

Fourier transform infrared spectroscopy, a new method for rapid determination of total organic and inorganic carbon and biogenic silica concentration in lake sediments

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Abstract We demonstrate the use of Fourier transform infrared spectroscopy (FTIRS) to make quantitative measures of total organic carbon (TOC), total inorganic carbon (TIC) and biogenic silica (BSi) concentrations in sediment. FTIRS is a fast and cost-effective technique and only small sediment samples are needed (0.01 g). Statistically significant models were developed using sediment samples from northern Sweden and were applied to sediment records from

Sweden, northeast Siberia and Macedonia. The correlation between FTIRS-inferred values and amounts of biogeochemical constituents assessed conventionally varied between $r = 0.84$ – 0.99 for TOC, $r = 0.85$ – 0.99 for TIC, and $r = 0.68$ – 0.94 for BSi. Because FTIR spectra contain information on a large number of both inorganic and organic components, there is great potential for FTIRS to become an important tool in paleolimnology.

Keywords Fourier transform infrared spectroscopy · FTIRS · Biogeochemistry · Biogenic silica · Carbon · Paleolimnology · IR spectroscopy

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Introduction

Lake sediments are useful archives for studies of past climatic and environmental changes (Battarbee 2000). For a robust interpretation of paleolimnological data it is important to use a multiproxy approach because each technique has advantages and limitations. Some analyses require large sample sizes, which can make multiproxy investigations difficult, especially high-resolution studies in which only small amounts of sediment are available. Furthermore, some lakes contain several hundred meters of sediment, including Lake Baikal (Peck et al. 1994; Colman et al. 1995; Williams et al. 1997), Lake Tanganyika (Cohen et al.

1993), Lake Biwa (Fuji 1988), Lake El'gygytyn (Niessen et al. 2007; Gebhardt et al. 2006), and Lake Ohrid (Krstel personal communication), which would require analysis of very large numbers of individual samples. As a consequence, multiproxy studies in paleolimnology can be both time consuming and expensive.

Fourier transform infrared spectroscopy (FTIRS) allows detailed structural and compositional analysis of both organic and inorganic compounds using only small samples (0.01 g). The basic principle of the FTIRS technique is that infrared radiation excites vibrations in molecules and as a consequence of the quantum mechanical behaviour this radiation is absorbed at specific wavelengths. Because molecules and minerals have unique chemical compositions and structures, they display unique infrared spectra. FTIR spectra of sediment consist of spectral signatures from all the sediment compounds and are the sum of the characteristic infrared (IR) "fingerprints" of each compound present. FTIRS has been applied to sediment for analysis of silica and other minerals (Sifeddine et al. 1994; Bertaux et al. 1996; Wirmann and Bertaux 2001; Mecozzi et al. 2001) and for assessment of tree-line changes and TOC in lake water (Rosén and Persson 2006). FTIRS has also been used to characterize humic materials (Braguglia et al. 1995; Belzile et al. 1997; Calace et al. 1999; Mecozzi and Pietrantonio 2006), and for the quantitative determination of sodium carbonate (Na_2CO_3). Vogel et al. (2008) demonstrated the potential to use FTIRS to assess quantitatively the TOC, TIC, TON and BSi content in long sediment records from Lake El'gygytyn (Siberia) and Lake Ohrid (Macedonia), using internal calibration sets. However, these models were only applied to these specific lakes.

The aim of this study is to assess the generality of FTIRS models to assess quantitatively total organic carbon (TOC), total inorganic carbon (TIC) and biogenic silica (BSi) in sediment from lakes in very different settings. Calibration sets from northern Sweden are applied to a 350-kyr sediment sequence from Lake El'gygytyn, and to a 40-kyr sediment sequence from Lake Ohrid, as well as to more recent records from northern Sweden. To validate the FTIRS method, results are compared to concentrations measured by previously established traditional methods.

