

Fourier transform infrared spectroscopy, a new cost-effective tool for quantitative analysis of biogeochemical properties in long sediment records

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Abstract Measurements of Fourier transform infrared spectroscopy (FTIRS) in the mid-infrared (MIR) region were conducted on sedimentary records from Lake El'gygytgyn, NE Siberia, and Lake Ohrid, Albania/Macedonia. Calibration models relating FTIR spectral information to biogeochemical property concentrations were established using partial least squares regression (PLSR). They showed good statistical performance for total organic carbon (TOC), total nitrogen (TN), and biogenic silica (opal) in the sediment record from Lake El'gygytgyn, and for TOC, total inorganic carbon (TIC), TN, and opal in sediments from Lake Ohrid. In both cases, the calibration models were successfully applied for down-core analysis. The results, in combination with the small amount of sample material needed, negligible sample pre-treatments, and low costs of analysis, demonstrate that FTIRS is a promising, cost-effective tool that allows high-resolution paleolimnological studies.

Keywords Fourier transform infrared spectroscopy · Biogeochemistry · Biogenic silica · Paleolimnology · Lake El'gygytgyn · Lake Ohrid

Introduction

Lacustrine sediment records are valuable archives of past environmental changes. A few of these records, such as the well-known records from lakes Baikal (e.g. Peck et al. 1994; Colman et al. 1995; Williams et al. 1997), Tanganyika (Cohen et al. 1993), Malawi (Tiercelin and Lezzar 2002), Biwa (e.g. Fuji 1988), and Bosumtwi (Grieve et al. 1995) cover more than 1 million years. Recent studies have also shown that lakes Ohrid (Stankovic 1960; Watzin et al. 2002) and El'gygytgyn (Layer 2000) probably have sediment records more than 3 million years old.

The investigation of the sediment records of these ancient lakes requires several analytical methods, one of which comprises their biogeochemical properties. Analysis of biogeochemical properties in sediment records often involves intensive sample pre-treatment and incorporates several different analytical techniques, which makes the analytical process both time consuming and expensive. As one approach to develop a fast and cost-effective tool to obtain information on biogeochemical properties and related climate changes, near infrared spectroscopy (NIRS) has been applied successfully to marine (e.g., Chang et al. 2005; Jarrard and Vanden Berg 2006) and

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lacustrine (Malley et al. 1999, 2000; Korsman et al. 2001; Rosén et al. 2000; Rosén 2005; Rosén and Hammarlund 2007) sediments.

Fourier transform infrared spectroscopy (FTIRS) in the mid infrared region (MIR) is more sensitive to molecules present in minerogenic and organic material than NIRS (e.g., Farmer 1974; Colthup et al. 1990; Harris 1998; Kellner et al. 1998). FTIRS has been applied to sediments to infer quantitatively the concentrations of lake water total organic carbon (TOC) (Rosén and Persson 2006), silicate minerals (Sifeddine et al. 1994; Bertaux et al. 1996; Wirmann et al. 2001), carbonates (Mecozzi et al. 2001), and humic substances (Braguglia et al. 1995; Belzile et al. 1997; Calace et al. 1999, 2006). The potential to use FTIRS as a rapid and cost-effective tool for the analysis of biogeochemical properties on long lacustrine sediment records has yet to be tested.

Within the scope of this study, we aim (1) to test if calibration models for the determination of TOC, total inorganic carbon (TIC), total nitrogen (TN), total sulphur (TS), and opal concentrations in Lake El'gygytyn and Lake Ohrid sediments can be established using FTIRS and (2) to test the calibration models on down-core sediment samples by comparing the results to values measured by established analytical methods.

Study sites

Lake El'gygytyn (67°30'N, 172°05'E) is situated in northeastern Siberia, in a 18-km-wide crater, which was formed by a meteorite impact 3.6 Ma ago (Layer 2000). The bedrock of the crater is formed by felsic to intermediate igneous rocks of Late Cretaceous age (Ispolatov 2004). Where Tertiary or Quaternary sediments prevail in the vicinity of the lake, the continuous permafrost reaches depths between 100 and 300 m (Nolan and Brigham-Grette 2007). The lake is located in the southeastern part of the crater and has a diameter of 12 km and a maximum depth of 175 m. The lake probably formed shortly after the meteorite impact and is believed to have never been inundated by quaternary ice sheets (Brigham-Grette et al. 2007; Glushkova and Smirnov 2007). Due to the harsh climate the lake remains ice covered for at least 9 months of the year (Nolan and Brigham-Grette 2007). The catchment of the lake is restricted

to the area formed by the crater rim and drained by 50 small ephemeral creeks during the short (2–3 month) summer period. The river Emnyaam forms the outlet of the lake in its southeastern corner. The sparse vegetation in the Lake El'gygytyn basin is dominated by lichen and herbaceous taxa, with rare occurrences of shrub forms of *Salix* and *Betula* in protected areas (Lozhkin et al. 2007).

Lake Ohrid (41°01'N, 20°43'E) is a transboundary lake located between the Republics of Albania and Macedonia. The lake is c. 30 km long, c. 15 km wide and has a maximum depth of c. 280 m. Lake Ohrid is believed to be 2–5 Ma old (Stankovic 1960; Watzin 2002). It contains more than 200 endemic species (Stankovic 1960; Watzin et al. 2002) and has reacted sensitively to recent environmental change (Matzinger et al. 2006). The lake basin is located within an active tectonic graben system (Watzin et al. 2002) and surrounded by high mountain ranges reaching up to 2,300 m above sea level. Strongly karstified limestones and clastic sedimentary rocks of Mesozoic age as well as metamorphic rocks of Paleozoic age crop out in the watershed of Lake Ohrid (Robertson and Shallo 2000; Watzin et al. 2002). According to Matzinger et al. (2006), Lake Ohrid is fed by karst aquifers, surface runoff, and direct precipitation on the lake surface. Surface outflow (60%) to the River Crn Drim to the north and evaporation (40%) are the main hydrologic outputs. Mediterranean vegetation with clear indications of anthropogenic degradation is characteristic for the Lake Ohrid region (Stankovic 1960).

Both Lake Ohrid and Lake El'gygytyn are large, old, deep, and oligotrophic lakes. However, their geographic locations, hydrological regimes, catchment dynamics, tectonic frameworks, vegetation, and climatic conditions differ significantly, leading to considerably different sediment characteristics.

