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Recent changes in sedimentary organic matter from Lake Neuchâtel (Switzerland) as traced by Rock-Eval pyrolysis

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Key words: lake sediments, rock-eval pyrolysis, eutrophication, organic matter, talc.

ABSTRACT

Recent changes in the composition of sedimentary organic material (OM) from a well-oxygenated lake (Lake Neuchâtel, Switzerland) were investigated using the new generation Rock-Eval pyrolysis (Re6). Although Re6 offers a range of new analytical parameters, the classical hydrogen and oxygen indices (HI and OI) prove to be most useful for the kind of material analysed. For a rapid screening of lake sediment cores we propose an additional parameter, $POI=S3/(S1+S2a)$, which reflects most of the observed changes in the nature of the OM, but can be calculated from the pyrolysis step alone.

In the Lake Neuchâtel sediment cores the HI values and total organic carbon (TOC) are low in samples older than ca. 1880 (HI: 150-200; TOC: 0.7%), and thereafter gradually increase. The HI and TOC values stabilize in the 1960's (HI: 300-350; TOC: 1.7%). This latter age is inferred from the location of a layer enriched in talc, originating from a paper mill. This local time marker horizon is dated to 1952. The OI curve is by and large inversely correlated with the HI. Together, the HI, OI and TOC curves trace the change from an oligotrophic lake, where the relative contribution of terrestrial OM is important, towards a more eutrophic system with steadily increasing autochthonous OM with an important diatom component.

A horizon (ca. 1960's) containing allochthonous material introduced by dumping of excavation material was identified based on its mineralogy and on the soil-type HI-OI values of the OM present.

RESUME

Les changements récents de la composition de la matière organique (MO) sédimentaire du Lac de Neuchâtel (Suisse) ont été analysés par pyrolyse Rock-Eval (Re6, nouvelle génération). Bien que le Re6 permette la détermination de nombreux nouveaux paramètres analytiques, les indices classiques tels que l'index d'hydrogène (HI) et l'index d'oxygène (OI) fournissent les informations les plus utiles pour la caractérisation de cette MO. Pour une analyse rapide, nous proposons néanmoins un paramètre supplémentaire – $POI=S3/(S1+S2a)$ – paramètre qui ne nécessite uniquement un cycle de pyrolyse (sans oxydation de la MO résiduelle).

Dans les carottes courtes analysées, les valeurs du HI ainsi que la quantité totale de matière organique (TOC) sont faibles dans les échantillons antérieurs à, approximativement, 1880 AD (HI: 150-200; TOC: 0.7%). Après cette date, ces valeurs augmentent pour se stabiliser aux alentours des années 1960 (HI: 300-350; TOC: 1.7%). La datation des sédiments les plus récents est basée sur l'observation d'une couche particulièrement riche en talc d'origine industrielle. Les apports maximaux de talc sont datés de 1952 AD. La courbe du OI montre, de manière globale, une corrélation négative avec celle du HI. L'ensemble des courbes du HI, OI et TOC témoignent de la transition d'un lac initialement oligotrophe vers une situation plus riche en nutriments. Alors qu'au stade oligotrophe les apports détritiques représentent une contribution importante de la MO, ultérieurement la production autochtone (notamment la production de diatomées) devient la source majeure de MO.

Les indices HI-OI ont également permis d'identifier une couche riche en MO d'origine terrestre (issue du déversement de matériaux d'extraction au début des années 1960).

1.- Introduction

Almost every Swiss lake experienced more or less pronounced eutrophication during the last century. Measurements of total P concentrations in the water column showed dramatic increases between 1950 and ca. 1980 with values as high as 500 $\mu\text{g P/l}$ (Liechti 1994). The transition from oligotrophic to eutrophic conditions is well documented for many of the strongly affect-

ed lakes reaching a true eutrophic (or even hypertrophic) state (e.g. Teranes et al. 1999, Hollander et al. 1992). Here we report on the recent changes in the organic matter (OM) preserved in the sediments of Lake Neuchâtel – a lake which experienced only a moderate increase in its trophic level, and which in the last century did not develop full eutrophic condi-

