Varved lake sediments and diagenetic processes

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Abstract

Varved (annually laminated) sediments are of great interest for inference of past environmental conditions, as they provide dated records with high time resolution. After deposition, the sediment varves are affected by diagenesis; i.e., chemical, physical and biological changes that occur within the sediment. An important premise when reconstructing past environmental conditions using lake sediments is that the signal of interest is preserved in the sediment. In this thesis I have used a unique collection of ten stored freeze cores of varved lake sediment from Nylandssjön in northern Sweden, collected from 1979 to 2007. The suite of cores made it possible to follow long-term (up to 27 years) changes in iron (Fe), sulfur (S), carbon (C), nitrogen (N), $\delta^{13}C$ and $\delta^{15}N$ in the sediment caused by processes that occur in the lake bottom as the sediment ages. The sediment geochemistry and resulting changes were followed in years for which there are surface varves in the core series. Fe and S concentrations analyzed by X-ray fluorescence spectroscopy showed no diagenetic front in the sediment and the data do not suggest a substantial vertical transport of Fe and S in the sediment. A model based on thermodynamic, limnological, and sediment data from the lake, showed that there are pe (redox) ranges within which either FeS (reduced specie) or $Fe(OH)_3$/FeOOH oxidized species) is the only solid phase present and there are pe ranges within which the two solid phases co-exist. This supports the hypothesis that blackish and grey-brownish Fe-layers that occur in the varves were formed at the time of deposition. C and N analyzed with an elemental analyzer showed that within the first five years after deposition the C concentration of the sediment decreased by 20% and N by 30%, and after 27 yr in the sediment, there was a 23% loss of C and 35% loss of N. The C:N ratio increased with increasing age of the sediment; from ~ 10 in the surface varves to ~12 after 27 years of aging. $\delta^{13}C$ and $\delta^{15}N$ analyzed on a mass spectrometer showed that $\delta^{13}C$ increased by 0.4-1.5‰ units during the first five years, after that only minor fluctuations in $\delta^{13}C$ were recorded. Another pattern was seen for $\delta^{15}N$, with a gradual decrease of 0.3-0.7‰ units over the entire 27-year-period. The diagenetic changes in the stable isotope values that occur in Nylandssjön are minor, but they are of about the same magnitude as the variation in the isotopic signal in the varves deposited between 1950-2006.

My results show that diagenesis does not change the visual appearance of the varves, except for varve thickness; the varves get thinner as the sediment ages. As the color of Fe in the varves likely reflects the environmental conditions at the time of deposition this creates possibilities for deciphering high-temporal-resolution information of past hypolimnetic oxygen conditions from varves. My findings on C, N, $\delta^{13}C$ and $\delta^{15}N$ will have implications for interpretations of paleolimnological data. The diagenetic effects should be carefully taken into consideration when C, N, $\delta^{13}C$ and $\delta^{15}N$ in sediment cores are used to study organic matter sources or paleoproductivity, in particular when dealing with relatively small and recent changes.

In addition to the significance of diagenetic effects on sediment parameters, a comparison of the varves in Nylandssjön and the adjacent lake Koltjärnen, and the two deep basins of Nylandssjön show that subtle features in the lakes and their catchments affect the appearance of the varves, which make interpretation of varves complicated.

Key words: Varved (annually laminated) lake sediment, diagenesis, varve appearance, iron, sulfur, chemical speciation, iron cycling, carbon, nitrogen, stabile isotopes, $\delta^{13}C$, $\delta^{15}N$

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Picture on cover: Nylandssjön in July 2003. Photo by Veronika Gälman.

List of papers

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals.

I. Gälman V, Petterson G, Renberg I. 2006. A comparison of sediment varves (1950–2003 AD) in two adjacent lakes in northern Sweden. J Paleolimnol 35: 837-853.

II. Gälman V, Rydberg J, Shchukarev A, Sjöberg S, Martínez-Cortizas A, Bindler R, Renberg I. 2009. The role of iron and sulfur in the visual appearance of lake sediment varves. J Paleolimnol. Doi: 10.1007/s10933-008-9267-6.

III. Gälman V, Rydberg J, Sjöstedt de-Luna S, Bindler R, Renberg I. 2008. Carbon and nitrogen loss rates during aging of lake sediment: Changes over 27 years studied in varved lake sediment. Limnol Oceanogr 53: 1076-1082.

IV. Gälman V, Rydberg J, Bigler C. Decadal diagenetic effects on δ^{13}C and δ^{15}N studied in varved lake sediment. Limnol Oceanogr Accepted.

Contents

Introduction

In deep basins of lakes where no sediment mixing occurs, seasonal variety in the properties of the deposited material may give rise to varves. Often seasonal layers can be distinguished (Nipkow 1920, Renberg 1976, O´Sullivan 1983, Saarnisto 1986, Petterson 1996, Ojala et al. 2000). A varve consists of material deposited during one annual cycle. Formation processes of the type of varves studied in this thesis were outlined by Renberg (1981a). As varved lake sediments provide the highest time resolution for paleolimnological records they are of great interest as environmental archives. A verified varve chronology has the lowest error of any dating method (Woodhouse and Overpeck 1998). Varved lake sediments have been found all over the world, and these deposits have been used for a variety of paleolimnological applications, but in most of those, the varves have been used primarily as a tool for dating. Some examples of such applications are: inference of past land use (e.g., Huttunen 1980, Tolonen 1981, Segerström et al. 1984, Wallin 1996), eutrophication (e.g., Simola 1981, Liukkonen et al. 1993, Teranes and Bernasconi 2000, Lehman et al. 2002), paleoproductivity (e.g., Lücke et al. 2003), lake-water pH (Tiljander et al. 2006), pollution (e.g., Renberg 1986, Brännvall et al. 1999, Outridge et al. 2005), and paleoclimatology (e.g., Leemann and Niessen 1994, Hardy et al. 1996, Ohlendorf et al. 1997, Zolitschka 1998, Desloges 1999, Snowball et al. 1999, Hughen et al. 2000, Lamoureux 2000, Moore et al. 2001, Snowball et al. 2002, Chu et al. 2005, Kienel et al. 2005, Finsinger et al. 2006, Larocque et al. 2009).