Materials and methods

Core recovery and composition

Core PG1351 from Lake El'gygytyn was recovered during an expedition in 1998. It was collected from the lake ice in the central part of the lake, where a water depth of 175 m was measured. The sediment composite core is 1,290 cm long and composed of a gravity core (Uwitec Ltd., Austria) from the

uppermost sediments and several successive percussion piston cores (Uwitec Ltd., Austria) of up to 300 cm length from deeper sediments. The sediment consists of clastic mud with low, but variable amounts of organic matter (Melles et al. 2007). Massive horizons of olive grey alternate with laminated horizons of brown and dark grey colors (Asikainen et al. 2007; Melles et al. 2007). Core PG1351 has already been investigated for lithology, sedimentology, physical properties, palynology and geochemistry to assess past climate changes in the region and changes in the catchment and water column using a multiproxy approach (Nowaczyk et al. 2002; Asikainen et al. 2007; Lozhkin et al. 2007; Melles et al. 2007; Minyuk et al. 2007). The biogeochemical properties are some of the most valuable proxies for reconstructing changes in regional temperature and humidity (Melles et al. 2007). The base of core PG1351 at 1,290 cm sediment depth is dated to 250 ka (Nowaczyk et al. 2007).

Sediment cores from Lake Ohrid were taken from a floating platform in 2005, in the southeastern part of the lake, where a water depth of 105 m was measured. A 1,075-cm-long composite core (Lz1120) was sampled using the same coring equipment as described above. Core Lz1120 was subdivided into two units with distinctly different sediment composition. The lower Unit I (1,075–552 cm) with a basal age of c. 40 ka before present (BP) consists of poorly sorted, massive, medium to coarse silt of grayish color. Carbonates and plant macrofossils are typically absent, and organic material is sparse in Unit I. The upper Unit II (545–0 cm) consists of medium to coarse-grained silt, with finely-dispersed organic material, and carbonaceous remains of fossil ostracode and mollusc valves. Color changes repeatedly from light grey to brownish-black in Unit II (Wagner et al. in press). Variations of biogeochemical properties throughout this sedimentary record clearly reflect climate-induced changes in the catchment and water column of Lake Ohrid (Wagner et al. unpubl. data).

Biogeochemistry (conventional methods)

Both cores PG1351 and Lz1120 were sub-sampled at 2-cm intervals. The samples were freeze-dried and

ground to a particle size below 63 μm using a planetary mill. Concentrations of total carbon (TC), TN, and TS were measured with a combustion CNS elemental analyzer (VARIO Co. and EuroVector Co.). Samples for TOC analysis were pre-treated with HCl (10%) at a temperature of 80°C to remove carbonates and then analyzed using a Metalyt-CS-1000-S (ELTRA Corp.). TIC was calculated by subtracting TOC from TC. Opal measurements were conducted using the leaching method described by Müller and Schneider (1993).

FTIRS

The basic principle of the FTIRS technique is that vibrations in molecules containing polar bonds are excited by infrared (IR) radiation. The wavelengths at which molecules are excited are dependent on the structural and atomic composition of the molecule leading to the absorbance of IR radiation at molecule-specific wavelengths (e.g. Colthup et al. 1990; Kellner et al. 1998).

FTIRS measurements were performed on a subset of 161 samples collected at 6-cm intervals from core PG1351 (Lake El'gygytgyn), and 505 samples at 2-cm intervals from core Lz1120 (Lake Ohrid). To avoid variations in measurement conditions caused by temperature, all samples were placed in the same thermostated laboratory ($25 \pm 0.2^\circ\text{C}$) as the FTIRS device for at least 5 h immediately prior to analysis, in order to adapt to the same temperature as the FTIRS device. For FTIRS analysis 0.5 g potassium bromide (KBr) (Uvasol®, Merck, Germany) was mixed with 0.011 g freeze-dried and ground sample material using a mortar and pestle. The mixing of KBr and sample material was performed without any safety precautions since KBr is rated as a non-toxic substance. KBr is transparent in the IR region and is used as a diluting substance to avoid distortions that are caused by optical effects (Griffiths and De Haseth 1986). The processed, powdered samples were placed into a sample cup and analyzed by means of the diffuse reflectance FTIRS technique using a Bruker IFS 66v/S FTIR spectrometer (Bruker Optik GmbH, Germany) equipped with a diffuse reflectance accessory (Harrick Inc., USA). For each sample, data were collected at 4 mbar vacuum conditions for wavelengths between 2,666 and 25,000 nm, or from 3,750

to 400 cm^{-1} or reciprocal centimeters, with an analysis each 2 cm^{-1} , yielding 1,737 data points per sample.

Numerical analysis

FTIR spectra were normalized using baseline correction and multiple scatter correction (MSC). Internal variations of the FTIRS device during analysis can cause baseline-shifts and tilting between the sample spectra. In order to get the same baseline for all spectra, independent of measurement conditions, baseline correction performs a linear correction of the spectra, by setting two points ($3,750$ and $2,210$ – $2,200\text{ cm}^{-1}$) to zero. Since this correction is done for two points of the spectra it corrects for both baseline-shifts and tilting. MSC removes spectral variation arising from varying effective path lengths between the sample surface and the detector and particle size (Geladi et al. 1985; Martens and Næs 1989; Geladi and Dåbakk 1999). The aim of this method is to remove variation in spectra caused by between-sample scatter variation. Thus, MSC linearizes the spectra and eliminates variation caused by noise. The remaining variation is supposed to relate solely to the chemistry of the samples. Using spectral data from many samples enables the distinction between absorption and scatter. The scatter for each sample is estimated relative to that of an ‘ideal’ sample, taken as the mean spectrum of all sample spectra. Each sample spectrum is then corrected to the same scatter level as the ‘ideal’ sample. SIMCA-P

(Umetrics AB, SE 901-91 Umeå, Sweden) software was used for all statistical analysis.