Materials and methods

Study area

A calibration set of 94 lakes from northern Sweden ($67^{\circ}07'–68^{\circ}48'N$) was used to assess the correlation between FTIR spectra of lake sediment and total organic matter ($\text{LOI}_{550^{\circ}\text{C}}$) and biogenic silica (BSi) concentration of lake sediments. The surface sediment from the calibration set has $\text{LOI}_{550^{\circ}\text{C}}$ values between 3 and 87% and BSi concentrations varying between 2 and 61% of dry weight (dw). The range in altitude is from 170 to 1,180 m above sea level (a.s.l.), annual precipitation varies from 300 to 1,900 mm/year, and mean July air temperatures vary from 7 to 14.7°C (Bigler and Hall 2002). Correlation between the $\text{LOI}_{550^{\circ}\text{C}}$ and BSi is $r = 0.32$ for the surface sediment calibration set. The lakes are mainly small (<20 ha) headwater lakes situated on similar bedrock (mainly granite and gneiss), with maximum depths ranging from 1.5 to 16 m. All lakes are from an area with low human impact.

Due to low content of TIC in the 94-lake calibration set, 55 Holocene sediment samples from Lake Badsjön, northern Sweden were used to assess the relationship between FTIR spectra and $\text{LOI}_{950^{\circ}\text{C}}$, from which TIC was calculated. Lake Badsjön is situated in the sub-alpine birch forest, 400 m a.s.l., with a maximum depth of 2.3 m (Table 1). To compare the $\text{LOI}_{950^{\circ}\text{C}}$ values with measured TIC from downcore samples, all $\text{LOI}_{950^{\circ}\text{C}}$ values were transformed to TIC using the equation:

$$\text{TIC} (\%) = \text{LOI}_{950^{\circ}\text{C}} * (12/44) \quad (1)$$

where 44 is the molecular weight for the carbon dioxide coming from carbonate, and 12 is the atomic weight for C (Bengtsson and Enell 1986; Heiri et al. 2001). The TIC concentration of Lake Badsjön's sediment varies between 0 and 11% of dry weight.

To test the FTIRS models, sediment archives from the Swedish lakes Sotaure, Lundsjön, Seukokjaure, Vuolep Njakajaure, Makkasjön and Inre Harrsjön (unofficial names) were used (Table 1). To test if the FTIRS models also are applicable to large lakes outside the region of the calibration set, sediment from the Siberian Lake El'gygytyn and Macedonian Lake Ohrid were used. A lake from the calibration set Lake C57 (unofficial name) was used to show FTIR spectra

Table 1 Location and environmental characteristics of the study lakes

Variables	94-lake cal. set	Badstjörn	Sotaure	Sweden		Vuolep Njakajaure	Makkasjön	Inre Harsjön	Siberia El'gygytgyn	Macedonia Ohrid
				Lundsjön	Seukok- jaure					
Latitude (°N)	67°07'– 68°48'N	68°20'N	66°43'N	66°42'N	67°46'N	68°20'N	66°43'N	68°21'N	67°30'N	41°01'N
Longitude (°E)	23°52'– 17°48'E	18°45'E	20°36'E	20°36'E	17°31'E	18°45'E	20°35'E	19°03'E	172°05'E	20°43'E
Altitude (m a.s.l.)	170–1,180	400	425	425	670	408	415	351	492	693
Lake area (ha)	<20	0.4	2	3	11	13	3	2	29 300	35 800
Catchment vegetation	Boreal to alpine	Subalpine birch forest	Boreal forest	Boreal forest	Alpine	Subalpine birch forest	Boreal forest	Permafrost/mire/ subarctic	Alpine/ permafrost	Mediterranean, anthropogenic
Bedrock	Mainly granite, gneiss	Hard shales/ dolomite	Granite	Granite	Granite/ syenite	Hard shales/ dolomite	Granite	Dolomite/ Sandstone	Volcanic rocks	Limestone/ metamorphites/ ultramafites
Maximum depth (m)	<16	2.3	9	8	6.1	13.7	15	5	175	280
Sediment core length (m)	Surface sed.	3.5	0.7	1.2	1.8	3.2	1.2	0.25	16.5	10.8
Sampling year	1997–1998	2006	2003	2003	2006	2005	1995	2005	2003	2005

