deep meso- to eutrophic lake with a steep marginal bathymetry (Gaupp and Wilke, 1998). The deposition of black shales requires anoxic conditions in the epilimnion and relatively low detrital input. The lack of larger woody fragments points to a hydrologically closed lake without major tributaries.

A research well, drilled in 1996 near the geophysically predicted center of the lake deposit, sunk through the entire lake sequence and revealed a total sediment filling of 140 m.

Olive-brown to black-coloured, organic-rich and mostly laminated oil shales are frequently interlayered by clastic redeposition sections which build up almost 3/4 of the entire sedimentary column. This event-deposits with variable thickness ranging from cm-scale to several meters, underline the steep morphology of the lake basin (Felder et al., 1998). Although they can reach substantial thickness, they are believed to represent only local events which do not affect the entire lake.

For this study, only the oil shale lithologies (approximately 35 cumulative core-meters) were investigated in a set of 102 samples. To obtain a representative record over the whole deposit, sampling positions were chosen with respect to sedimentological changes within the oil shale. Each sample represents a homogenized 1- to 5-cm interval of macroscopically uniform oil shale.

A flow chart diagram summarizing the analytical work-up is given in Fig. 2.

All samples were freeze-dried, ground to analytical grain size and subjected to elemental analysis (C, N, S) by combustion in a LECO CS 225 (C, S) and a HERAEUS Vario EL (C, N) instrument. Total organic carbon (TOC) was determined after removal of carbonate carbon by acidification with 32% HCl; carbonate carbon (TIC) was calculated by difference between total carbon (TC) and TOC. Sediments of the Enspel oil shale deposit are virtually free of carbonate despite rare siderite bands of less than 1-cm thickness (Felder et al., 1998). Rock Eval analysis was carried out on a VINCI Rock Eval II instrument applying standard methods as described in Espitalié et al. (1985) or Bordenave et al. (1993).

Dried samples were sequentially extracted by accelerated solvent extraction (ASE) using dichloromethane and methanol/chloroform (1:1, v/v) at 75 °C and 50 bar pressure. An aliquot of the highly polar extract fraction and the extraction residue was saponified with 1 N KOH in methanol under reflux for one hour to obtain bound lipids. Total extracts were fractionated into carboxylic acid and neutral fraction by low-pressure liquid chromatography on a KOH-impregnated silica column (15×1.5 cm) using dichloromethane as mobile phase. Acids were recovered from the basic column by elution with 1% formic acid in dichloromethane. Neutral fractions were further chromatographed by middle-pressure liquid chro-

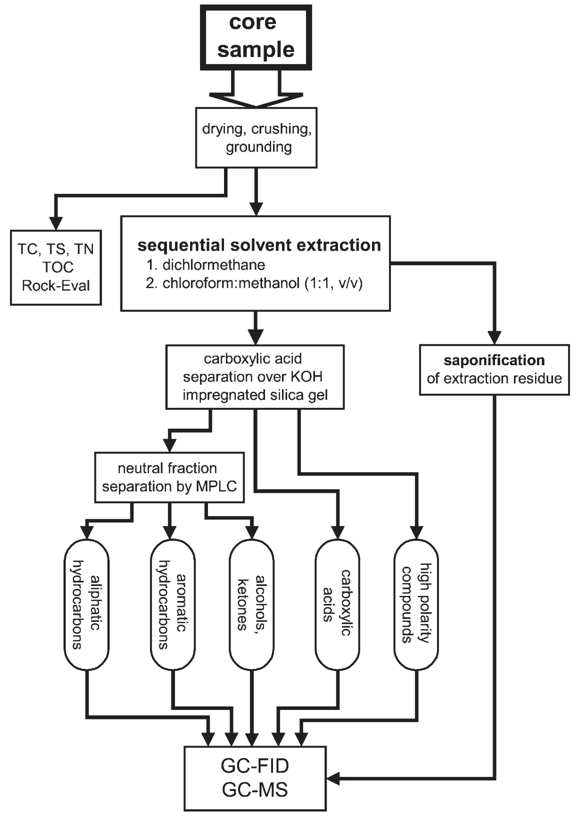


Fig. 2. Analytical flow chart diagram. About 100 samples were analysed for rapid screening data including elemental and Rock Eval analysis. Sequential solvent extraction and saponification of extraction residue followed by GC-FID and GC/MS analysis was carried out on a reduced set of 24 representative samples.

matography (MPLC) (Radke et al., 1980) to obtain aliphatic hydrocarbon, aromatic hydrocarbon, ketone and alcohol fractions. After derivatization with diazomethane or bis-silyl-trifluoracetamid (BSTFA), for carboxylic acids and alcohols, respectively, fractions were analysed by gas-chromatography with flame-ionisation detection (GC-FID) and gas chromatography–mass spectrometry (GC/MS).