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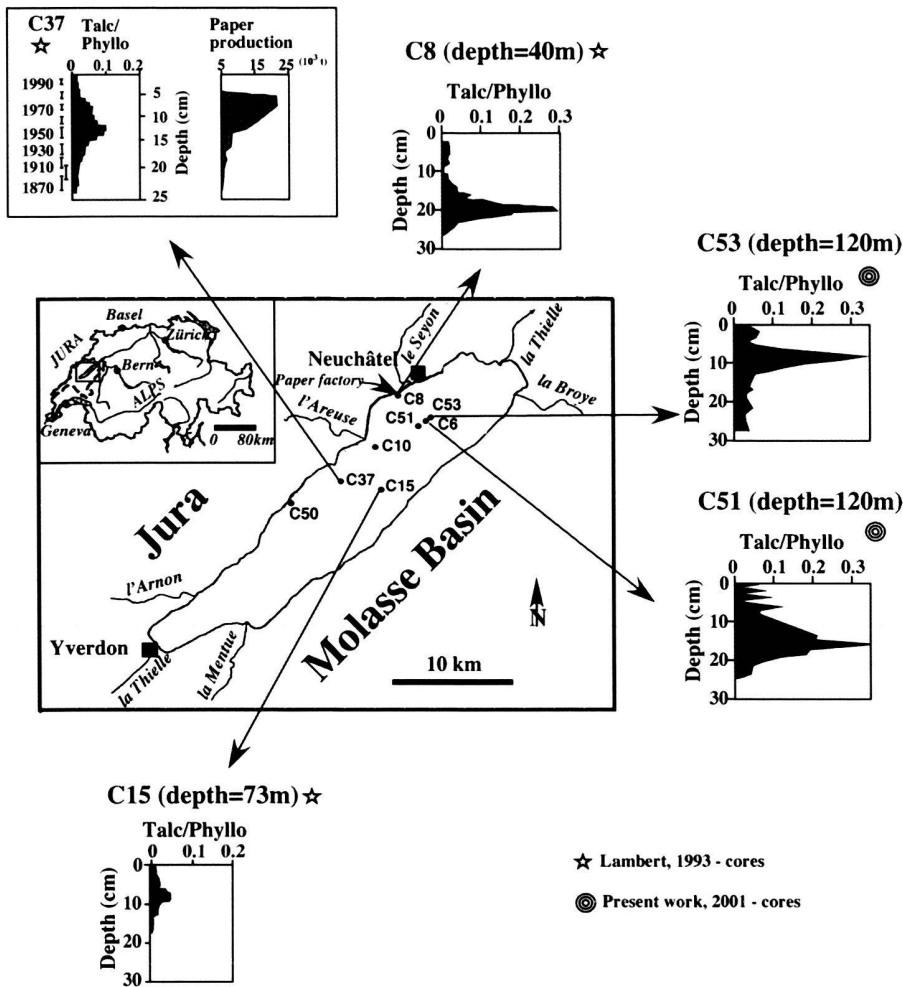


Fig. 1. Location of the short cores and selected talc/Σphyllosilicates profiles (measured in the 2-16 μm size fraction). The cores C51/C53 have been collected in 2001 (this study); core 50 was collected in 2000 (water depth 60 m); cores C8 to C37 were collected in 1993 (Lambert 1999). Core C8 is located closest to the paper mill at Serrière, which was the most important source of talc to the lake at the time. Core C37 has been dated using Cs-137 and Pb-210 (Lambert 1999).

tions nor bottom water anoxia. Based on phosphorous concentrations, Lake Neuchâtel changed from oligotrophic to mesotrophic conditions (with P concentrations of >20 μg P/l) in the 1960's. By 1980 the phosphorous concentrations reached 60 μg P/l and from then on declined again to values around 20 μg P/l in the mid-90's (Liechti 1994), and around 10 μg P/l in the most recent years (Pokorni-Aebi 2002).

Lake Neuchâtel (429 m a.s.l., 215 km², max. water depth 153 m, volume 13.77 km³) is located at the southern foot of the Jura Mountains, Switzerland (Fig. 1). The orientation of this holomictic lake is parallel to the major wind directions, resulting in a good oxygen supply even to bottom waters. Calcium concentrations are around 1.3 mM and calcite precipitation occurs during the summer. The trend toward more nutrient-rich conditions is manifested in the sediments of Lake Neuchâtel by an increase in the size of precipitated calcite

(Lambert 1999). Authigenic calcite grains > 4 μm appear in the L2 interval (dated ca. 1800-1920, Fig. 2) and rhombohedral calcite grains (8-16 μm) in the L1 interval (younger than 1920, Fig. 2).