On core PG1351, calibration models for TOC and TN are based on 96 out of 100 samples and for opal on 64 out of 100 samples from the topmost 764 cm, respectively (Table 1). TIC was absent in core PG1351. For core Lz1120, calibration models were constructed in a different way since the sediment characteristics of Units I and II are different. Hence, a calibration model built upon samples from Unit II cannot be applied for Unit I and vice versa. Thus, on core Lz1120, calibration models for TOC, TIC, TN, and TS are based on 102 samples in 10-cm intervals and for opal on 58 samples in c. 20-cm intervals throughout the core. Partial least squares regression (PLSR) (e.g. Martens and Næs 1989 and references therein) was used to establish calibration models between FTIR-spectra of sediment samples and corresponding conventionally-measured biogeochemical property concentrations. Quantitative validation of the internal statistical performance of the calibration models was carried out using cross validation (CV). In CV, 90% of the conventionally measured dataset with biogeochemical property concentrations and their corresponding sample spectra are used for the calibration model. The model is then used to predict biogeochemical property concentrations of the remaining 10% of the sample set by solely using their recorded FTIR-spectra. Root mean square error of cross validation (RMSECV) and the cross-validated coefficient of determination R^2_{CV} were used to describe the best fit for internal model predictions. RMSECV was calculated according to Eq. 1:

Table 1 Descriptive statistics for calibration models for the estimation of biogeochemical properties of core PG1351 and Lz1120 from FTIR-spectra

Statistic	TOC (%)		TIC (%)		TN (%)		TS (%)		Opal (%)	
	PG1351	Lz1120	PG1351	Lz1120	PG1351	Lz1120	PG1351	Lz1120	PG1361	Lz1120
PLS components	6	1	–	1	5	2	–	2	4	1
Samples (<i>n</i>)	96	102	–	102	96	102	–	102	64	58
Min	0.12	0.48	–	0.00	0.00	0.07	–	0.02	6.22	0.10
Max	1.94	2.40	–	9.64	0.17	0.31	–	0.36	22.72	7.84
Gradient	1.82	1.92	–	9.64	0.167	0.240	–	0.340	16.50	7.74
Mean	0.54	1.19	–	2.85	0.067	0.160	–	0.090	13.07	3.39
RMSECV	0.07	0.25	–	0.69	0.017	0.022	–	0.047	1.76	1.02
RMSECV (% gradient)	3.79	13.15	–	7.11	10.45	9.21	–	13.91	10.66	13.22
R^2_{CV}	0.96	0.81	–	0.96	0.68	0.69	–	0.26	0.75	0.63

$$\text{RMSECV} = \frac{1}{n} \sqrt{\frac{\sum_{i=1}^n (y_i - x_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}} \quad (1)$$

with n the number of samples, y_i the conventionally-measured property concentration for sample i , x_i the FTIRS-inferred property concentration for sample i , and \bar{y} the mean conventionally-measured property concentration for all samples.

Adjacent to CV, in a second validation procedure, FTIRS calibration models were used to assess the concentrations of biogeochemical properties on sediment samples not included in the model and compared with measurements using conventional methods. To verify the robustness of the calibration models, 61 FTIRS-inferred concentrations for each property were compared to conventionally-measured concentrations in the section between 1,290 and 772 cm of core PG1351. For this purpose, 60 samples with conventional TOC and TN measurements and 18 samples with conventional opal measurements were available.

Calibration models for TOC, TIC, TN, and TS were verified on 403 interspersed samples with conventional measurements available for core Lz1120. Since only 119 conventionally-measured opal concentrations were available throughout core Lz1120 the calibration model for opal built upon 58 samples was verified on the remaining 61 conventionally-measured samples. Then, the opal model was applied to infer opal concentrations in the sample set not measured conventionally.

The coefficient of determination (R^2) between the conventionally-measured and the FTIRS-inferred property concentrations, as well as the standard error of estimate of y on x ($\text{SE}_{y,x}$), were calculated to get a quantitative estimate about how the calibration model performs if the property concentrations in the samples are derived from FTIR spectra. The $\text{SE}_{y,x}$ was calculated according to Eq. 2:

$$\text{SE}_{y,x} = \sqrt{\frac{\sum (y - x)^2}{n}} \quad (2)$$

with n the number of samples, y the primary biogeochemical property concentration, and x the FTIRS-inferred biogeochemical property concentration. Loadings or weight vector (w^*c) values of the PLS component 1 (PLSC1), the most important principal

component equivalent in PLSR, which explains most of the correlation between the sample spectra and the concentration of the regarded biogeochemical property, were plotted against wavenumbers to identify the spectral region contributing most to the calibration models.

Results and discussion

Spectral information

Lake El'gygytgyn

The FTIR spectra of the MIR-region from Lake El'gygytgyn sediments show only little variation and generally the highest absorbance at wavenumbers between 1,000 and 1,150 cm^{-1} (Fig. 1a). This region of the spectrum as well as regions between 400 and 650 cm^{-1} and centered at 800 cm^{-1} can be attributed to absorbance caused by SiO (Farmer 1974) or organic material (Colthup et al. 1990). In Lake El'gygytgyn organic compounds are only minor constituents of the sediment (<2.5% TOC) (Melles et al. 2007) whilst minerogenic material containing SiO such as chlorite, smectite, illite (Asikainen et al. 2007), kaolinite, quartz, feldspar (Dehnert 2004) and opal (Melles et al. 2007) is dominant. Hydroxyl ions are major constituents of clay minerals, opal, and of organic substances present in lake sediments. Within the recorded spectra of Lake El'gygytgyn the absorbance maximum centered around 3,600 cm^{-1} and further absorbance between 3,000 and 3,750 cm^{-1} can be mostly attributed to hydroxyl vibrations (Farmer 1974; Kellner et al. 1998). Molecules present in organic substances show absorbance in a large part of the whole MIR-region. Carbon hydrogen bonds show absorbance between 2,850 and 3,000 cm^{-1} (Colthup et al. 1990) (Fig. 1a). Absorbance in the 1,600–1,800 cm^{-1} region is characteristic for CO bonds, such as those originating from carbonates (Mecozzi et al. 2001) or carboxyl-groups of humic substances (Calace et al. 1999). Since carbonates are almost absent in Lake El'gygytgyn (Melles et al. 2007) absorbance in the 1,600–1,800 cm^{-1} region is probably related to the occurrence of humic substances. Further determination of chemical bonds present in organic substances is difficult in Lake El'gygytgyn, as the high concentration of minerogenic