GC-FID was performed on a Hewlett-Packard 5890 Series II GC applying splitless injection onto a 50-m fused silica column (0.25 mm ID) coated with 5% phenylsiloxane (0.25 μm film thickness). Helium was used as carrier gas with constant flow of 1.5 ml/min. Temperature was programmed from 80 to 140 °C at 10 °C/min and then to 320 °C at 4 °C/min, followed by 30-min isothermal temperature. Chromatographic conditions for GC/MS were identical to GC-FID analysis. The mass spectrometer was operated in electron-ionisation mode at 70 eV, scanning from 50 to 650 amu. Compound identification was achieved by injection of authentic standards and standard mixtures, supplemented by comparison of mass spectra and elution orders with published data.

3. Results

Sediments from fossil Enspel Lake are composed of low amounts of detrital input derived from eroded Devonian shales and siltstones, variable amounts of volcanoclastic tuffs and tuffites and organic matter. Macrofossils found in the investigated core almost exclusively comprise deciduous plant leaves (Fig. 3), which according to Köhler (1997) belong to the arcto-tertiary floral assemblage with East Asian elements.

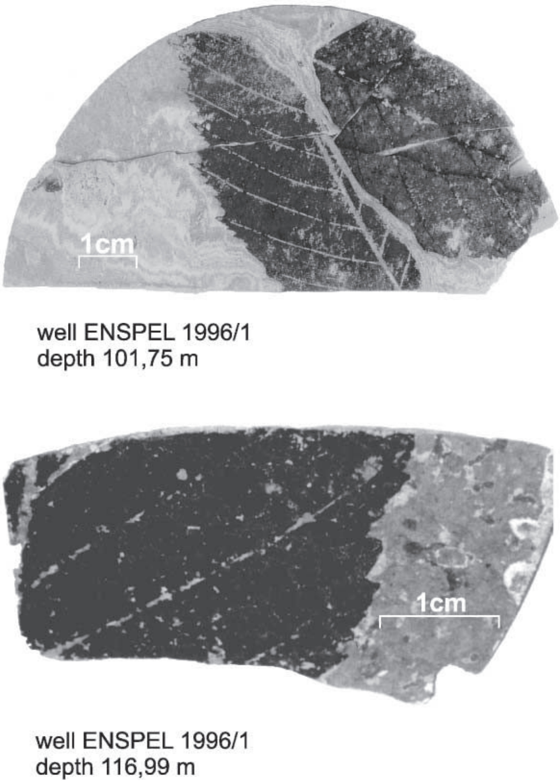


Fig. 3. Photographs of cores split parallel to bedding plane containing frequent plant debris, especially deciduous tree leaves.

Microscopical investigation reveals the presence of diatomaceous algae (Schiller, in press), some *Botryococcus*-like algae, occasionally dinoflagellates, and few examples of other algae (Clausing, 1998).

The TOC contents of 102 representative samples vary between 2% and 34%. Total nitrogen (TN) ranges from 0.06% to 0.85%, and total sulphur (TS) was found to fluctuate between 0.2% and 3.5%, except for one sample at the base of the lacustrine sequence yielding 6.1% TS (Fig. 4a). Low sulphur concentration as compared to TOC are typical for sulphate-depleted lacustrine settings (Leventhal, 1983; Berner and Raiswell, 1984) and except for two basal samples all data points plot in the freshwater field (Fig. 4a) as defined by Berner and Raiswell (1984). A crossplot of total nitrogen vs. TOC reveals a good correlation between both elemental concentrations and allows calculating an averaged molar C/N-ratio of 32 (Fig. 4b). C/N-ratios are widely applied to organic matter source characterisation (Tyson, 1995; Meyers and Ishiwatari, 1993; Meyers and Lallier-Vergès, 1999) with low values of 5–8 being characteristic for lacustrine algae and values between 20 and approximately 100 being indicative of terrestrial land plant input. Microbial activity can significantly influence the C/N-ratio (Meyers and Ishiwatari, 1993; Meyers, 1994; Tyson, 1995) during settling through the water column and during early diagenesis but generally the starting values are retained in the preserved organic matter (Meyers and Eadie, 1993; Meyers, 1994). Molar C/N-ratios between 21.5 and 53 (Fig. 4b) as determined for Enspel lake sediments therefore represent terrigenous-derived organic matter with only minor contribution of autochthonous algal material.