Primary productivity of the lake was measured at 24°C gC m⁻²a⁻¹ in 1988 when phosphorous concentrations were around 30 μg P/l (Liechti 1994). The biomass 0-20 m is 23.8 g/m² (average for 1999-2001; B. Pokorni, pers. comm.). Total organic carbon (TOC) concentrations in the most recent sediments typically remain below 2%. During its Late Glacial and Holocene history the lake has known several periods of high productivity, as indicated by planktonic diatom assemblage (Schwalb et al. 1998).

The present paper focuses on the application of the new generation Rock-Eval pyrolysis (Rock-Eval 6) to the study of the recent Lake Neuchâtel sediments. For age dating

we rely on lithological correlation with a horizon enriched in talc (and kaolinite), which had its origin in a significant release of these minerals by a local paper mill peaking around 1950 (Lambert 1999).

2.- Methods

2.1. Sediment cores

Short sediment cores were collected using a Kullenberg type sampler (Kelts et al. 1986). Two parallel cores, C51 and C53, were taken in October 2001 at the deepest part of the Neuchâtel sub-basin at a water depth of ca. 130 m. Core C50 was taken in 2000 at a water depth of ca. 60 m. Figure 1 shows the location of these cores and the cores previously collected by P. Lambert (C6 – C37; Lambert 1999).

2.2. X-Ray Diffraction

Sample processing for whole rock and clay mineral XRD analyses (SCINTAG XRD 2000 Diffractometer) follows the procedure outlined by Kübler (1987) and Adatte et al. (1996). Random powder of bulk samples was used for characterization of whole rock mineralogy. The sediment samples were dried at a temperature of 60°C and then ground in an agate mortar to a homogenous powder (clasts > 2 mm were removed before grinding). The method for semi-quantitative analysis of the bulk rock mineralogy used external standards, which gave an error varying between 5-10% for the phyllosilicates and 5% for grain minerals.

For clay mineral analyses the carbonate fraction was reacted with 1.25 N HCl at room temperature until all the carbonate was dissolved (ca. 20 minutes with intermittent ultrasonic disaggregation). For an estimate (error ca. 5%) of the proportion of the clay minerals (chlorite, illite, kaolinite, smectite, talc, illite-smectite and chlorite-vermiculite irregular mixed-layers), the intensities of selected, characteristic XRD peaks were measured. Determination of chlorite, kaolinite and talc was obtained (when necessary) by deconvolution of their 001, 002 and 004 peaks, respectively located at 9.4 ° (talc), 24.9° (kaolinite) and 25.2° (chlorite).

2.3. Rock-Eval pyrolysis

During Rock-Eval pyrolysis ca. 100 mg of ground and homogenised sample is subject to a pyrolysis step followed by the complete oxidation of the residual sample. A FID detector measures the hydrocarbon released during pyrolysis, while CO₂ and CO are detected by infrared absorbance during both steps. In the here applied standard cycle for “whole rock” (IFP 2001), pyrolysis starts isothermally at 300°C for 3 minutes, after which the sample is heated to 650°C. The oxidation step

starts isothermally at 400°C (3 min) and then heats up to 850°C. Organic carbon decomposition results in 4 main peaks: the S1 peak (hydrocarbons released during the isothermal phase), the S2 peak (hydrocarbons produced between 300 and 650°C), the S3 peak (CO₂ from pyrolysis of OM up to 400°C), and the S4 peak (CO₂ released from residual OM below ca. 550°C during the oxidation step). Mineral carbon decomposition is recorded by the S3' peak (pyrolysis-CO₂ released above 400°C), and the S5 peak (oxidation-CO₂ released above ca. 550°C).