from sediment without diatoms preserved. The Swedish test lakes were all small headwater lakes (2–13 ha) situated in the same region as the calibration set, with a maximum lake water depth of 4.5–15 m. Lake El'gygytyn is 175 m deep and 29,300 ha in size and Lake Ohrid is 280 m deep and 35,800 ha in size. For further details about Sotaure, Lundsjön and Makkasjön see Rosén and Hammarlund (2007), for Seukokjaure see Rosén and Persson (2006), for Vuolep Njakajaure see Barnekow (2000), for Lake Inre Harrsjön see Karlsson et al. (submitted) and for Lake El'gygytyn and Lake Ohrid see Vogel et al. (2008).

Field and laboratory methods

Surface sediment samples (0–1 cm) from 94 lakes were sampled during the summers in 1997–1998 from the deepest part of the lakes using a gravity corer (Renberg 1991). Sediment cores from Swedish lakes were taken from the deepest part of the lakes (Table 1) using a Russian peat corer. Surface sediment cores were taken using a gravity corer or a freeze corer (Inre Harrsjön). The sediments from Lake El'gygytyn and Lake Ohrid were taken using a gravity corer (Uwitec Ltd., Austria) for the uppermost sediments and several successive percussion piston cores (Uwitec Ltd., Austria) of up to 3 m length for the deeper sediments.

Prior to FTIRS analysis, all calibration samples and samples used to test the models were freeze-dried, ground and mixed with oven dried (80°C) potassium bromide (KBr), which is transparent in the IR region. All samples from Sweden were ground by hand. The samples from Lake El'gygytyn and Lake Ohrid were ground to a particle size <63 µm using a planetary mill. The weight ratio between sediment and KBr (0.02) was chosen to avoid very high absorbances (>2), which results in low intensities of IR light reaching the detector, and thus produces noisy data and possibly spectral distortions (Herbert et al. 1992). Samples were analyzed by diffuse reflectance FTIRS under vacuum (4 mbar) conditions, using an FTIR spectrometer (Bruker IFS 66v/S) equipped with a diffuse reflectance accessory (Harrick Inc.). Each sample was scanned 64 times at a resolution of 2 cm⁻¹ for wavelengths between 2,666 and 25,000 nm, or from 3,750 and 400 cm⁻¹ (reciprocal centimetres) yielding 1,735 data points per sample. To avoid variations in measurement

conditions caused by temperature, all samples were placed in the same temperature-controlled laboratory (25 ± 0.2°C) as the FTIRS device for at least 5 h prior to analysis.

For comparative purposes, reference spectra of biogenic silica were also obtained by FTIR microspectroscopy on single diatom frustules in sediment samples from Lake El'gygytyn and a lake (Lake C98-57, unofficial name) in the 94-lake calibration set. These spectra were recorded on a Bruker Equinox 55 spectrometer equipped with a microscopy accessory and a 64 × 64 focal plane array (FPA) detector (Hyperion 3000), providing a maximum spatial resolution of approximately 5 µm at about 4,000 cm⁻¹. Visual photographs for spectral overlay were snapshots of live images taken with a Sony Exwave HAD color digital video camera mounted on the top of the microscope. The sample tray was boxed and the chamber was continuously purged with dry air. The samples were applied onto polished rectangular BaF₂ windows. Spectra were recorded in transmission mode over the range of 850 to 3,850 cm⁻¹ with a spectral resolution of 4 cm⁻¹. The detector system has a cut-off at 850 cm⁻¹ hence the spectra quality from the microscopy technique is low below 1,000 cm⁻¹ and should not be interpreted. Also, the quality above 3,000 cm⁻¹ is comparatively poor and of limited value. For each image, 100 interferograms were co-added to obtain high signal to noise ratios. Background spectra were recorded for each sample at a nearby empty spot on the BaF₂ crystal, prior to sample measurement, with the same number of scans.