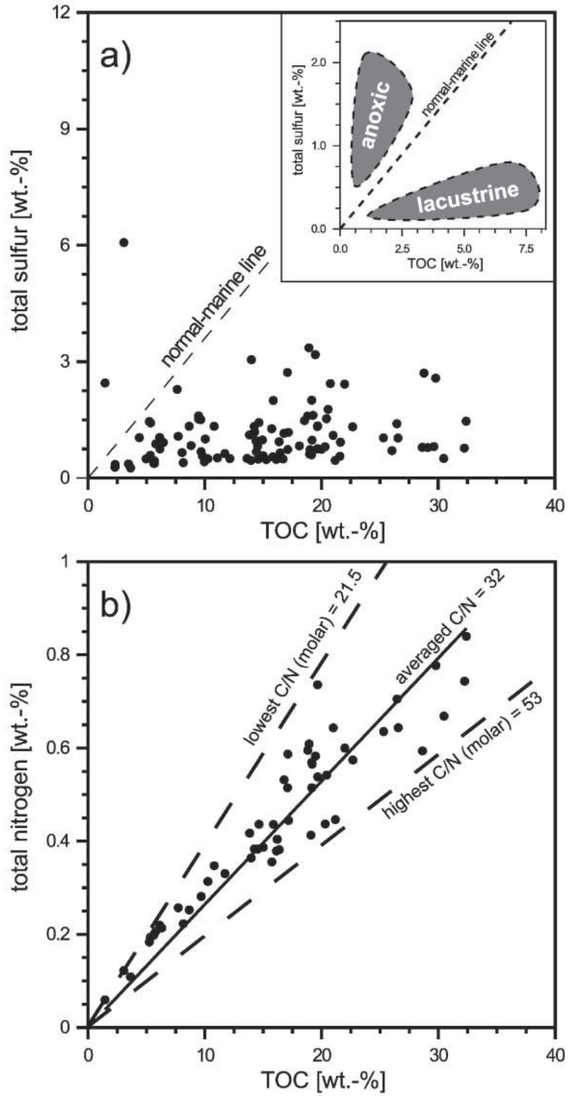


Fig. 4. Crossplots of (a) TOC vs. total sulphur and (b) TOC vs. total nitrogen. Fields for normal marine, anoxic and freshwater conditions are according to Berner and Raiswell (1984). Total nitrogen and TOC values are given in weight percent, C/N-ratios are calculated on molar base.

Rock Eval analysis of bulk samples provided HI-values of 250 to 600 [mg HC/g TOC] and OI values of 20 to 70 [mg CO_2/g TOC] except for one sample with an OI of 120 (Fig. 5). When plotted in a standard HI/OI-discrimination diagram (Espitalié et al., 1977, 1985; Tissot and Welte, 1984), half of the data points are located in the type II organic matter field. For immature Quaternary sediments, this is characteristic for predominately autochthonous algal organic matter. A trend of decreasing HI and complementary increasing OI values (Fig. 5) is noted for the remaining samples. Such a distribution is commonly interpreted as a result of either mixing of variable proportions of type I and III organic matter or increasing degradation/oxidation of type I or II organic material. In both cases a lacustrine algal end-member with HI-values around 650–700 [mg HC/g TOC] is postulated by extrapolation of the distribution trend shown in Fig. 5. Extrapolation of the observed trend towards highly

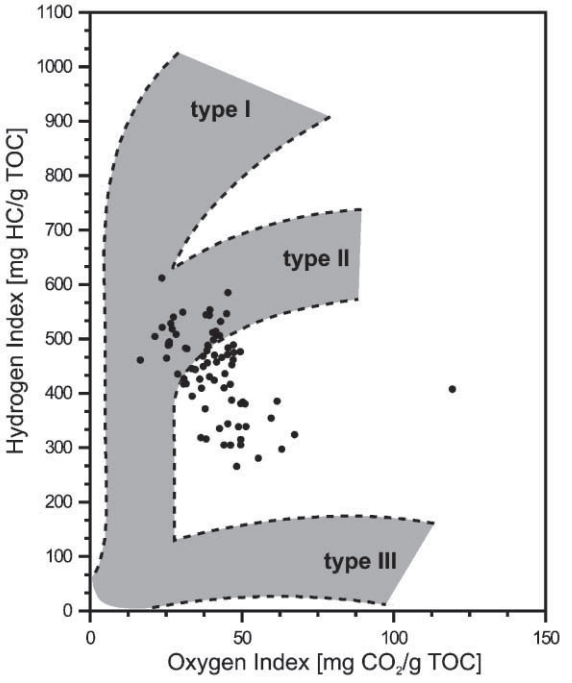


Fig. 5. HI vs. OI crossplot often referred to as pseudo-van Krevelen diagram with indications for diagenetic evolutionary pathways for type I, II and III organic matter.

oxidized organic matter composition or exclusively terrigenous organic matter will result in a non-linear increase in OI and decrease in HI-values.