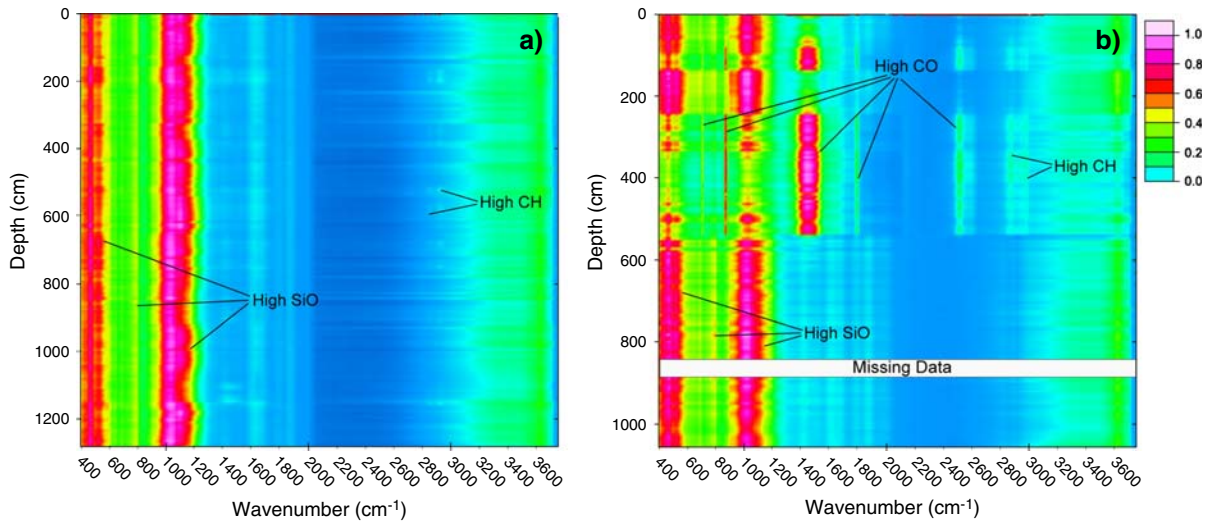


Fig. 1 2D plot of FTIR spectra from cores (a) PG1351 and (b) Lz1120. Wavenumbers are displayed on the x-axis, sediment depths are shown on the y-axis, and absorbance is indicated by a color chart with red/violet indicating highest and blue

indicating lowest absorbance. SiO equals silicon oxygen bond, CO equals carbon oxygen bound, and CH equals carbon hydrogen bound

components leads to overlapping spectra in regions where organic substances absorb.

Lake Ohrid

FTIR spectra from Lake Ohrid generally show the highest absorbance in the $1,450\text{ cm}^{-1}$ region for the uppermost 550 cm sediment depth (Fig. 1b). This spectral region ($1,450\text{ cm}^{-1}$) as well as absorbance centered at 710, 880, 1,800, and $2,520\text{ cm}^{-1}$ (Fig. 1b) can be attributed to CO vibrations of calcite (White 1974). Calcite is one major component of Lake Ohrid sediments within the uppermost 550 cm, reaching concentrations of up to 80wt% (Wagner et al. in press). The region between 1,000 and $1,050\text{ cm}^{-1}$ (Fig. 1b) shows highest absorbance from 1,075 to 550 cm sediment depth. This spectral region as well as absorbance maxima at 800, and between 400 and 650 cm^{-1} (Fig. 1b) are related to SiO vibrations mainly from quartz, feldspars, clay minerals and opal. Absorbance between 3,000 and $3,750\text{ cm}^{-1}$ with a characteristic maximum at $3,600\text{ cm}^{-1}$ (Fig. 1b) is due to OH vibrations and shows the highest absorbance values in samples with low carbonate content and correspondingly high amounts of silicate minerals. Absorbance in the $2,850\text{--}3,000\text{ cm}^{-1}$ region, in

particular visible in the uppermost 550 cm of core Lz1120 (Fig. 1b), can be attributed to CH vibrations.

Model development

The statistical performance for the calibration models by means of the root mean square error of cross-validation (RMSECV), RMSECV as percentage of the calibration set gradient (the gradient is the difference between minimum and maximum concentrations of the regarded property within the sample set used for the calibration model), R^2_{CV} , and the number of PLS components is presented in Table 1 for both lakes.

Lake El'gygytgyn

For Lake El'gygytgyn, the correlation is high between the FTIRS-inferred and conventionally-measured TOC ($R^2_{CV} = 0.96$), TN ($R^2_{CV} = 0.68$), and opal ($R^2_{CV} = 0.75$) concentrations. Correspondingly the RMSECV is low for TOC (0.07%, 3.79% of the gradient), TN (0.017%, 10.45% of the gradient), and opal (1.76%, 10.66% of the gradient). Model performance for TS ($R^2_{CV} = 0.11$) was low so a correlation was not performed.

Lake Ohrid

The statistical performance of the calibration models for Lake Ohrid is high for TOC ($R^2_{CV} = 0.81$), TIC ($R^2_{CV} = 0.96$), TN ($R^2_{CV} = 0.69$), and opal ($R^2_{CV} = 0.63$). Correspondingly the RMSECV is low for TOC (0.25%, 13.15% of the gradient), TIC (0.69%, 7.11% of the gradient), TN (0.022%, 9.21% of the gradient), and opal (1.02%, 13.22% of the gradient). The statistical performance of the TS model ($R^2_{CV} = 0.26$) is poor and the FTIRS model is therefore not good enough for quantitative estimations of TS in the sediment from Lake Ohrid.

Relationships between FTIRS models and biogeochemical properties

Lake El'gytgyyn

Since the FTIRS model uses similar wavenumbers for TOC and TN these elements can probably not be assessed independently. Especially the regions around 500, 850–1,000, 1,400–1,800, 2,850–3,000, and 3,600 cm^{-1} are important for the PLSR models (Fig. 2). The regions between 1,400–1,800 and between 2,850–3,000 cm^{-1} are sensitive to molecules present in organic substances. This indicates that the models are partly based on a direct relationship between spectral variation and organic matter content. In contrast, spectral regions at around 500 and between 850–1,000 cm^{-1} are indicative for absorbance mainly caused by SiO, and absorbance in the 3,600 cm^{-1} region is mainly caused by OH vibrations. This indicates that indirect relationships are also important for the calibration models. Spectral bands between 600–800 and 1,040–1,240 cm^{-1} are anti-correlated to the TOC and TN concentrations (Fig. 2). Absorbance in these spectral regions is mainly due to SiO groups in silicate minerals.