These peaks are used to calculate the amount of total organic carbon (TOC) and the amount of mineral carbon (MINC). In addition, the so-called hydrogen index (HI = S2/TOC) and oxygen index (OI = S3/TOC) are calculated. The HI and OI indices are proportional to the H/C and O/C ratios of the organic matter, respectively, and can be used for OM classification in Van-Krevelen-like diagrams (Espitalié et al. 1985/1986).

The calibration standard used was the IFP-55000 (Institut Français du Pétrole; IFP 2001), a Jurassic marine sediment. Unfortunately there are no certified lake sediments available as Rock-Eval standards.

2.4. Alternative Rock-Eval parameters

Rock-Eval pyrolysis was developed to study petroleum source and reservoir rocks (Espitalié et al. 1985/1986). In these rocks the organic matter (OM) consists of a mobile fraction of free hydrocarbons and a more complex kerogen fraction. These two fractions are adequately separated by the peaks S1 (volatilisation of free hydrocarbons) and S2 (cracking of kerogen). Furthermore, the temperature of the maximum yield of S2 (T_{max}) offers a useful tool to estimate the degree of kerogen thermal maturity.

For OM in young lake sediments this interpretation is not appropriate. First, the sediments contain low amounts of free hydrocarbons and most of the S1 signal is due to the pyrolytic decomposition of more complex but immature organic molecules. (For that reason it would be justified to include S1 in the calculation of the HI value. However, since in our samples the S1/S2 ratio is relatively constant, we used the original definition of HI = S2/TOC.) Second, there is no unique T_{max} but the FID signal is a more complex curve with several peaks appearing at different temperatures. The deconvolution of the FID curve into 4 major peaks has, indeed, been successfully applied to characterize soil organic matter (Sebag et al. 2002). Our own measurements of sediment trap material and soil organic matter show at least 3 peaks: a S1 (during the 300°C isotherm), S2a (between 300-400°C, peaking at ca. 365°C) and a S2b (above 400°C, peaking at ca. 465°C). In these materials, the ratio of the S1, S2a and S2b peaks is highly variable: sediment trap material recovered in summer is dominated by the S2a peak, while OM in the deeper part of a soil profile shows a

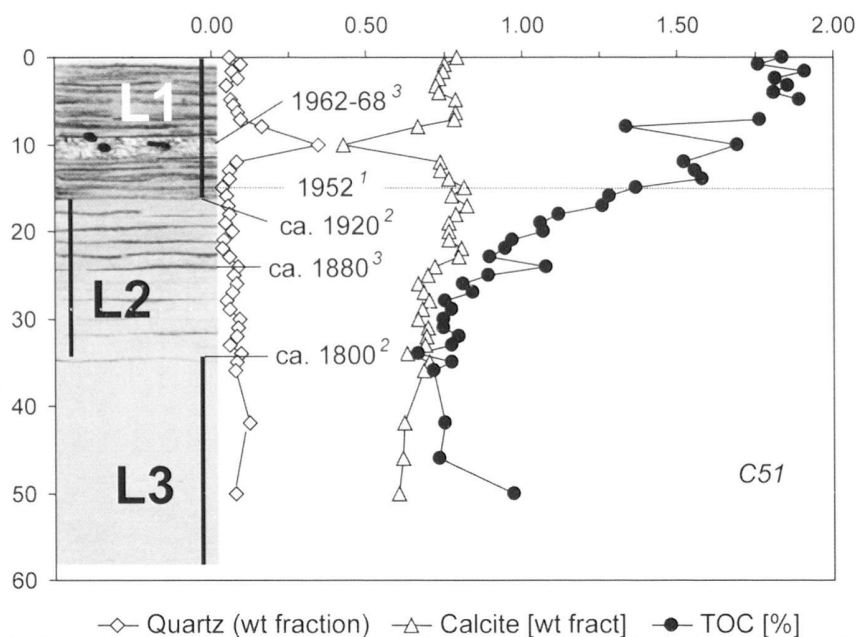


Fig. 2. Core C51: Concentration of quartz, calcite and total organic carbon (TOC). The intervals L1-L3 indicated in the lithological column are discussed in the text. Ages are inferred from (1) a local time marker horizon ("talc peak"; Lambert 1999), (2) lithological correlation with dated cores (Lambert 1999), and (3) comparison with sedimentation history (this study). Scale is in centimeters.

strong S2b peak. The lake sediments from this study, in contrast, show much more uniform FID-spectra. The $(S1+S2a)/S2b$ ratio is little higher in the upper samples (L1 interval) than lower down in the core. However, the magnitude of these change is small and deconvolution of the FID curve does not add significant new information for the samples in this study.