There are, however, a number of investigations of varved sediments where properties of individual varves were analyzed and assessed in terms of past environmental conditions. Relationships between varve thickness and meteorological data have been established by, e.g., Itkonen and Salonen (1994), Zolitschka (1996), Lotter and Birks (1997), Boës and Fagel (2008), Chutko and Lamoureux (2008). Past climate changes and land use have also been inferred from varve features such as: periodicities in varve thickness (e.g., Anderson 1993, Vos et al. 1997, Prasad et al. 2006, De Batist et al. 2008, Bird et al. 2009), mineral grain size (e.g., Francus et al. 2002, Ohlendorf et al. 2003, Besonen et al. 2008), variation in sediment components like aluminum (Al), silica (Si), manganese (Mn) (e.g., Dean 1993, Dean et al. 2002), the stability of mercury (Hg) and methylmercury (Rydberg et al. 2008), variation in organic/minerogenic content (e.g., Tiljander et al. 2003, Haltia-Hovi et al. 2007), and sediment color (e.g., Zhai et al. 2006).

At first glance it may seem simple and straightforward to assess past environmental conditions from varve features such as varve thickness, mineral grain size and sediment color, but with closer scrutiny there are factors that make it complicated. Generally, we have a too limited knowledge about varve formation processes and how lake and catchment conditions are recorded in the varves. An important factor that must be considered is diagenesis, i.e. the chemical, physical, or biological change that the sediment undergoes after its initial deposition. To be able to understand the link between varves on the one hand and the catchment and lake on the other hand, it is crucial to understand how diagenesis alters the sediment and hence the varves. The overall objective of this thesis is to contribute to the knowledge of how the information in the varves themselves can be interpreted, and the focus in this thesis is how diagenesis affects the varves.

Specific aims of the thesis

The main tasks in the research were to:

- Establish a pertinent study object for analysis of sediment diagenesis; a lake with thick, legible varves and with little or no spatial variation of varves in the deep basin.
- Assess whether the color of the seasonal layers of the varves reflects the conditions at the sediment–water interface at the time of deposition.
- Assess whether long-term diagenesis affects the C and N content of the sediment.
- Assess whether long-term diagenesis affects the $\delta^{13}C$ and $\delta^{15}N$ signal in the sediment.

Study sites

Nylandssjön (62°57′N, 18°17′E) and Koltjärnen (62°57′N, 18°18′E) are dimictic soft-water lakes formed by land-upheaval (34 and 30 m above sea level, respectively) situated at the coast of the Baltic Sea. The mean annual air temperature is 4°C and the mean annual precipitation is 800 mm. The lakes are small (0.28 and 0.16 km^2, respectively), separated by a distance of 2 km, and connected by a small stream flowing from Nylandssjön into the drained and very shallow lake Bergsåkerstjärn before it enters Koltjärnen. Nylandssjön has no permanent inlet streams, only small inlets with short duration during spring flood and periods of continuous rain. The landscape is characterized by a hilly terrain, where the low-lying areas are used for cultivation and pasture, and the hills are forested (Norway spruce and birch) and some clearings occur. Nylandssjön has two deep basins with depths of about 17.5 and 14.3 m, and the maximum depth of Koltjärnen is 17.5 m, and varves are formed in all three deep basins. In a survey from 1986, about 25 % of the 3.5 km^2 catchment around Koltjärnen was cultivated, compared to 15 % of the 0.95 km^2 catchment around Nylandssjön (Wallin, personal communication); and no substantial changes have occurred since.

Materials and methods

The purpose of **Paper I** was to lay the foundation for the diagenetic studies that follow in papers II, III, and IV. Paper I consists partly of unpublished data from Gunilla Petterson (Petterson 1999), who compared the varves of the deep basins of Nylandssjön and Koltjärnen. My contribution to the paper was a comparison of the varves in the two deep basins in Nylandssjön, as well as an evaluation of the data and publication. Three replicate cores were cored from each basin. N04:17a, N04:17b, and N04:17c from the 17.5 m deep basin, and N04:14a, N04:14b and N04:14c from the 14.3 m deep basin.

These six sediment cores were sampled on 30 January 2004 from the lake-ice surface, with a freeze corer (Renberg 1981*b*). The cores were stored carefully wrapped and frozen at -18˚C until subsampling. All work with subsampling took place in a freezer room. The cores were split in two core slabs, which gives pseudo-replicates of the replicates, i.e. there are two parts of the cores e.g., N04:17a 1 and 2. One core slab from each basin (N04:17c1 and N04:14b2) was used for image analysis. Before subsampling the sediment slab was cleaned with a woodworker's hand plane. After cleaning the cores were documented with a digital camera, and then the individual varves were scraped off manually with a steel scalpel, following Renberg (1981*b*). To facilitate accurate subsampling a magnifying glass was used. The uppermost surface of the black winter layer, which forms during November to April, was used as the divider between years. The thick surface varves were easy to subsample accurately, but due to sediment compaction and declining varve thickness, in practice it was difficult to subsample individual varves older than 35 years in each core with high accuracy. After subsampling the samples were freeze dried.

Carbon (C) and nitrogen (N) concentrations were analyzed with a Perkin Elmer 2400-CHNS/O elemental analyzer and analytical quality was verified against certified standard materials. The analyses were made at the Department of Ecology and Environmental Science, Umeå University.

Grey-scale values for the image analysis were acquired with a Nikon D70 camera with a AF-S Nikkor 18–70 mm 1:3.5-4.5 ED objective. Before image acquisition the freeze cores were cleaned and polished. To make a nonlinear grey-scale calibration, a Kodak Q-13 grey-scale zone card (zone 7-19) was included in every picture. The images were converted from NEF-files (Nikon Electronic Image Format) to TIFF-files (RGB 8-bits) using Nikon Capture Editor 4. For conversion to grayscale and image analysis the program ImageJ (http://rsb.info.nih.gov/ij) was used. For acquiring grey-scale data for the comparison of Nylandssjön and Koltjärnen, the varves were digitized and grey-scale records produced following the method described by Petterson et al. (1993, 1999).

After the initial paper my work focused on the 17.5 m deep basin of Nylandssjön, where a unique collection of ten stored freeze cores, collected in 1979, 1980, 1985, 1989, 1993, 1997, 2002, 2004, 2006, and 2007 were used. The cores had been stored frozen, and subsampling was performed in 2004-2007 in the same way as described for Paper I. The top varve in the 1979 core is the material that was deposited in 1978, the top varve in the 1985 core is material deposited in 1984, etc. This suite of cores made it possible to follow long-term changes in iron (Fe), sulfur (S), and titanium (Ti) (Paper II), C and N (Paper III), and $\delta^{13}C$ and $\delta^{15}N$ (Paper IV) in the sediment, caused by processes that occur in the lake bottom when the sediment is aging. The time window studied was from 0.5 to 27 yr after sediment deposition.