Within the calibration model for opal, spectra between 1,050 and 1,350 cm^{-1} (Fig. 2), explain most of the variation, however the region between 3,000 and 3,500 cm^{-1} and the small peak centered around 1,675 cm^{-1} (Fig. 2) also contribute to the correlation. Opal shows characteristic SiO absorbance maxima at 480, 790, and in particular at 1,100 cm^{-1} (Moenke 1974; Gendron-Badou et al. 2003). The absorbance around 1,100 cm^{-1} is probably the most important

region for the FTIRS opal model. The absorbance between 3,000 and 3,500 cm^{-1} can be linked to OH molecular vibrations (Moenke 1974), which are also important constituents of opal. Thus it can be assumed that the model is predominantly based on a direct relationship between opal concentration and spectral variation. The regions between 400–1,000 cm^{-1} and at 3,600 cm^{-1} are anti-correlated to the concentration of opal (Fig. 2). Even though the 400–1,000 cm^{-1} region is also indicative for SiO it is difficult to define specific silicate minerals causing absorbance in this region. Absorbance at 3,600 cm^{-1} is due to OH and in this particular region it is negatively correlated to opal concentrations.

Even though the variation observed in the raw spectra is very low the models for TOC and TN on the one hand and the model for opal are clearly distinguishable regarding the wavenumbers used by the models. This shows that spectral variation, even if it is not clearly visible to the human eye, can contain

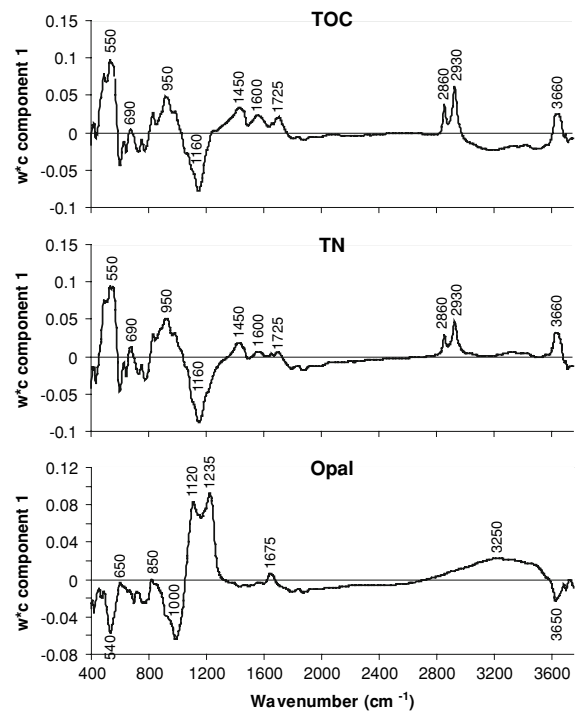


Fig. 2 Loadings expressed by weight vectors (w^*c) of the PLSC1 (y-axis) for the FTIRS-inferred properties of sediment from core PG1351. The figure shows the spectral regions important for the predictive models. Positive loadings indicate wavelengths positively correlated to the property of interest and negative loadings indicate wavelengths negatively correlated to the property

important information on the concentration of biogeochemical properties.

Lake Ohrid

The FTIRS models for TOC, TIC, TN, TS, and opal use similar wavenumbers (Fig. 3), which indicates that these models may not be independent of each other. In particular the wavenumbers indicative for carbonate at 710, 880, 1,470, 1,800, and 2,520 cm^{-1} (White 1974; Gaffey 1986) are clearly the most important wavenumbers for all calibration models (Fig. 3). Whereas TOC, TIC, and TN are positively correlated, opal is negatively correlated to these wavenumbers. This is probably due to the dominance of calcium carbonate in the uppermost 550 cm of the Lz1120 record (Wagner et al. in press) and changes in carbonate concentration have a large impact on the relative concentration of other compounds.

Predictions

The results for the predictions of biogeochemical properties solely using FTIR spectral information is displayed by means of the SE y,x , the SE y,x as percentage of the prediction set gradient (the gradient is the difference between minimum and maximum concentrations of the regarded property within the prediction set) and the R^2 between FTIRS-inferred and conventionally-measured property concentrations in Table 2.

Lake El'gytgyn

The FTIRS calibration models for TOC ($R^2 = 0.79$), TN ($R^2 = 0.62$), and opal ($R^2 = 0.76$) show good statistical performance and can be used to reproduce general trends in down-core analysis (Figs. 4, 5). The SE y,x is low for TOC (0.12%, 8.28% of the gradient), TN (0.010%, 12.46% of the gradient), and opal (2.17%, 13.22% of the gradient), showing that the reproducibility with respect to absolute values is good. The statistical performance for TOC calibration models decreases substantially with a difference of 0.17 (TOC) between the R^2_{CV} (0.96) of the calibration model and the R^2 (0.79) in down-core