As an additional useful parameter to characterize lake sediments, we propose to calculate the ratio of CO_2 to hydrocarbons released during the pyrolysis of OM up to $400^\circ C$ (i.e. $S3/(S1+S2a)$). This ratio – here referred to as "pyrolysis oxidation index" or POI - is indicative for the O/H ratio of readily pyrolysable OM in the sample. Besides being a more meaningful measure for immature organic matter, the principle advantage of the POI index is, that it can be calculated from the pyrolysis step alone, making it an ideal tool for a rapid screening of sediment cores. As will be shown below (Fig. 3), the POI - resembling the OI - is a very sensitive indicator for the changes in the OM of the here studied sediment cores.

Although the classical Rock-Eval parameters HI and OI can successfully distinguish between different types of OM from a single setting, comparison of absolute values, obtained from samples of different environments, should be done with caution. Matrix effects (clay-rich vs. carbonate-rich sediments), peak overlap ($S3'-CO_2$ from carbonates may "contaminate" the $S3$ peak), and even instrumentation (old Re2 instrument with trapping of CO_2 followed by TCD detection vs. Re6), all introduce sources of systematic differences, which

are not necessarily linked to the nature of the OM present in the sample.

3.- Results and discussion

3.1. The investigated sediment cores

The recovered sediments consist of carbonate-rich silts with visible, but often disturbed, diffuse lamination towards the top of the cores. In core C51 (Fig. 2), a thin brownish surface layer of oxidized sediment is underlain by a 16 cm thick dark zone with a diffuse lamination. Within this zone, a ca. 2 cm thick horizon containing pebbles and mud-pebbles up to 0.5 cm in diameter, as well as some 30 % of quartz (Fig. 2), more than 10 % of plagioclase, and nearly 5 % of K-feldspar in the < 2 mm fraction. From 16-24 cm the sediment is of somewhat lighter colour but still with a visible lamination (caused by mm-thick dark layers separated by cm-thick light layers). From 24-34 cm the colour of the sediment is still lighter, with only faintly visible lamination. Below 34 cm the sediment is light-coloured, carbonate-rich, quite homogeneous silt. Core C53 shows the same features, but it is not complete at its top (ca. 8 cm are missing).

Based on the lithology, the TOC content, and the peak in talc concentration (discussed below) we can correlate the above-described lithological variations with the general

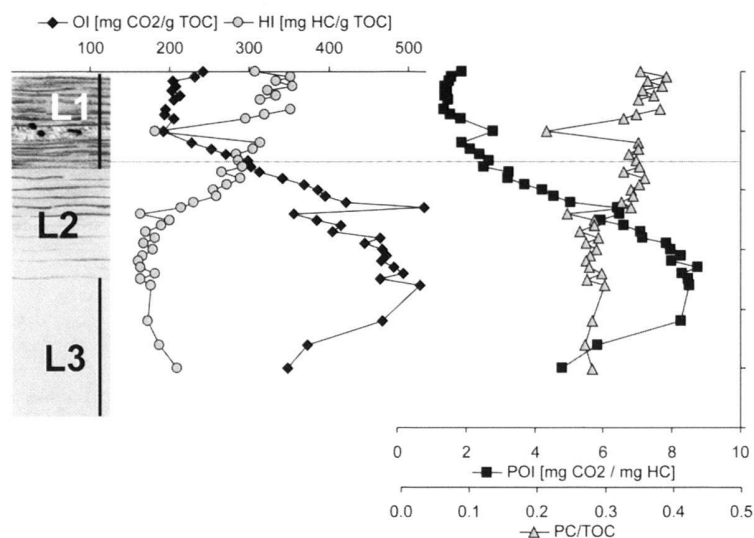


Fig. 3. Core C51: Hydrogen index (HI) and oxygen index (OI) as obtained from Rock-Eval pyrolysis, together with the proposed pyrolysis oxidation index (POI = pyrolysis- CO_2 / pyrolysis-hydrocarbons) and the relative proportion of pyrolysable organic carbon (PC/TOC).