To assess diagenetic effects, on Fe, S, Ti, C, N in the varves, as the sediment ages, changes in concentrations were followed in years for which there is a surface varve in the core series. For example, the composition of the material deposited in 1978 (surface varve in the 1979 core, sampled in April 1979) was compared to the 1978 varve in the core taken in 1985 (after six years in the lake bottom), in the 1989 core (after 11 years), and so on until the 2007 core (after 27 years). The change with time is expressed as percentage loss (–) or percentage gain (+) relative to the concentration of the original surface varve and the change is plotted against time, i.e. the number of years that has elapsed since the material was a surface varve. The change in $\delta^{13}C$ and $\delta^{15}N$ was also followed in the core series, expressed as the deviation in $\delta^{13}C$ and $\delta^{15}N$ compared to the value of the surface varve (set to zero), plotted against the number of years the surface varve has been in the sediment.

In **Paper II** seven freeze cores were used, cored in 1979, 1985, 1989, 1993, 1997, 2002 and 2004. For determination of Fe, S and Ti concentrations an energy dispersive X-ray fluorescence spectroscopy (XRF) analyzer was used (Cheburkin and Shotyk 1996, 2005).

Accuracy and precision were assessed using standard reference materials. The analyses were performed at the RIAIDT lab at the University of Santiago de Compostela, Spain.

Oxygen profiles in the water column were measured with an Oxyguard Handy Delta oxygen meter. Redox potential and pH was measured using a pH 197 WTW probe. Fe and SO_4^{2-} in lake water samples were analyzed according to Swedish national standards using ICP-AES for Fe and ion chromatography for SO_4^{2-} at the Department of Environmental Assessment, Swedish University of Agricultural Sciences, Uppsala.

Modeling of Fe and S was performed based on thermodynamic data and available lake-water and sediment data from the lake, by professor Staffan Sjöberg. The equilibrium calculations were accomplished by means of WinSGW (Karlsson and Lindgren 2006), which is a computer-code based on the SOLGASWATER algorithm of Eriksson (1979).

In **Paper III** ten freeze cores sampled in 1979, 1980, 1985, 1989, 1993, 1997, 2002, 2004, 2006 and 2007 were used. C and N analyses were performed as described for Paper I. The modeling of C and N degradation was done by the mixed-model module in the statistical software package SPSS 14.0 (SPSS Inc.) by Dr Sara Sjöstedt-de Luna. The C:N ratio used is calculated to C:N atomic ratio.

In **Paper IV** eight freeze cores collected 1979, 1980, 1989, 1993, 2002, 2004, 2006 and 2007 were used. For $\delta^{13}C$ and $\delta^{15}N$ analyses the freeze dried samples were combusted with a Carlo Erba NC2500 analyzer connected via a split interface to reduce the gas volume to a Finnigan MAT Delta plus mass spectrometer, at the Department of Geology and Geochemistry, Stockholm University. The analyzer was calibrated against certified reference materials, $\delta^{13}C$ was referenced to Vienna Peedee belemnite (VPDB), and $\delta^{15}N$ to air, which is regarded as 0‰. The analytical quality was controlled using internal standards and the precision of the analyses, calculated as one standard deviation (n=24), was ±0.2‰ for $\delta^{13}C$ and ±0.1‰ for $\delta^{15}N$. To test the homogeneity of the samples a replicate sample for each tenth sample was included, giving a total of 13 replicates. All values for the replicate samples were within ±0.2‰ for $\delta^{13}C$ and ±0.1‰ for $\delta^{15}N$.

A brief description of the content of the papers

Paper I compares the varves of the deep basins of two adjacent lakes, Nylandssjön and Koltjärnen, as well as the varves of the two deep basins of Nylandssjön.
Paper II assess the long term effect of diagenesis on Fe and S in the Nylandssjön varves; whether the color and the speciation of Fe in the varves reflect the environmental conditions at the time of deposition, or whether these are determined by chemical processes in the sediment as the sediment ages and undergoes diagenesis.
Paper III follows the long-term loss of C and N from the sediment of Nylandssjön due to processes that occur in the lake bottom as the sediment ages.
Paper IV assesses the long-term effects of sediment aging on $\delta^{13}C$ and $\delta^{15}N$ in the sediment of Nylandssjön.

Results and discussion

The varved sediment and its spatial distribution

Lake and catchment characteristics appear very similar for the two lakes Nylandssjön and Koltjärnen, and as they are closely situated one would expect the sediment varves to be similar. The comparison of the varves from the two lakes shows that water content, varve thickness, annual accumulation rates of organic matter and nitrogen are correlated for the period (1950–1996). Annual accumulation rates of dry mass, biogenic silica, minerogenic matter, and within-varve successions in grey-scale differ between the lakes. The differences can be explained by differences in catchment size, catchment-to-lake material fluxes, lake productivity and land-use influence, which gives different conditions for varve formation.

The comparison of the two basins of Nylandssjön shows that water content, varve thickness, annual accumulation rates of organic matter and nitrogen are correlated for the period (1970–2003). In about 50 % of the varves the grey-scale curves are clearly similar. The varves of the two basins have many features in common, but the differences suggest local influences on the individual basins from the catchment or within the lake.

However, when varves from different cores within each of the two basins of Nylandssjön are compared, the varves are very similar. They are similar on a small-scale (split core samples) as well as between cores that may have been taken tens of meters apart. The cores were not collected at exactly the same site in the basins because most of the cores in the core series were collected before global positioning system (GPS) receivers were common. The spatial uniformity of the varves in the 17.5-m basin is easily demonstrated by photographs of the cores taken different years, Fig. 1. As the varves of the 17.5 m basin of Nylandssjön have small spatial variation, and are thick and distinct, they are highly suitable for the type of study design I have used for assessing the effect of diagenesis on the varves.

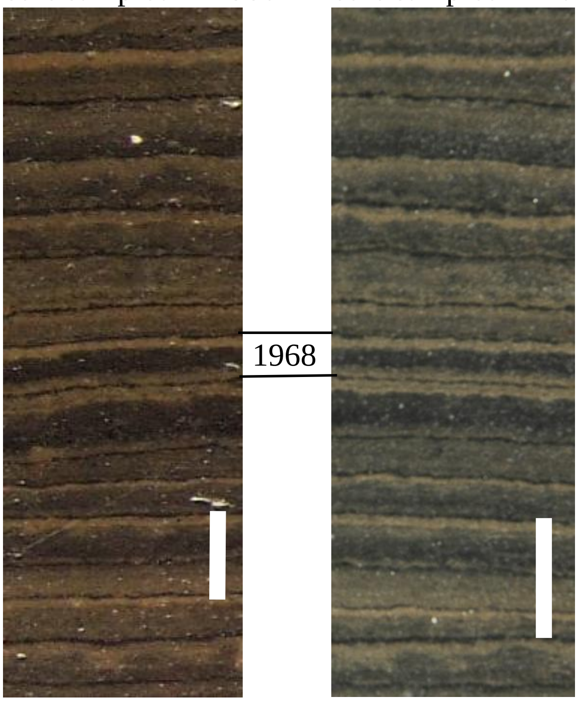

Figure 1. Varve sequence covering the period 1961-1975 in two separate cores, one sampled in 1980 and the other in 2002. The visual comparison of the varves of the two cores was facilitated by an enlargement of the photo of the varve sequence in the 2002 core, to match the varve thicknesses in the core sampled in 1980. In the core from 1980 the varves were less compacted due to shorter time in the lake bottom prior to coring. White bars in each image represent 1 cm. The figure is from Paper II.