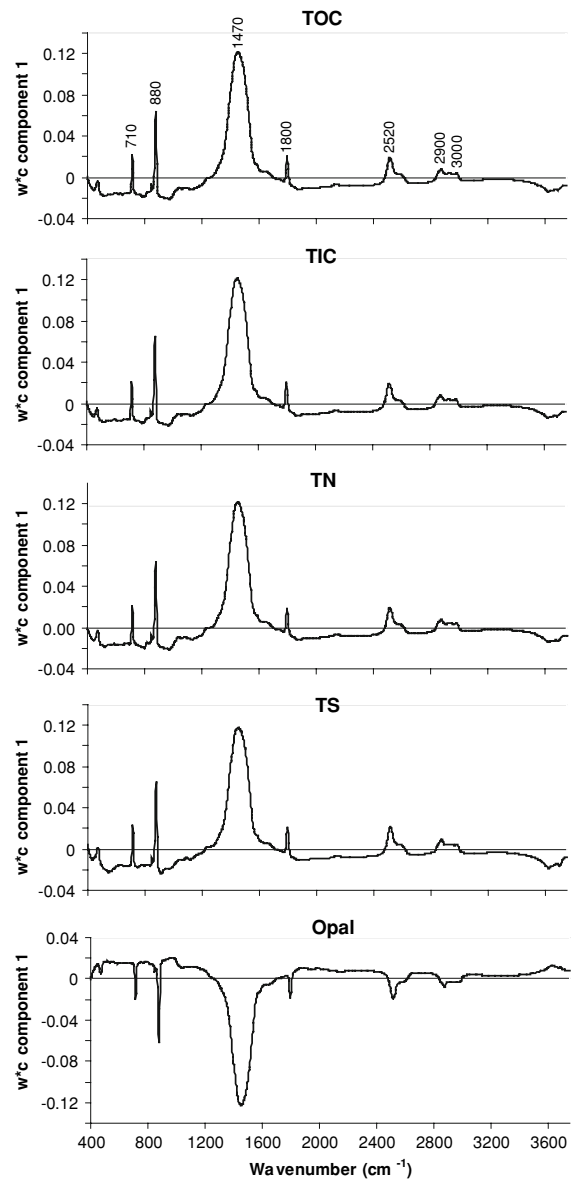


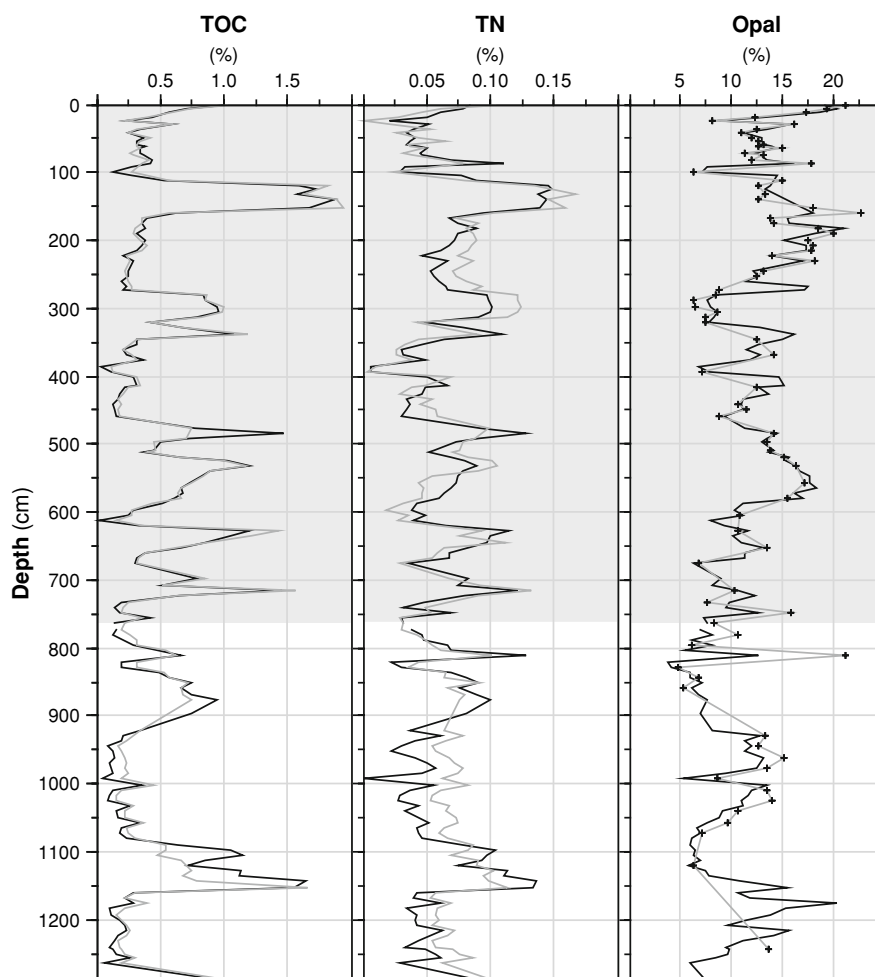
Fig. 3 Loadings expressed by weight vectors ($w \cdot c$) of the PLSC1 (y-axis) for the FTIRS-inferred properties of sediment from core Lz1120. The figure shows the spectral regions important for the predictive models. Positive loadings indicate wavelengths positively correlated to the property of interest and negative loadings indicate wavelengths negatively correlated to the property

predictions (Fig. 5), due to 7 outliers between 1,089 and 1,144 cm sediment depth (Fig. 4). By removing these 7 outliers, the difference is reversed and the R^2 (0.96) in down-core predictions equals the R^2_{CV} (0.96) of the internal calibration model validation. Since the gradient as well as maximum and minimum

Table 2 Descriptive statistics for the prediction of biogeochemical properties estimated by applying calibration models to samples not included in the calibration models for core PG1351 and core Lz1120

Statistic	TOC (%)		TIC (%)		TN (%)		TS (%)		Opal (%)	
	PG1351	Lz1120	PG1351	Lz1120	PG1351	Lz1120	PG1351	Lz1120	PG1351	Lz1120
Samples (<i>n</i>)	60	403	–	403	60	403	–	403	18	61
Min	0.16	0.48	–	0.00	0.03	0.07	–	0.01	4.71	0.68
Max	1.66	2.85	–	9.72	0.11	0.30	–	1.39	21.15	6.74
Gradient	1.50	2.37	–	9.72	0.084	0.230	–	1.380	16.44	5.79
Mean	0.39	1.20	–	2.75	0.07	0.16	–	0.10	10.72	3.18
SE y,x	0.12	0.25	–	0.48	0.010	0.020	–	0.090	2.17	0.68
SE y,x (% gradient)	8.28	10.48	–	4.96	12.46	8.63	–	6.50	13.22	8.78
R^2	0.79	0.84	–	0.98	0.62	0.84	–	0.21	0.76	0.78

Fig. 4 Down-core plot of biogeochemical properties measured with conventional techniques (grey line) and inferred using FTIRS (black line) of core PG1351. The interval on which the calibration model has been performed is indicated by the grey background for the uppermost 764 cm. Due to the few samples analyzed by conventional methods, opal concentrations measured by conventional method are indicated by crosses



concentrations are covered by the calibration model, the discrepancy between FTIRS-inferred and conventionally-measured concentrations might be due to

inconsistency in the conventionally-measured TOC concentrations. Another possibility could derive from low quality FTIRS data for this sediment sequence.