lithologic scheme for late Holocene sediments from lake Neuchâtel developed by Lambert (1999). Our top 16 cm of dark sediments correspond to his L1 interval (younger than ca. 1920). The lighter sediments from 16-34 cm correspond to interval L2 with less TOC but still visible lamination. The estimated age range of the L2 interval is ca. 1800- ca. 1920. The lithological boundary found at 24 cm in core C51 might coincide with changes in the lake hydrology due to the “first correction of the Jura waters” including a lake level drop of 2 m in 1880 (Peter 1922). Our fourth layer (below 34 cm) can be correlated to Lambert’s L3 interval, which is described as OM-poor silts with rare laminations. The mineral carbon content decreases within Lambert’s L3 downcore, with a minimum above the transition from L3 to L4. The fact that we do not see an increase in carbonate at the very bottom of core C51 suggests that we did not reach the L4 interval, and, therefore, our youngest sediments are younger than the L4/L3 boundary dated at approximately 1250 A.D. (Lambert 1999).

As for the pebble horizon at 10 cm depth the presence of very coarse grains and the mineralogical composition clearly point to an allochthonous source. According to the “talc layer” this material was deposited in the 1960’s. The origin of this horizon is most likely the dumping of excavation material during the “second correction of the Jura waters”. In the frame of this engineering work two nearby canals were widened and deepened between 1962 and ca. 1968 (Ehrsam 1974). The authorized dumping site for the excavation material was located approximately 4 km upslope to the east of the coring site.

3.2. A talc-enriched layer as a marker horizon in Lake Neuchâtel

A special feature of lake Neuchâtel sediments is the presence of a talc-enriched layer appearing somewhere between 5 and 25 cm depth, slightly above the transition from L2 to L1 (Lambert 1999). This layer is easily identified when plotting the vertical distribution of the talc/ Σ phyllosilicate ratio (Fig. 1). The talc/ Σ phyllosilicates peak is due to the release of talc (together with kaolinite) by a paper-mill located in Serrière, just west of Neuchâtel (Bapst 1987, Ruch et al. 1989). According to Lambert (1999), the first appearance of talc in the sediments is around 1860/1870 and corresponds to the beginning of the use of talc in the paper mill. The paper production stopped in 1981 but due to replacement of talc in the manufacturing process and to improved waste management practices, the release of talc into the lake diminished well before. The resulting peak in the talc/ Σ phyllosilicate ratio has been observed in cores from all over the lake basin and has been dated to the year 1952 (± 4) by comparison with 137-Cs and 210-Pb profiles (Fig. 1; Lambert 1999). The magnitude of the peak is greater in proximity to the source than in more distant locations (e.g. compare cores C8 and C37 in Fig. 1).

3.3. Organic matter

The concentrations of TOC is low in the interval L3 (ca. 0.75 %), during the interval L2 TOC roughly doubles, and continue to increase during L1 reaching values around 1.7 % in the top 5 cm (Fig. 2). The scatter of the TOC data near 10 cm depth is mainly caused by the dilution of the sediment with coarse-