In sediments, strong mineral matrix effects are often observed during Rock Eval analysis, causing a retardation of pyrolytically released compounds and thus underestimation of the hydrogen index (Langford and Blanc-Valleron, 1990). In order to obtain a corrected HI-value, a plot of S_2 vs. TOC is generated and the slope of the regression line taken as representative hydrogen index (Langford and Blanc-Valleron, 1990). For the investigated sample set, an average HI of 550 [mg HC/g TOC] is obtained by this method, with all samples plotting in the organic matter type II field (Fig. 6). In organic matter-rich lacustrine sediments, waxy high molecular components are ubiquitous (Tissot and Welte, 1984). These free lipid compounds by definition do not contribute to particulate organic matter (proto-kerogen) and should be released during the thermo-vaporization phase of Rock Eval analysis to be quantified within the S_1 peak. However, high boiling points of C_{30+}

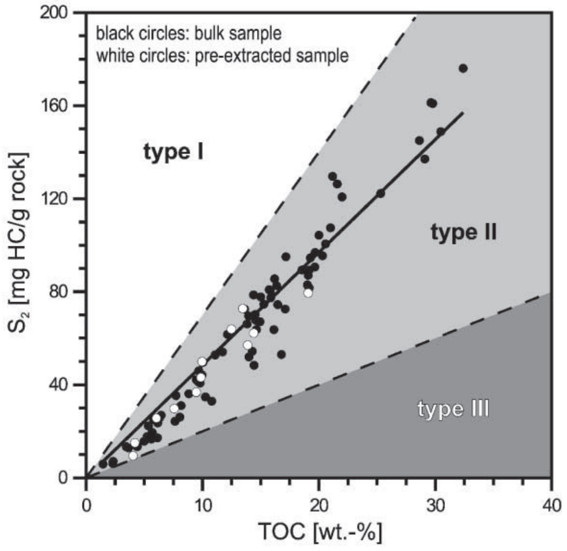


Fig. 6. Improved organic matter typing diagram based on crossplotting of TOC and S_2 data. In this approach mineral matrix effects are minimised and an averaged HI-value can be calculated from the slope of the regression line.

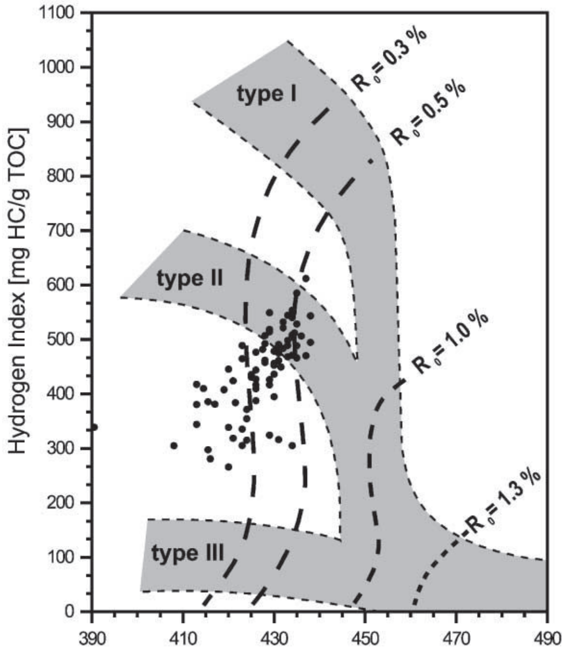
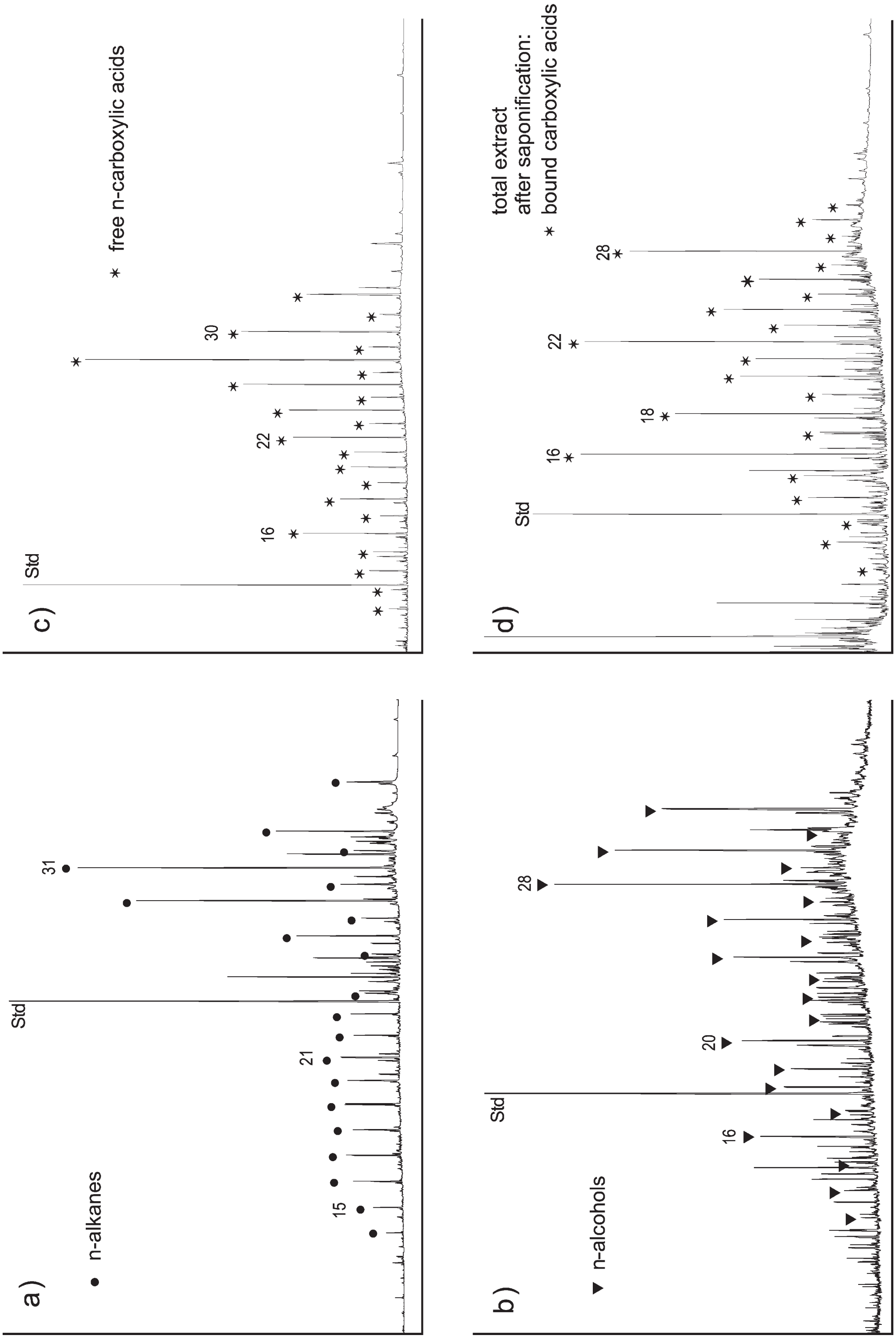