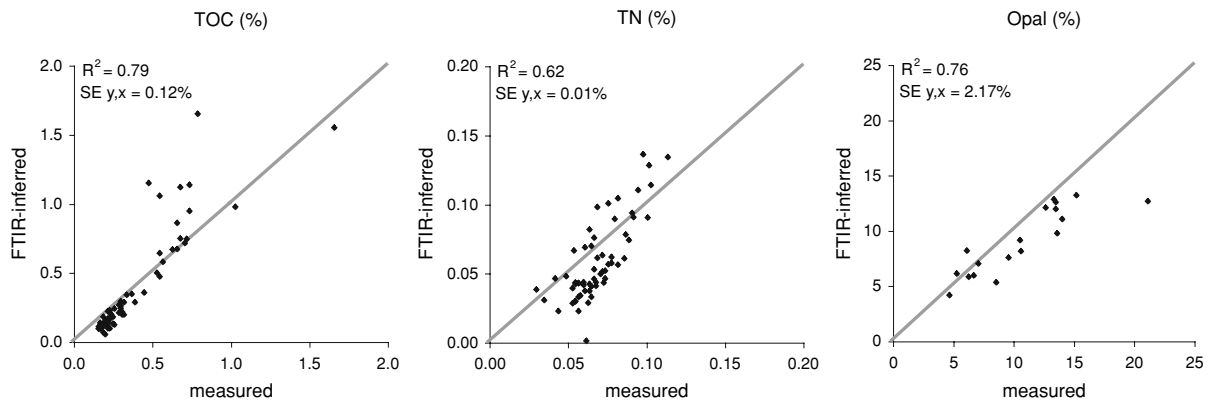


Fig. 5 Scatter plots of conventionally-measured (x-axis) versus FTIRS-inferred (y-axis) TOC, TIC, TN, TS, and opal concentrations for core PG1351

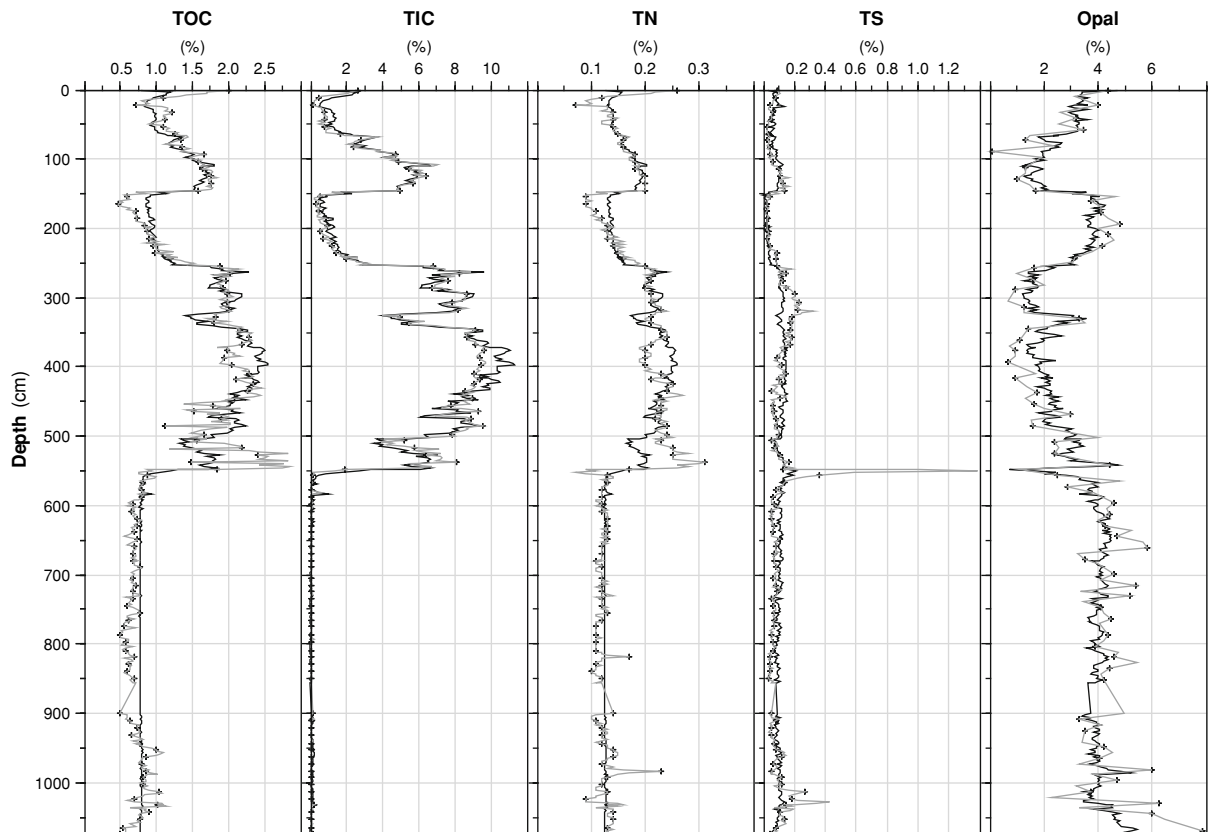


Fig. 6 Down-core plot of biogeochemical properties measured with conventional techniques (grey line) and inferred using FTIRS (black line) of core Lz1120. Black crosses indicate the samples used for the calibration models

However, no peculiarities were observed during analysis and among the collected spectra, further predictions for TN and opal within the same sediment sequence do not show similar discrepancies.

Lake Ohrid

The FTIRS calibration models for TOC ($R^2 = 0.84$), TIC ($R^2 = 0.98$), TN ($R^2 = 0.84$), and opal ($R^2 = 0.78$)