Diagenetic effects on Fe and S

Fe in different species has different color. In reducing conditions Fe is reduced to ferrous iron (Fe^{2+}), which can form black iron sulfide (FeS) in the presence of sulfide (S^{2-}).

In oxidizing conditions ferric iron (Fe^{3+}) can form grey-brownish iron hydroxide ($Fe(OH)_3$). Renberg (1982) hypothesized that grey-brownish $Fe(OH)_3$ layers visible in the varves were deposited in spring and autumn during water circulation, and that black FeS layers were formed in winter and summer during stagnation. He further suggested that these layers could be permanently preserved in the sediment. Does the color of Fe compounds in the varves reflect the environmental conditions at the time of deposition, or is the color influenced by chemical processes in the sediment as the sediment ages and undergoes diagenesis? To assess this question, long-term changes in total concentration of Fe and S in the varve series were followed (Fig. 2a, c). No diagenetic front of iron was found in the sediment and the data do not suggest that there is a substantial vertical transport of Fe and S in the sediment, which goes against the common view. In a number of studies a Fe peak near the sediment surface was found and was suggested to be caused by an upward migration of reduced iron and re-precipitation of Fe (e.g., Sasseville and Norton 1975, Kemp et al. 1976, Carignan and Flett 1981). The changes in Fe and S concentration with time in the varves of Nylandssjön (Fig. 2a, c) is ascribed to small-scale spatial variability in sediment deposition, rather than to substantial transport within the sediment. A support for this argument is the curves for Fe and the non-mobile element Ti which show a clear resemblance and have a high Pearson correlation (r = 0.87) (Fig. 2a, b).

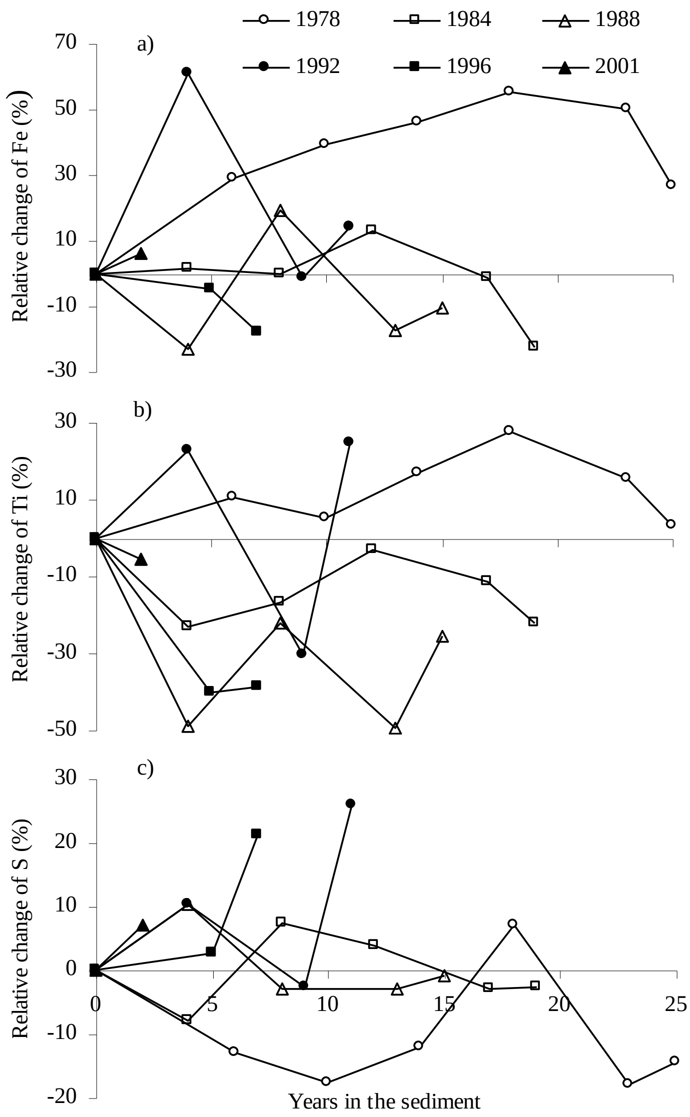

Figure 2. The curves illustrate the relative change of a) Fe, b) Ti, and c) S with time in six individual varves: 1978, 1984, 1988, 1992, 1996 and 2001 (i.e. the surface varve of cores sampled in 1979, 1985, 1989, 1993, 1997 and 2002), when these surface varves are followed in each core collected in subsequent years. The change is expressed as percent of the initial concentration (– = loss, + = gain). For example, the 1978 varve in the core taken in 1985 contains 30% more Fe than the 1978 varve had when it was a surface varve in the core taken in 1979, in the core from 1989 the concentration gain was 40%, and so on, and in the 2004 core it was about 25% more than in the 1979 core. The curves of the non-mobile element Ti show a clear resemblance with the Fe curves, and the two elements have a high Pearson correlation (r = 0.87). The figure is from Paper II.

Modeling of Fe and S based on thermodynamic, limnological, and sediment data from the lake, showed that there are pe (redox) ranges within which either FeS or $Fe(OH)_3$/FeOOH is the only solid phase present and there are pe ranges within which the two solid phases can co-exist. The findings support the hypothesis that the blackish and grey-brownish layers that occur in the varves were formed at the time of deposition.

The results agree with the findings of Shchukarev et al. (2008) that showed a presence of Fe^{3+}, but absence of Fe^{2+} in the spring and autumn layers. This indicates that the layers are preserved despite the low pe in the sediment and in the overlying hypolimnetic water during periods of stratification. The findings give new possibilities for deciphering high-temporal-resolution environmental information from varves, such as how oxygen/redox conditions in the hypolimnion were in the past.