Fig. 7. Organic matter type discrimination diagram based on crossplot of Tmax and hydrogen index.


a)
● n-alkanes
15
21
Std
31
b)
▼ n-alcohols
16
Std
20
28
c)
✶ free n-carboxylic acids
Std
16
22
30
d)
total extract
after saponification:
✶ bound carboxylic acids
Std
16
18
22
28

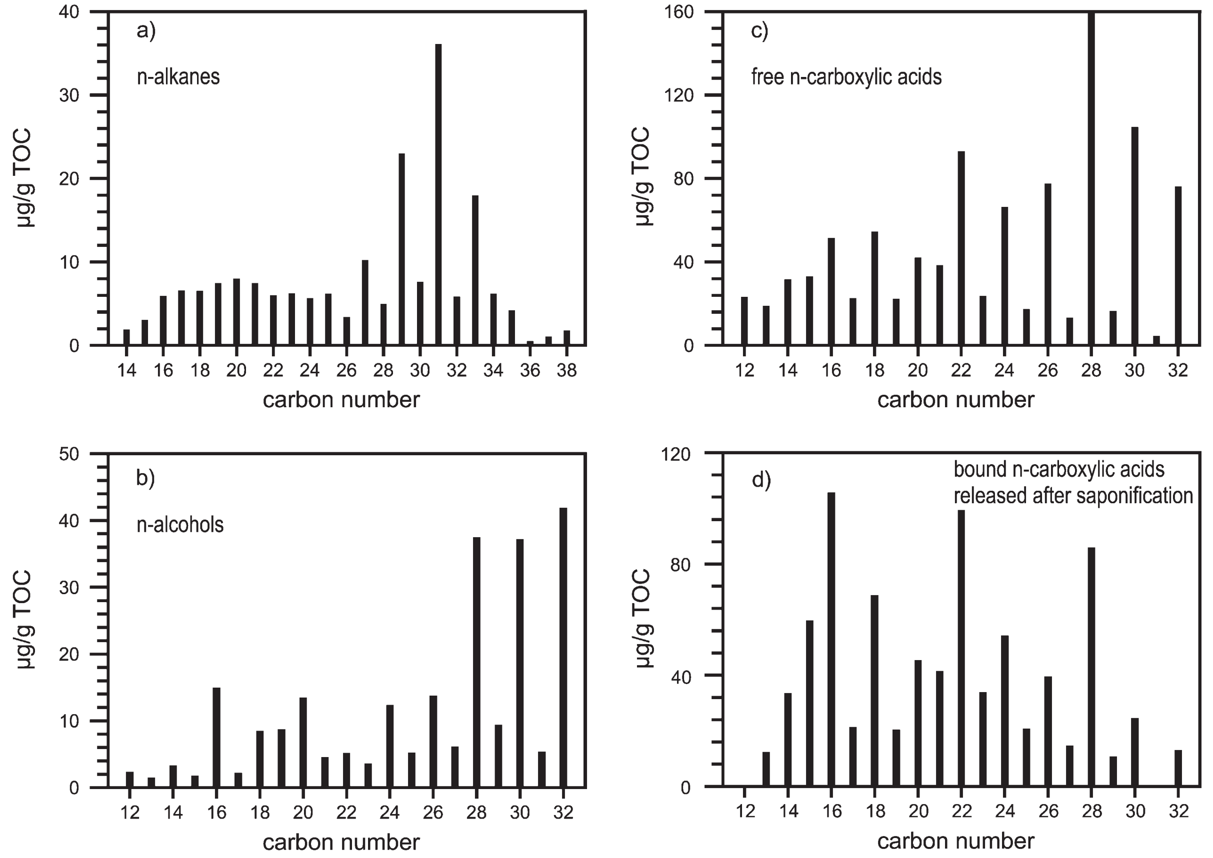


Fig. 9. Bar charts showing the absolute concentrations of individual compounds normalized to TOC from the homologous series of (a) *n*-alkanes, (b) *n*-alcohols, (c) *n*-alkanoic acids of the free lipid fractions and (d) bound lipids released by saponification. Numbers denote chain length of respective components. Sample 980065 shown here yields the highest proportion of bound acids for all samples investigated.

organic compounds often prevent complete thermovaporisation. These compounds then will not contribute to the S_1 peak but consequently to the S_2 peak upon temperature increase during the pyrolysis step. Solvent extraction removes such high molecular weight free lipids and data points for selected pre-extracted samples are given in Fig. 6. No significant change in organic matter type is recognized with pre-extracted samples.

Determination of oxygen indices of subrecent sample material during Rock Eval analysis might cause analytical problems. S_3 values can be overestimated when samples contain high proportions of bound water or if significant amounts of thermally labile carbonate species are present (Bordenave et al., 1993; Espitalié et al., 1977). The obtained HI- vs. OI-plots are thus incorrect and for such samples alternative discrimination diagrams have been developed. The comparison of Tmax-temperatures with HI-indices allows defining three organic matter evolution pathways (Espitalié et al., 1985). At the same stage of thermal maturity, type I organic matter exhibits higher Tmax values than type II kerogen. Tmax values for this data set are affected by the presence

Fig. 8. (a–c) Gas-chromatograms (sample 980065; 100.89 m) of free lipid fractions: aliphatics, alcohols and carboxylic acids; (d) total lipids obtained after saponification of sample 980065 dominated by *n*-carboxylic acids. Homologous series of each compound class is denoted by symbols above peaks.

of significant amounts of free lipids and impregnation of kerogen with these compounds leads to low Tmax values around 410 °C (Fig. 7). Comparable to the HI- vs. OI-diagram, a mixture between type I and type III organic matter may be deduced from the HI- vs. Tmax-plot.