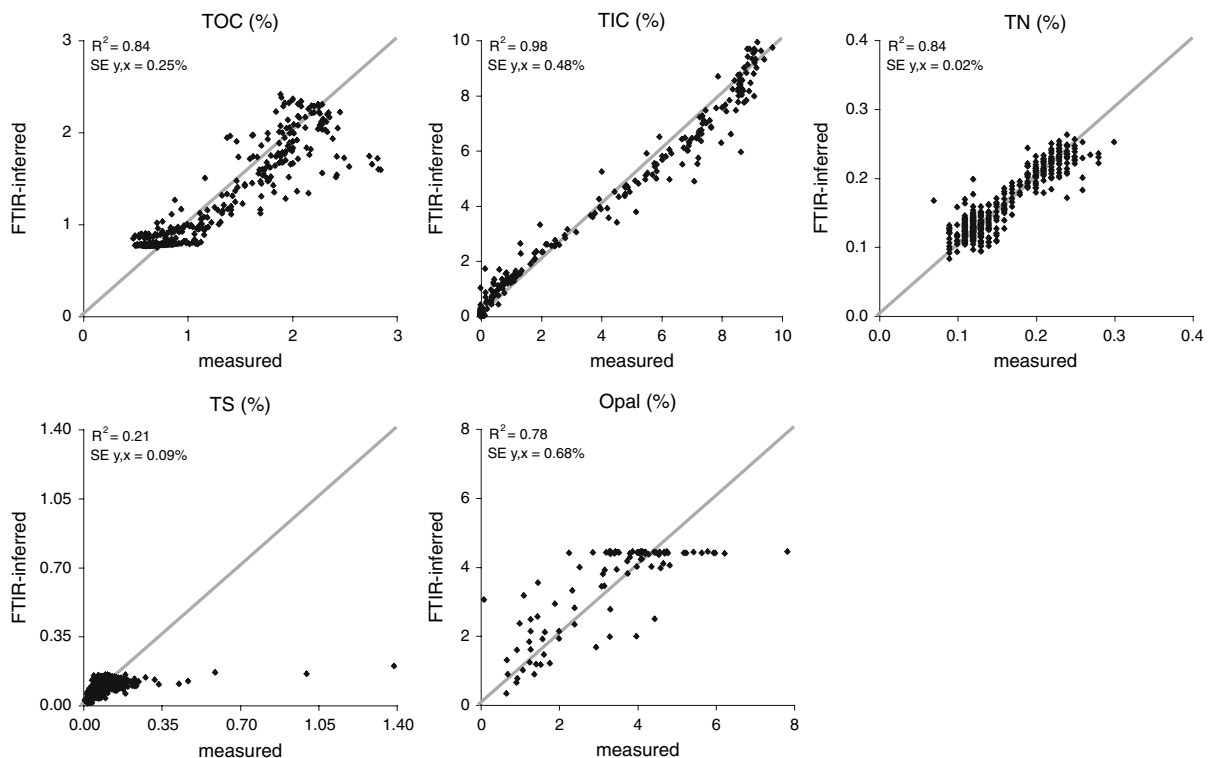


Fig. 7 Scatter plots of conventionally-measured (x-axis) versus FTIRS-inferred (y-axis) TOC, TIC, TN, TS, and opal concentrations for core Lz1120

show good statistical performance (Figs. 6, 7). Correspondingly, the $SE_{y,x}$ is low for TOC (0.25%, 10.48% of the gradient), TN (0.020%, 8.63% of the gradient), opal (0.68%, 8.78% of the gradient), and especially low for FTIRS-inferred TIC (0.48%, 4.96% of the gradient) concentrations. The small difference between conventionally-measured property concentrations and FTIRS-inferred concentrations for TOC, TN, and opal is probably related to the indirect relationship established by the models. The carbonates show strong absorbance in the MIR region and the concentration is highly variable in Lake Ohrid. Therefore it can be difficult to make independent models for TOC, TN, and opal from the Lz1120 core. The detection limit for FTIRS-inferred opal as seen in Fig. 7 is likely due to the dependency of the model on the carbonate concentration. The TS calibration model ($R^2 = 0.21$) shows rather poor statistical performance and can thus not be used for predictions. Possible reasons for the poor predictability of TS is its low concentration in most samples, the large gradient combined with only very few high values (Figs. 6, 7),

and the indirect relationships based on the carbonate-specific wavenumbers used by the model.

Advantages of FTIRS compared to conventional analytical techniques

This study demonstrates that reliable FTIRS calibrations for TOC, TIC, TN, and opal can be established and might be applied in high-resolution studies of lake sediments. FTIRS calibrations for TS could not be established due to the low concentrations of this property for cores from Lakes El'gygytyn and Ohrid, however the establishment of TS FTIRS calibrations might be possible for sediment sequences containing higher amounts of TS.

Due to simultaneous analysis of several biogeochemical properties and negligible sample pre-treatments, FTIRS is significantly faster and costs are distinctly lower (both by factors of about three) compared to conventional methods. A limiting factor of the method is that FTIRS calibration models need

to cover the whole gradient of the relevant property concentration. Thus calibration models developed for a certain sediment sequence can only be applied to sediment sequences in which the composition of the properties of interest is within the same range.

FTIR spectra contain information on minerals and thus calibration models relating the spectral information and absolute concentrations of minerals can also be established and applied as a tool for quantitative analysis. The approach of using FTIR spectra for the quantitative determination of crystallized and amorphous silicate (Bertaux et al. 1996; Wirth et al. 2001) as well as carbonate minerals (Mecozzi et al. 2001) has been demonstrated in earlier studies.

A significant advantage of FTIRS compared to conventional analytical methods is the fact that FTIRS provides information on mineralogical as well as organic components in lake sediments, which enables fast overviews of sediment composition without incorporating numerous analytical techniques and sample pretreatments. Given the current knowledge about FTIRS, low-resolution data from conventional analytical methods should always be used to verify the FTIRS-inferred results. Future research will include a large number of lakes with varying sediment properties to make more specific models with selected wavenumbers for different sediment properties.

Conclusions

This study demonstrates that FTIR-spectra in the MIR region can be used to reconstruct quantitatively TOC, TIC, TN, and opal in sediments from lakes El'gygytyn and Ohrid. Calibration models relating FTIR spectra to the concentrations of TOC, TN, and opal in sediments from Lake El'gygytyn showed good statistical performance. The most important wavenumbers used by the calibration model correspond well to known molecular vibrations of molecules indicative of the predicted biogeochemical properties. In sediments from Lake Ohrid, calibration models relating FTIR spectra to the concentrations of TOC, TIC, TN, and opal show good statistical performance, however the models for Lake Ohrid are predominantly dependent on the carbonate concentrations since all calibration models are based on known absorbance bands for carbonate. Hence, the

spectral regions used by the calibration models differ greatly for both lakes depending on the sediment characteristics. Statistical performances for TS calibration models could not reproduce results from conventional methods.

Furthermore it was demonstrated that FTIR spectra contain information on mineralogical as well as organic constituents in lake sediments. FTIRS is faster and costs are lower compared to conventional analytical methods, particularly when multiple sediment compounds need to be determined quantitatively. The amount of sample material needed for FTIRS is small (0.01 g). Therefore FTIRS can be applied in high-resolution studies of sediments or as a prescreening tool enabling a rapid determination of important sediment components. However, since calibration to the regional peculiarities and verification with conventional methods is still required at present, FTIRS cannot yet entirely replace conventional analytical tools in paleolimnology.

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