Diagenetic effects on C and N

The long-term loss of C and N due to processes that occur in the lake bottom as sediment ages was followed. The concentration of C and N in the sediment decreased by 20% and 30%, respectively within the first five years after deposition, and after 27 years in the sediment there was a 23% loss of C and 35% loss of N (Fig. 3a, b). This is a slightly lower loss rate than found in previous studies, which reported loss rates for C of 25-45% and for N of 40-70% after 1-3 years e.g., Hamilton-Taylor and Willis (1984), Jonsson and Jansson (1997), and Teranes and Bernasconi (2000).

When comparing our results with previous studies, it is important to notice that our starting sediment material had an average age of several months up to a year, while other studies have used sediment trap material and compared that to sediment cores. Another aspect is that Nylandssjön is a soft-water lake without whitening events (many studies are conducted in calcareous lakes). Oxic versus anoxic hypolimnion also matters. Anoxic Lake Lugano had a net loss of C of 15-20%, which is ~30% less than Baldeggersee (with artificially aerated hypolimnion). Both are varved, eutrophic and calcareous lakes (Teranes and Bernasconi 2000, Lehmann et al. 2002).

The relative loss of C with time was smaller than the loss of N, and hence the C:N ratio increased with increasing age of the sediment (Fig. 3c). Sediment in the varves at the sediment-water interface had a C:N ratio of 10, which then increased to 12 as the sediment aged. The findings in this study clearly demonstrate that diagenesis changes the C:N ratio of sediment with time. Thus, changes in C:N ratio down-core in cores of recent sediment should not be uncritically interpreted as a shift over time in the proportion of organic matter sources, such as increased influx of algae or decreased influx of terrestrial organic matter (with a high C:N ratio). The loss of C and N with time does not, however, affect the visual appearance of the varves, even if it affects the varve thickness. It could on the other hand have implications for interpretations of paleolimnological data where the elements in the sediment are associated with organic matter. This was demonstrated in a study by Rydberg et al. (2008), where the effect of diagenesis on total mercury and methylmercury was assessed using the same core series.

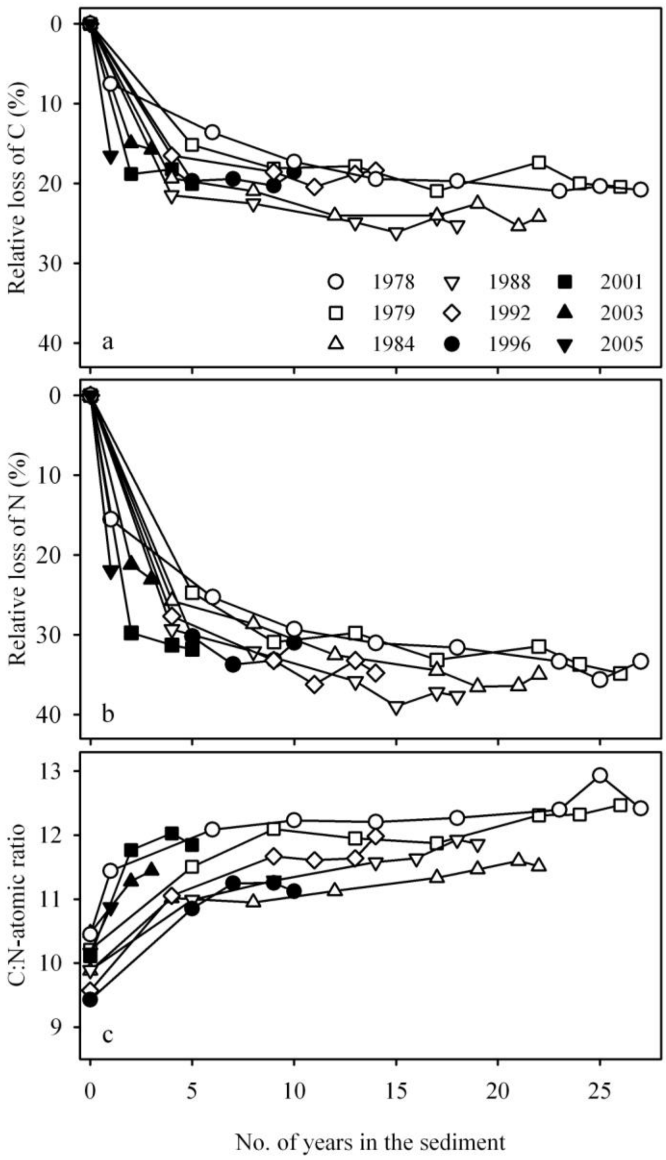

Figure 3. Curves illustrating the relative loss of (a) C and (b) N with time. The diagrams are constructed in the following way: The C and N concentration, respectively, of the surface varve for each core is followed in subsequent cores, and the loss of C and N of this surface varve in each subsequent core is calculated relative to the surface varve (expressed as percent). For example, the varve deposited in 1978 (1979 core) is followed in the core taken in 1980 (loss after 1 year), in the core taken in 1985 (loss after 6 years), and in subsequent cores until 2006. The x-axis represents the number of years the surface varve has been in the sediment. (c) The C:N ratio of the surface varves is followed in the same way in subsequent cores and the C:N ratio plotted against time in the sediment. Figure is from Paper III.

Diagenetic effects on $\delta^{13}C$ and $\delta^{15}N$

Changes in sediment δ^{13}C and δ^{15}N are used to derive information on organic matter sources, changes in nutrient availability, and paleoproductivity in lakes (Meyers and Lallier-Vergès 1999, Meyers and Teranes 2001, Meyers 2003). Here the long-term effects of sediment aging on δ^{13}C and δ^{15}N were assessed. The varve series shows that δ^{13}C increases by 0.4-1.5‰ units during the first five years and thereafter fluctuate without any obvious trend (Fig. 4a). δ^{15}N on the other hand, gradually decreases by 0.3-0.7‰ units over the entire 27-year-period encompassed by the dataset (Fig. 4b). Diagenetically caused isotopic depletion of ^{15}N in residual sediment material in an anoxic lacustrine environment was also reported by Lehmann et al. (2002). Contrary to the results from Nylandssjön the Lehman study reported an isotopic depletion of δ^{13}C, but as their starting material was fresh when the comparison started, that is expected.

To evaluate how important the initial properties of the sediment is for the extent of change in δ^{13}C and δ^{15}N over time, the δ^{13}C change and δ^{15}N change were correlated with parameters of the initial material of the surface varves such as: total C and N concentrations, $\delta^{13}C$ and $\delta^{15}N$, and C:N ratio. The results of the correlations indicate that the magnitude of change in $\delta^{13}C$ is controlled by the composition of the source material, whereas the extent of the $\delta^{15}N$ change seems to be rather independent of the composition of the initial sediment material.