An influence of detrital Devonian organic matter input from the surrounding basement on the analytical results can be neglected. C_{org} content of the Lower Devonian siliciclastic sediments is very low compared to the oil shale and input of reworked Devonian sediments is found to be rather low (Felder et al., 1998). A significant contribution of Devonian-derived organic matter to the Oligocene lake sediments would be recognized by higher Tmax values indicating enhanced maturity of organic matter affected by the Variscan orogenesis.

Extraction of lipids using polar organic solvents allows determining the relative distribution of several homologous series of biomarkers in various compound classes and evaluating their biological precursors. Addition of internal standards enables the absolute quantification of biological markers in the different extracts or fractions, which is mandatory for accurate source interpretation. Biomarker results are presented for sample 980065 (100.89 m core depth), which represents a suite of 24 Enspel sediments studied by molecular geochemistry. Gas-chromatograms of various fractions are shown in Fig. 8a–c for the free and Fig. 8d for bound lipids released by saponification of extraction residue. For clarity, absolute concentrations of homologous series of *n*-alkanes, *n*-alcohols and *n*-carboxylic acids are shown for sample 980065 in bar chart diagrams (Fig. 9).

The distribution of free aliphatic hydrocarbons is dominated by long chain *n*-alkanes with odd predominance in their carbon chain length (Figs. 8a and 9a). This is clear evidence for an origin from terrestrial plant waxes (Eglinton and Hamilton, 1967; Tissot and Welte, 1984). Short-chain *n*-alkanes attributed to a lacustrine algal input (Meyers and Ishiwatari, 1993; Silliman et al., 1996) occur in low concentrations only and are virtually absent in many Enspel oil shale sample. The absolute amount of *n*-alkanes is low compared to those of functionalised lipids (Fig. 9). Fingerprint distribution of free alcohols (Figs. 8b and 9b) in a similar manner is dominated by long chain components in the C_{24} to C_{32} range with a predominance of even numbered homologues. These lipids also originate from land plant waxes and cuticles (Eglinton and Murphy, 1969; Matsuda and Koyama, 1977; Meyers and Ishiwatari, 1993) when found in lacustrine settings. The distribution pattern of *n*-carboxylic acids reveals high abundance of even numbered long chain analogues in the C_{24} to C_{32} range (Figs. 8c and 9c), indicative for a land plant origin as well (Matsuda and Koyama, 1977; Kawamura and Ishiwatari, 1985; Meyers and Ishiwatari, 1993). Preferential removal of algal derived labile lipids during settling of organic matter through the water column and during early diagenesis in surface sediments may lead to a bias in the landplant-derived components of free lipid distribution obtained during extraction (Eglinton and Murphy, 1969; Cranwell, 1978; Meyers