Total organic carbon and inorganic carbon were analysed by LOI_{550°C} and LOI_{950°C}, respectively, using standard methods (Heiri et al. 2001). For Makkasjön, total elemental carbon content was measured using a Costech Instruments ECS 4010 elemental analyzer (Rosén and Hammarlund 2007). As the lake is situated on granite and has a pH of ~6, we assumed that the sediment does not contain carbonates and that the TC results from Makkasjön reflect total organic carbon (TOC). The accuracy is within ± 5% of the reported values based on replicate analyses of standard material. The FTIRS-inferred LOI_{550°C} values for Makkasjön were transformed to TOC using the equation:

$$\text{TOC (\%)} = \text{LOI}_{550^\circ\text{C}} * 12/30 \quad (2)$$

assuming an average atomic ratio of CH₂O for the sediment organic matter. The atomic weight for

carbon is 12 and the molecular weight for CH₂O is 30. For Lake El'gygytgyn and Lake Ohrid, concentrations of total carbon (TC) 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. Biogenic silica (BSi) in N Sweden samples (surface and long core) was measured using Na₂CO₃ according to the DeMaster (1981) method, as modified by Conley and Schelske (2001). BSi from Lake Ohrid and Lake El'gygytgyn was digested using NaOH according to the method described by Müller and Schneider (1993). Comparable BSi concentrations are obtained using the different methods (Conley 1998). Unfortunately we do not have a quantitative estimate of the relative abundance of diatoms and other contributors to BSi such as sponge spicules, but our experience is that diatoms generally form the major part of BSi visible in microscope slides from the study region (Wagner et al. 2008; unpublished data).

Numerical analyses

FTIR spectra were normalized using baseline correction and multiple scatter correction (MSC) to get the same baseline for all spectra, independent of measurement conditions. Baseline correction performs a linear correction of the spectra so that two points (3,750 and 2,210–2,200 cm⁻¹) equals zero. MSC removes spectral variation arising from different effective path lengths and particle sizes (Geladi et al. 1985; Martens and Næs 1989; Geladi and Dåbakk 1999). The aim of the method is to remove variation in spectra caused by between-sample variations to linearize spectra and eliminate variation caused by noise. Remaining variation should contain solely chemical information about the samples.

Partial least square regression (PLS) (e.g. Martens and Næs 1989) was used to develop a transfer function between FTIRS spectra of the sediment and measured values of LOI₅₅₀, LOI₉₅₀ and BSi. To normalize the data, all LOI₉₅₀ values were square root-transformed and all BSi values were log₁₀-transformed prior to analysis. The number of significant components in PLS was assessed by cross-validation (CV) with ten groups, e.g. 10% of the calibration lakes were used as a

prediction set and the model was built on the remaining 90% of the lakes. This was repeated a total of 10 times as each group, in turn, was set aside. Root mean squared error of cross validation (RMSECV) was used as an estimate of prediction error. RMSECV was calculated as:

$$\text{RMSECV} = \frac{1}{I} \sqrt{\frac{\sum_{i=1}^I (y_i - \hat{y}_i)^2}{\sum_{i=1}^I (y_i - \bar{y})^2}} \quad (3)$$

where I is the number of lakes, y_i is the measured TOC for lake i , \bar{y} is the mean TOC for all lakes and \hat{y}_i is the predicted TOC. SIMCA-P 10.0 (Umetrics AB, SE-907 19 Umeå, Sweden) was used for all multivariate data analysis.

Results and discussion

The results clearly show that FTIR-spectra contain information on TOC (LOI_{550°C}), TIC (LOI_{950°C}), and biogenic silica (BSi) concentrations and can be used to determine the quantitative concentrations of these compounds in lake sediment.