When plotting the $\delta^{13}C$ change against the C loss (Fig. 5a) $\delta^{13}C$ increases as the total C decreases. The C concentration becomes stable after 5-10 years, and the change in $\delta^{13}C$ almost stops. This together with the results from the correlation analysis suggests that the $\delta^{13}C$ change is caused by a higher proportion of isotopically lighter (^{12}C) material in the easily degradable fractions of the organic matter in the sediment. When the C loss stops, the change in $\delta^{13}C$ therefore also stops. Further more, there seems to be no correlation between the magnitude of the $\delta^{13}C$ change and the change in C:N ratio (Fig. 4b). There is however, a tendency that the change in C:N ratio during the first year is accompanied by a change in $\delta^{13}C$, while the later change in C:N ratio does not give rise to any change in $\delta^{13}C$. A reasonable explanation may be that the N loss, and consequently also the C:N ratio change continues for a longer time than the C loss.

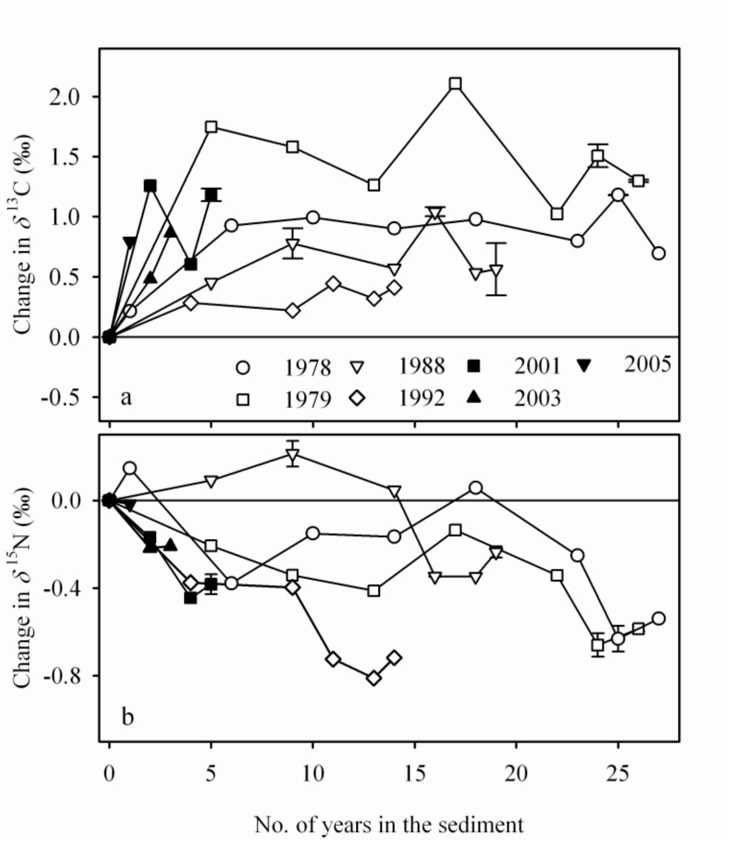

Figure 4. Curves illustrating the change of (a) $\delta^{13}C$ and (b) $\delta^{15}N$ with time. The surface varve deposited in 1978 (1979 core) is followed in the core taken in 1980 (change after 1 year), in the core taken in 1989 (change after 10 years), and in subsequent cores until 2006. The x-axis represents the number of years the surface varve has been in the sediment. The figure is from Paper IV.

When plotting the $\delta^{15}N$ change against the total N loss over time (Fig. 5c), it behaves differently compared to the $\delta^{13}C$ change against C concentration loss (Fig. 5a). During the initial phase with a large loss of N from the sediment the $\delta^{15}N$ does not change to a large extent. The main shift in $\delta^{15}N$ occurs when the N loss more or less has ceased. The decoupling between the N loss rate and the $\delta^{15}N$ change indicates that a microbial process is responsible for the fractionation of $\delta^{15}N$, in which the microbes continue to reuse the N in the sediment even when the N loss has more or less stopped. This would explain the relatively linear appearance of the $\delta^{15}N$ change (Fig. 4b) and the continued $\delta^{15}N$ decrease even when the N loss has subsided (Fig. 5c). It would also explain the weak correlation of the quality of the initial material and the magnitude of the $\delta^{15}N$ change and why there is some correlation between $\delta^{15}N$ change and the latter part of the change in C:N ratio (Fig. 5d), which seems to be controlled by the small N loss ongoing even after 20 years.