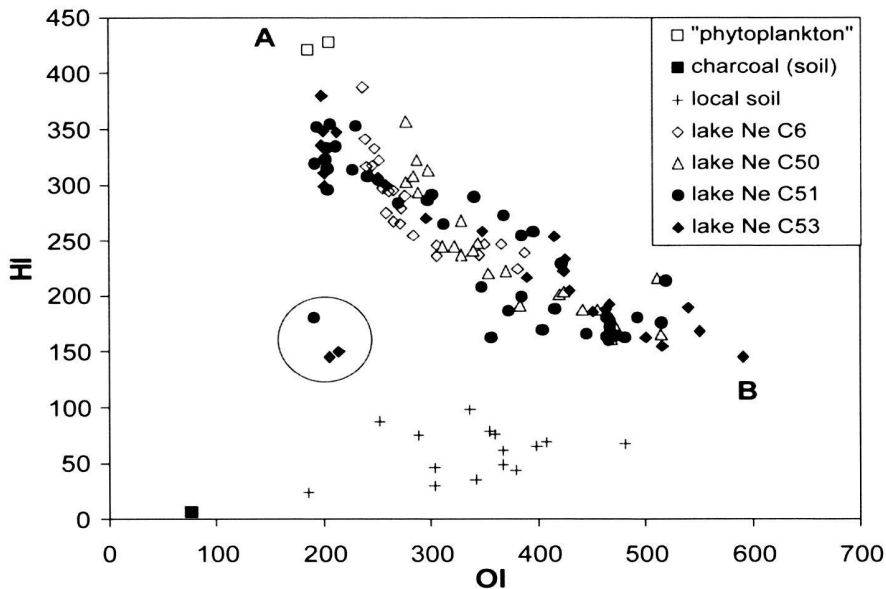


Fig. 4. Hydrogen index (HI) versus oxygen index (OI) for several short sediment cores from Lake Neuchâtel (C6, C50, C51, and C53; cf. Fig. 1). Two samples of lake suspended sediments ("phytoplankton" obtained by filtering lake water), samples from old soil (Neuchâtel region) and a sample of charcoal found in these soils are also plotted. The circled samples are those from the "dumping layer" observed in cores C51/C53. The points A and B indicate hypothetical end members of organic matter as discussed in the text.

grained detrital material (e.g. quartz, see Fig. 2).

The OI and HI records shown in Fig. 3 clearly document a shift in the composition of organic matter. The OI values decrease from around 450 at 30 cm (upper part of L3) to ca. 200 at 10 cm (within L1) and remain stable in the uppermost sediments. The HI values show an inverse behaviour. The HI values are low (150 – 200) below 25 cm and then increase between 25 cm and 12 cm depth, the onset of the increase being somewhat later than the observed decrease in OI values. Above 12 cm the HI values are high (>300). A very similar behaviour of these Rock-Eval parameters has been observed in the other pyrolysis-analysed cores from lake Neuchâtel (C6, C10, C50, cf. Figs. 1 and 4).

When plotted in a HI versus OI diagram, the samples from the sediment cores C51 and C53 plot on a line between two points labelled A and B in Fig. 4. Figure 4 includes two more cores from lake Neuchâtel, showing same general relationship. Sedimentary OM from Lake Neuchâtel appears to be a mixture of a hydrogen-rich end member (point A) and a more oxidized type of OM (point B). As mentioned above, the classical interpretation of the different fields of the HI-OI diagram as proposed by Espitalié (1985/1986) is not applicable to recent lake sediments. For example, Ariztegui et al. (1995) reported that algal lacustrine material can be either type I (i.e. lacustrine) or type II (i.e. marine) according to the Rock-Eval classification.

Our interpretation of the lake Neuchâtel data is, that point A in Fig. 4 corresponds to algal phytoplankton, as confirmed by the analysis of suspended material from the lake

epilimnion (Fig. 4), as well as sediment trap material (data not shown). Point B in Fig. 4 corresponds to older samples (L3) of core C10. This core is located close to the Areuse river mouth (Fig. 1) and contains macrorests (leaves). Point B, therefore, represents OM with a significant component of terrestrial material mixed with autochthonous OM. Accordingly, the HI and OI curves (Fig. 3) indicate a transition from an oligotrophic system, where terrestrial inputs are relatively important (interval L3) towards a lake with more pronounced algal contribution in the upper part of L1. Because TOC increases parallel to the HI, the observed changes in the HI-OI signature of the sediments may be largely explained by an increasing contribution of autochthonous OM, while the terrestrial inputs remain rather constant. This is confirmed by calculations of the contributions of terrestrial and autochthonous OM, respectively, based on comparison of the HI/OI ratios of the samples with those of the "end members" A and B (Fig. 4).

The three samples of the "dumping horizon" plot outside of the general trendline in the HI-OI plot (circled data points in Fig. 4). These points correspond to highly degraded OM and lay in the vicinity of terrestrial OM, such as soil OM or even char coal. Thus, the Rock-Eval parameters clearly confirm a terrestrial source, in agreement with the above interpretation.