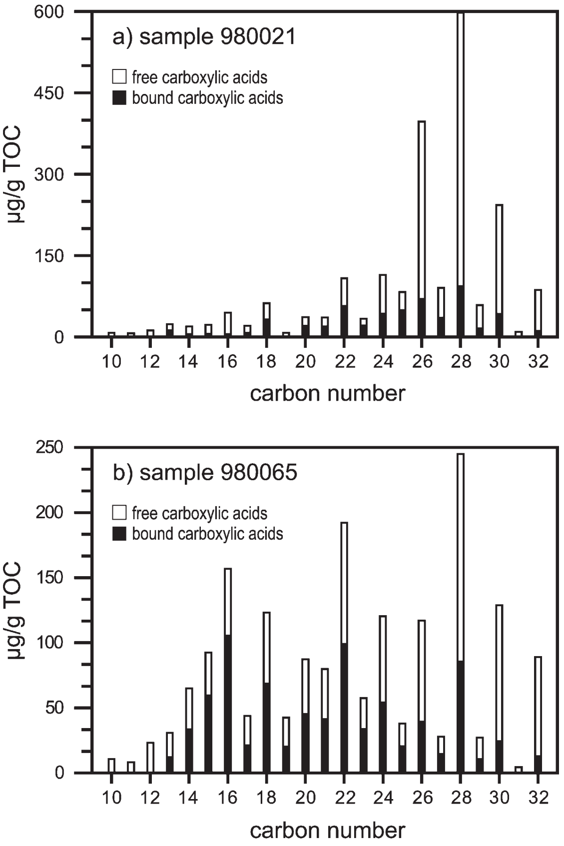


Fig. 10. Stacked bar chart of free and bound carboxylic acids for sample 980021 (29.22 m), representing the average Enspel oil shale, and sample 980065 (100.89 m), which yields the highest proportions of bound lipids.

and Ishiwatari, 1993). Therefore, saponification of extraction residues is recommended for integration of sequestered lipids (Eglinton and Murphy, 1969; Cranwell, 1978). Contribution of *n*-alkanes and aliphatic biomarkers to lipid distribution obtained after saponification is only minor but released *n*-carboxylic acids comprise the dominant lipid class of total extracts after saponification (Fig. 8d). For a few samples, especially no. 980065, the saponification extract reveals TOC-normalized amounts of *n*-carboxylic acids almost equal to those of the free lipid fractions (Fig. 9). However, the majority of samples reveal only minor amounts compared to the free carboxylic acid yields. Fig. 10 shows a cumulative distribution chart with stacked free and bound acid fractions for an average Enspel oil shale (sample 980021; 29.22-m core depth) and sample 980065. It is obvious that long chained *n*-alkanoic acids dominate the lipid distribution pattern. Therefore, the composition of aliphatic and functionalised biomarkers indicate an origin from terrestrial biomass for a large proportion of organic matter in fossil Enspel lake sediments.

4. Discussion

Organic matter in Oligocene sediments from the small Enspel maar-lake contains macroscopically identifiable leaf remnants. No larger plant fragments from stems, branches and roots are found which is in accordance with the lack of any tributary rivers into the lake (Gaupp and Wilke, 1998; Felder et al., 1998). Transportation energy only seems to have been sufficient to deliver deciduous tree leaves into the lake. Leaves are rich in hydrogen and poor in oxygen, due to lipid-rich wax coatings and cuticles. Oxygen bearing phenol moieties comprising the building blocks for woody plant material did not accumulate in high concentrations in the lake caused by the obvious lack of larger plant debris. Microscopically identified occurrence of autochthonous plankton in Enspel lake sediments includes diatoms, which seem to have been the main plankton producers (Schiller, in press; Gaupp and Wilke, 1998), *Botryococcus*-type algae (Gaupp and Wilke, 1998; Clausing, 1998), chrysophycean algae, and a newly described dinoflagellate species (Clausing, 1998; Köhler and Clausing, in press). Benthic algae and submerged macrophytes are rare or missing due to anoxic conditions prevailing in the water column and steep slopes accompanied by a very narrow (sub)littoral zone. Microbial mats of either a benthic type or those floating in the water column are reported by Wuttke and Radtke (1995) and may have contributed to the predominant amorphous organic matter found in lake sediments (Clausing, 1998).