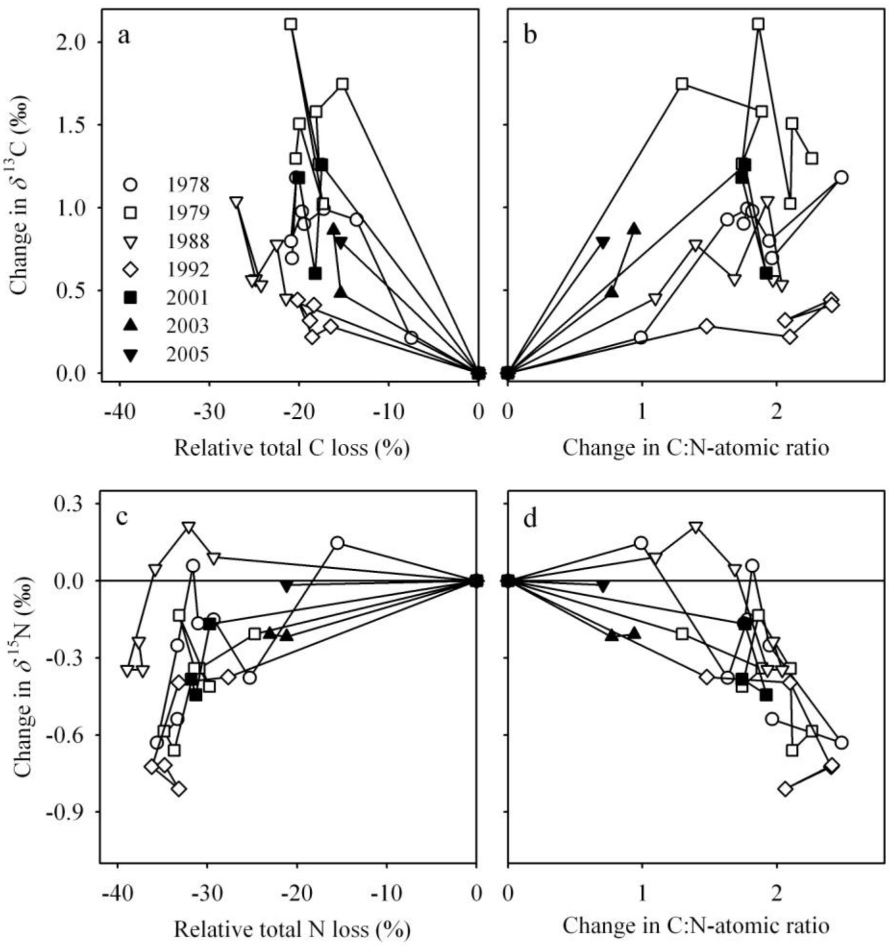

Figure 5. (a) $\delta^{13}C$ change vs. relative total carbon loss, (b) $\delta^{13}C$ change vs. C:N-ratio change, (c) $\delta^{15}N$ change vs. relative total nitrogen loss, (d) $\delta^{15}N$ change vs. C:N-ratio change. All changes are related to the initial material (i.e., surface varve) for that specific year. Figure is from Paper IV.

As already mentioned in the discussion on C and N it is hard to find suitable lakes to compare results as most previous studies were conducted over short time periods (Spooner et al. 1994, Bernasconi et al. 1997), have different starting points (Teranes and Bernasconi 2000, Lehmann et al. 2002), or were carried out in non-varved sediment. Even though the changes that occur in the stable isotope values as the Nylandssjön sediment ages seem small, the diagenetic effects should be carefully taken into consideration when $\delta^{13}C$ and $\delta^{15}N$ are used to interpret organic matter sources or paleoproductivity, especially when dealing with recent trends or small changes. For example, the diagenetic change with time in Nylandssjön is of the same magnitude as the total variation in the varves deposited between 1950-2006. A cautious recommendation for $\delta^{13}C$ is that when interpreting down core trends in lacustrine sediments, changes within the first five to ten years in the top sediment should not uncritically be interpreted as caused by changes in limnological conditions, as this study shows that they can be caused by diagenesis. When it comes to $\delta^{15}N$ it is difficult to give any recommendations, as the diagenetic change cover the whole surveyed period of 27 years. It can not be ruled out that the $\delta^{15}N$ change continues even after this period.

General discussion and future perspectives

The approach used in this thesis, where varves from a series of sediment cores sampled in the same deep basin over the course of 27 years are compared, is unique. It is a simple, well-controlled approach, which allows a high resolution comparison. However, with this approach we look only at a certain time window in the process of diagenesis. When the cores were sampled the material in the surface varve had an age from hours up to one year. The initial degradation of most of the sediment has already occurred. Likewise, what happens after 27 years cannot be studied. To study the processes that occur within the first year, sediment trap studies could be used. Actually, sediment trap data are available from Nylandssjön for the period 2001-2008, but were not analyzed as a part of this thesis. The study of the varved sediment of Nylandssjön started in 1979 with sediment coring by Professor Ingemar Renberg and co-workers. In 2001 the work was intensified with a limnological program, and in 2002 sediment traps were included. I am pleased that I had the opportunity to contribute to this time series with regular measurements of temperature and oxygen profiles, plankton sampling and sediment trap collecting. This limnological time series now spans over 8 years and makes a good foundation for the future assessment of varve formation. Long time series with a high time resolution are essential for the separation of the effect of land use versus climate on varve formation processes.

Are the findings about the effect of diagenesis on the varved sediment from Nylandssjön applicable to other lakes? When the results from this thesis are compared to other studies, there are a number of factors that must be considered: (1) *Bioturbation*. As the sediment is varved there is by definition no sediment mixing, fragmentation, and consumption by benthic invertebrates. The sediment of Nylandssjön is therefore not typical for most lakes. Studies of the effects of bioturbation on marine and lacustrine sediments suggest that mixing and the following oscillations in redox condition promote remineralization of organic matter (Aller 1994, Kristensen 2000, Stief 2007). (2) *Anoxic versus oxic conditions in the hypolimnion*. Incubation experiments have shown that for the most reactive organic matter, the degradation rate is the same in oxic and anoxic conditions (Andersen 1996, Kristensen and Holmer 2001, Lehman et al. 2002), but already degraded organic matter has a slower decomposition rate in anoxic conditions (Meyers and Ishiwatari 1993, Kristensen and Holmer 2001, Lehman et al. 2002). The importance of oxic versus anoxic conditions for the effect of diagenesis on stable isotopes is hard to evaluate as contrasting results on magnitude and direction of change have been reported. (3) *The initial composition of the sediment material,* i.e. the proportion between autochtonous and allochtonous material. A high lake productivity is a prerequisite for varve formation of the type of varve studied here, and Nylandssjön has a relatively higher productivity of algae than the typical boreal forest lake. The importance of the initial composition of the sediment material is illustrated by the fact that the loss rates for C and N vary somewhat between varves deposited different years; the loss rate after 10 years is about 5 % units larger in the varves that were deposited in 1984 and 1988, compared to the varves that were deposited in 1978 and 1979. Also, results from the isotopic study indicate that the magnitude of change in $\delta^{13}C$ over time is influenced by the composition of the source material. Another aspect to consider, which is not applicable to Nylandssjön, when discussing the initial composition of sediment material is calcite precipitation in the form of whiting events (when calcite crystals aggregate with phytoplankton algae and bacteria). This might lead to rapid sedimentation and reduced remineralization in the water column (Hodell and Schelske 1998, Dean 1999). A lake with whiting events can receive a higher proportion of easily degradable organic matter to the sediment than lakes without the

effect of a more rapid delivery system through the water column to the sediment, i.e., a higher proportion of easily degradable organic matter can give a higher decomposition rate.
A cautious assumption is that anoxia in the hypolimnion and absence of bioturbation lead to a slightly lower rate of degradation of organic matter in Nylandssjön than in non-varved lake sediments in the region. A possible design to test this assumption would be a comparative study in a lake with both a basin with varved sediment and a basin with mixed sediment. A difficulty that arises is, however, the dating of the non-varved sediment.

Even though Nylandssjön and Koltjärnen are situated close to each other and look very similar, the appearance of grey-scales and sediment characteristics such as the annual accumulation rate of dry mass, minerogenic matter and biogenic silica, differed between the lakes. This is explained by differences in catchment size, catchment-to-lake material fluxes, lake productivity and land-use influence. A further assessment of this explanation is provided by the comparison of the two basins of Nylandssjön. Although sediment parameters such as varve thickness, water content, annual accumulation rates of dry matter, organic matter and nitrogen were correlated, the grey-scale curves of the varves were only similar in about 50 % of the varves. These between-lake and within-lake comparisons show that subtle features in the lakes and their catchments contribute to the appearance of the varves. This knowledge has implications for inferences of varve properties in sediment cores in terms of past environmental data and calls for more studies of varve formation processes and how contemporary conditions in the lakes and their catchments are preserved in varves.