The HI values of ca. 330 in the upper L1 agree reasonably well with those for diatom-dominated lake sediments found in the literature. In their study of diatom-dominated sediments from an alpine siliciclastic lake Ariztegui et al. (1995) reported HI values around 250-450. In a subsequent study of organic-rich

sediments from an Italian Lake (Albano), Ariztegui et al. (2001) found again diatom-dominated sediments with similar (type II) characteristics and HI values of ca. 300.

A direct argument for an increasing role of diatoms in Lake Neuchâtel is the increasing number of diatom tests found in a core from the central part of the lake (Lambert 1999). In this core, the number of diatom tests per mg of dry sediment augments considerably from less than 50 during interval L3, to ca. 10^4 in a sample from interval L2 (below the talc peak), and is even higher ($4 \cdot 10^4$) in the top interval L1 (diatom analyses by Jean-Claude Druart, INRA, Thonon-les-Bains).

Ariztegui et al. (1995 and 2001) also found that cyanobacteria-rich layers show higher and more variable HI values (Lake Greifen; HI 700-800; Lake Albano: HI 400-450). Massif blooms of cyanobacteria in Lake Neuchâtel were observed towards the end of the 1950's and early 1960's (B. Pokorni, pers. comm.). These are not apparent from the Rock-Eval parameters of cores C51 and C53, possibly due to the disturbance of the profiles by the deposition of excavation material (see below). Among the other investigated cores C6 shows a distinct maximum in HI values (up to 400) above the talc layer. This maximum might be due to the reported occurrences of cyanobacteria. A corresponding HI maximum, however, is less pronounced in C50 and not appearing in C10. In other words this short-term shift in the composition of the phytoplankton diatoms towards cyanobacteria seems less reliably recorded by the OI/HI indices.

The question arises to what extent the composition of the original sedimentary OM was altered by selective preservation and early diagenesis. Recent studies from marine environments indicate that protection of organic molecules by association with mineral surfaces (e.g. clay minerals) is very effective, and that preservation of OM can be largely non-selective (Hedges et al. 2001; Kennedy et al. 2002). As the particle flux in lacustrine environments is high, we could as well expect non-selective preservation, making HI and OI a reliable record of historical changes in the OM cycle of the lake.

The marked increase of the HI values start within the interval L2, at a depth corresponding approximately to 1880, and continues beyond the peak in talc (1952) to stabilize approximately in the 1960's. Most of the changes therefore occurred well before the lake reached a mesotrophic state with $P > 20 \mu\text{g/l}$.

Towards the very top, an inversion of the trends can be suspected, with a slight increase in OI and a possible decrease in HI. It is interesting to note that the timing as well as the trend of the observed changes from lake Neuchâtel are very similar to those observed in Lake Greifen, a lake with much higher trophic level and also higher TOC content of the sediments (Ariztegui 1995).

The changes in the quality of the OM are also clearly traced by the POI (Fig. 3). The POI curve is in general rather close to the OI curve, but shows less scatter and gives a dis-

tinct signal for the "dumping horizon". Therefore, the POI appears as a valuable tool for a rapid (only a pyrolysis step is required during the analyses) screening of qualitative changes in the composition of the OM.

3.4. Conclusions

The Rock-Eval parameters TOC, HI and OI trace the recent changes of sedimentary organic matter in Lake Neuchâtel as follows: The 19th century was largely characterized by an oligotrophic lake where allochthonous terrestrial materials represent a significant contribution to OM buried in the sediments. Towards the end of the century (possibly coinciding with the first correction of the Jura waters) the TOC contents start to increase. The fact that the HI values increase at the same time suggests that increased productivity (diatoms) is the major cause of this increased burial of OM. Both TOC and HI values stabilize in the second half of the 20th century, when the lake reached a mesotrophic status.

The terrestrial origin of OM contained in a horizon rich in coarse-grained detrital minerals (C51 and C53) is clearly identified. In contrast an increased occurrence of cyanobacteria during several years around 1960 is not unequivocally evidenced in all of the investigated.

The fact that many of these changes in the OM are recorded in the sediments of the well-oxygenated Lake Neuchâtel points to an effective shielding of OM by mineral particles leading to its non-selective preservation. Finally, we propose the use of the "pyrolysis oxidation index" (POI) as a quick and appropriate indicator for young, immature lacustrine organic matter.

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