Statistical performance and spectral information for the FTIRS/LOI_{550°C} model

The 94-lake calibration set shows a statistically significant correlation between FTIRS and the corresponding LOI_{550°C} values of lake sediment. A 4-component PLS model gives an $R_{cv}^2 = 0.83$ and a RMSECV of 6.5% (Table 2). The PLS component 1 (PLSC1) model shows strong positive loading values in the region 1,050–1,750, 2,800–3,000 cm⁻¹ indicating a positive correlation with LOI_{550°C}. The spectral regions between 400–1,000 and 3,500–3,700 cm⁻¹ showed strong negative loading values, indicating negative correlation with LOI_{550°C} (Fig. 1b).

The results are supported by spectra from sediment with high organic carbon concentration, which also shows high absorbance values between 1,050–1,750 and 2,800–3,000 cm⁻¹ and low absorbance between 3,500–3,700 and 500–1,000 cm⁻¹ (Fig. 1a) as well as loading values reported by Vogel et al. (2008). These findings also correspond well with known absorption bands for organic compounds. For example, peaks centered around 1,125 cm⁻¹ may originate from –C–O–C vibrations of complex carbohydrates and the

Table 2 Statistical performance of the calibration models for Loss-on-ignition 550°C (LOI_{550°C}), total inorganic carbon (TIC) and biogenic silica (BSi)

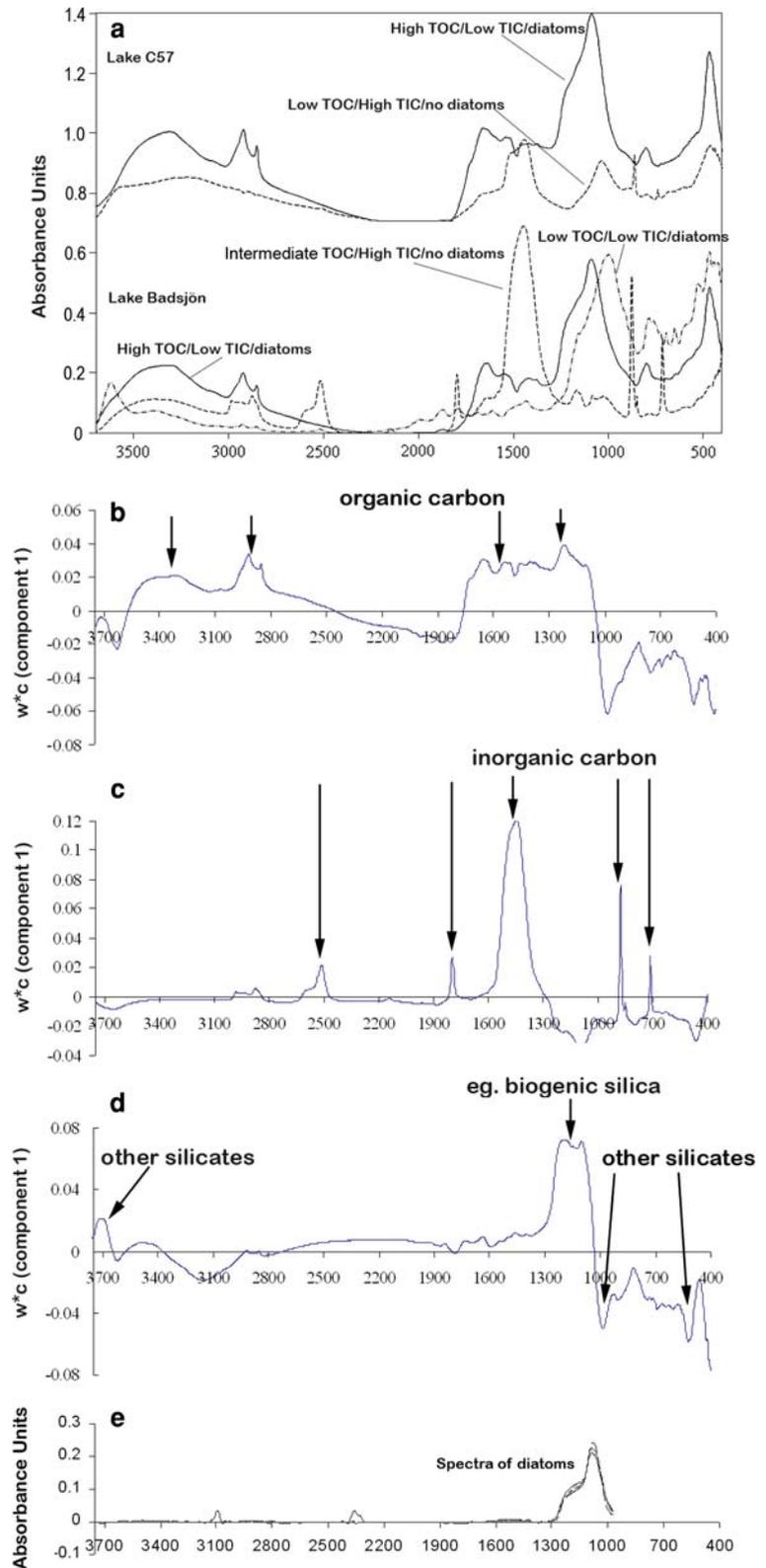
Statistics	LOI _{550°C}		TIC (%)		BSi (%)	
	All WL	Selected WL	All WL	Selected WL	All WL	Selected WL
PLS components	4	1	4	4	3	1
Samples (<i>n</i>)	94	94	54	54	94	94
Minimum	3	3	0	0	2	2
Maximum	87	87	11	11	61	61
Mean	42	42	3.0	3.0	23	23
RMSECV	6.5	8.9	0.5	0.5	7.1	7.9
RMSECV (% gradient)	7.7	11	5	5	12	13
R_{cv}^2	0.83	0.71	0.96	0.95	0.65	0.64
WL included (cm ⁻¹)	400–3,750	400–680; 740–840, 900–1,280; 1,570–1,770; 1,830–2,420; 2,650–3,750	400–3,750	700–725; 860–890; 1,300–1,560; 1,780–1,810; 2,460–2,640	400–3,750	1,050–1,250
Type of sediment	Surface sediment		Holocene core samples from Lake Badsjön		Surface sediment	
Transformation of sediment properties	No	No	lg-10(y)	lg-10(y)	Sqrt(y)	Sqrt(y)