Conclusions

- a comparison of the two closely situated lakes Nylandssjön and Koltjärnen shows that varves are rather different in the two lakes, i.e. that varve formation is controlled by very local factors such as catchment size, catchment-to-lake material fluxes, lake productivity and land-use
- a comparison of varves in the two deep basins of Nylandssjön shows that varves are similar but not consistently identical even within a lake
- the varves within each of the two deep basins of Nylandssjön have a minute spatial variation and are thick and distinct, which make them highly suitable for the type of study design I have used for assessing the effect of diagenesis on the varves
- the diagenetic study on Fe and S suggests that there is not a substantial vertical transport of Fe and S in the sediment of Nylandssjön; no diagenetic front of Fe was found in the sediment
- modeling of Fe and S in the sediment of Nylandssjön showed that there are pe ranges within which either FeS or $Fe(OH)_3$/FeOOH is the only solid phase present and there are pe ranges within which the two solid phases co-exist
- the color of Fe in the varves of Nylandssjön is not influenced by diagenesis; it reflects the environmental conditions at the time of deposition, which gives new possibilities for deciphering environmental information from varves
- within the first five years after deposition the concentrations of C and N in the sediment of Nylandssjön decreased by 20 % and 30 %, respectively, and after 27 year in the sediment, there was a 23 % loss of C and 35 % loss of N
- diagenesis increased the C:N ratio of the sediment with time, from ~10 to ~12

- the diagenetic influence on $\delta^{13}C$ in the varves of Nylandssjön was an increase by 0.4-1.5‰ units during the first five years, then only minor fluctuations without a trend in $\delta^{13}C$ were recorded
- $\delta^{15}N$ gradually decreased by 0.3-0.7‰ units over the entire 27-year-period covered by the data set
- the diagenetic changes of the stable isotope values of the Nylandssjön sediment were relatively small, but of the same magnitude as the down-core variation in isotopic signal in the varves deposited between 1950-2006
- diagenesis does not affect the visual appearance of the varves in Nylandssjön, except for varve thickness; the varves gets thinner with time

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Sammanfattning (Summary in Swedish)

Varviga sjösediment har stor potential som miljöarkiv för undersökningar av en rad miljöparametrar som vegetationsförändringar, markanvändning, övergödning, föroreningshistoria och långsiktiga klimatförändringar. Med hjälp av dessa arkiv kan man undersöka hur miljön var förr och hur den förändrats, både naturligt och genom människans påverkan. Varviga sediment utgör de bästa sedimentarkiven då de är lätta att datera genom varvräkning och har en hög tidsupplösning. När materialet som utgör varven deponerats, utsätts det för diagenes (nedbrytning), dvs. kemiska, fysikaliska, och biologiska förändringar. En viktig förutsättning om man ska undersöka historiska miljöförändringar med hjälp av sjösediment är att den parameter man är intresserad av inte förändras av diagenes. I min avhandling har jag använt en unik samling med varvigt sediment från Nylandssjön vid Höga kusten, provtaget mellan 1979 och 2007. Proppserien har gjort det möjligt att följa långsiktiga förändringar (upp till 27 år) hos järn (Fe), svavel (S), kol (C), kväve (N), och de stabila isotoperna $\delta^{13}C$ och $\delta^{15}N$. Analysen av järn och svavel visade att det inte finns en diagenetisk front för dessa ämnen i sedimentet, inte heller visade analysen på en omfattande vertikal transport i sedimentet. En modell baserad på termodynamiska och limnologiska data och sedimentdata från sjön, visade att det finns pe-intervall (redox potential) där antigen järnsulfid (FeS) eller järnhydroxid ($Fe(OH)_3$/FeOOH) är den fasta fasen, men det finns också pe-intervall där de båda faserna samexisterar i varven. Resultaten stöder hypotesen att de svarta (färgade av järnsulfid) och gråbruna (färgade av järnhydroxid) lager som finns i varven bildades vid tidpunkten för sedimentationen, dvs. färgen på dessa lager säger något om förhållandena i sjön vid tidpunkten för deras tillkomst. Analysen av kol och kväve visade att inom de första fem åren efter depositionen minskade koncentrationen av kol med 20 % och kväve med 30 %, och 27 år efter depositionen så var minskningen 23 % av kol och 35 % av kväve. Kvoten mellan kol och kväve ökade med ökande ålder på sedimentet, från ~ 10 i ytvarven till ~ 12 efter åldrande. $\delta^{13}C$ visade på en ökning motsvarande 0,4-1,5 ‰ enheter under de första fem åren, sedan konstaterades bara mindre fluktuationer. $\delta^{15}N$ visade ett annat mönster, med en gradvis minskning med 0,3-0,7 ‰ enheter som skedde under hela 27-års-perioden. De diagenetiska förändringar som skett med stabila isotoperna $\delta^{13}C$ och $\delta^{15}N$ i

Nylandssjön är till omfattningen små, men av ungefär samma storlek som variationen i isotopsignalen i varven som deponerats mellan 1950-2006.

Mina resultat visar att varvens utseende inte ändras av diagenes, förutom att varven blir tunnare när sedimentet åldras. Eftersom färgen på det järn som finns i varven troligen avspeglar de förhållanden som rådde i sjön vid tiden för materialets deposition, skapar detta nya möjligheter att uttolka högupplöst information om den miljö som en gång var. Däremot ändras koncentrationen av kol och kväve, kol-kväve kvoten, liksom isotopsammansättningen ($\delta^{13}C$ och $\delta^{15}N$) när sedimentet åldras. Det är en kunskap man har nytta av vid tolkning av paleolimnologiska data, eftersom de nämnda parametrarna brukar användas för att uttolka hur produktionen i sjön och transporten av material från sjöns omgivningar förändrats över tiden.

Förutom det faktum att diagenesens inverkan på en rad sedimentparametrar är av betydelse vid tolkning av paleolimnologiska data så visar en jämförelse mellan varven i Nylandssjön och den intilliggande Koltjärnen, liksom varven i de två djuphålorna i Nylandssjön, att subtila skillnader i sjöar, och deras avrinningsområden formar varvens utseende, något som gör tolkningen av varv komplicerad.

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