C/N-ratios from elemental analysis do not support a predominant autochthonous source for organic matter in Enspel lake sediments but point towards a significant terrigenous component, which is in agreement with the frequent observation of fossil leaves. C/N-ratios might however be affected by early diagenetic reactions of settling organic matter, leading to a nitrogen-depletion by preferential removal of labile proteins from descending algae. Elevated C/N-ratios in Mediterranean sediments have recently ascribed to strongly anoxic conditions, whereas terrigenous input was excluded (Bouloubassi et al., 1999). Interpretation of C/N-ratios thus does not provide an unambiguous tool for organic matter source characterization.

Hydrogen and oxygen indices of particulate organic matter determined by Rock Eval analysis categorizes the (proto)kerogen of Enspel lake sediments as mixed type I/III assemblage plotting in the type II field. Although a contribution from both sources is undisputed and supported by microscopical evidence, a dominance of algal-derived organic matter is regarded unlikely even for samples with HI-values around 500 to 600 [mg HC/g TOC]. This is based on a positive correlation of HI-index with the C/N-ratio (Fig. 11), which is exactly the opposite of what could be expected, if hydrogen-rich organic matter is primarily derived from algae with low C/N-ratios. On the other hand, if algae were the main contributors to organic matter accumulation in the lake, high C/N-ratios would have to result from severe algal matter degradation, which consequently would decrease the HI and increase the OI values.

Lipid geochemistry of Enspel lake sediments provides crucial and indisputable evidence for a predominantly terrigenous organic matter source. Long chain *n*-alkanes, *n*-alcohols and *n*-alkanoic acids must originate from plant waxes and plant cuticles, because aquatic organisms and bacteria do not synthesize such compounds (see review in: Meyers and Ishiwatari, 1993; Meyers and Lallier-Vergès, 1999). Sequestering

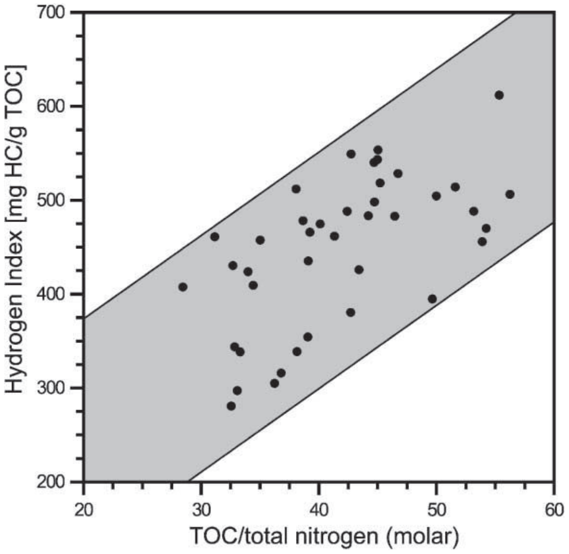


Fig. 11. Correlation between hydrogen index and C/N-ratio of fossil Enspel lake sediments.

of short chain algal-derived analogues of these compound classes was tested for by saponification and thus release of ester-bound lipids. For most samples no significant concentrations of algal-derived biomarkers were obtained and hence diagenetic sequestration of large amounts of algal biomass seems unlikely. In certain layers, enrichment of short chain lipids were recognized (sample 980065 in Fig. 10) corresponding to algal bloom periods.

Based on macroscopical evidence of frequent fossil leaf debris, high C/N-ratios, and long-chain biomarkers, it has to be concluded that high HI-values above 500–600 [mg HC/g TOC] in maar-type small lakes can be attributed to selective accumulation of hydrogen-rich landplant material. Small lakes often lack major tributaries and, by having small catchment areas, receive little run-off. This provides excellent depositional settings for exclusively wind blown input of plant debris. In maar-lakes and other small lakes with almost no fluvial input, nutrient supply may be low, especially when periods of pre-human perturbations of fossil ecosystems are encountered. Maar lakes often do not provide hospitable environments attributable to low pH-values of lake water, potential release of toxic substances during volcanic activity and morphological isolation. Conversely, small maar-lakes provide exquisite preservation potential for accumulating organic matter due to establishment of permanently anoxic lower water body and low dilution rate of organic matter by precipitation of carbonate and/or coarse-grained siliciclastic background sedimentation. In such environments, Rock Eval analysis-based typing of organic matter composition should not be approached by standard methods or interpretation schemes. Rock Eval in conjunction with isotopic and elemental analysis supported by biomarker studies in most cases will enable a precise characterization of organic matter sources in limnic settings.

5. Conclusions

Terrigenous-derived organic matter deposited in small lakes receiving little or no fluvial input might be strongly biased towards lipid-rich leaf waxes and cuticles.

Leaf-derived organic matter in lake sediments might mimic hydrogen and oxygen compositions commonly attributed to lacustrine algal sources, i.e. HI-values of 500 to 600 [mg HC/g TOC] and OI-values of 20 to 40 [mg CO_2/g TOC].

Identification of terrigenous plant-derived hydrogen-rich organic matter is possible by including C/N-elemental ratios and especially lipid biomarker data.

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