WL Wavelengths

spectral band centered around 1,250 cm⁻¹ may arise from –C–O stretching modes (Mecozzi and Pietrantonio 2006). Proteins display strong bands in the region 1,500–1,700 cm⁻¹, the so-called amide I and amide II vibrations, and these partly overlap with peaks around 1,650 cm⁻¹ originating from –C–O stretching vibrations in carboxyl groups common in humic substances (Calace et al. 1999; Mecozzi and Pietrantonio 2006). Bands centered on 1,715 cm⁻¹ are assigned to the stretching vibration of the –C=O group of fatty acids (Mecozzi and Pietrantonio 2006). Carbonates can also absorb in the 1,600–1,800 cm⁻¹ region, but because carbonates are almost totally absent in the 94-lake calibration set, we assume that humic compounds are more important. The band between 2,850 and 2,950 is due to C–H vibrations in –CH₃, –CH₂ and –CH groups of organic compounds. The regions 400–1,000 and 3,500–3,700 cm⁻¹, which exhibit negative correlation with LOI_{550°C}, correspond well with SiO and –OH molecular vibrations in silicates (Farmer 1974; Kellner et al. 1998). Because the LOI_{550°C} contains information on the relative proportions of organic and minerogenic matter in the sediment, the model

should perform best if spectral bands for both organic and minerogenic compounds are included. However, due to strong absorption bands for CaCO₃ in the FTIR spectra, these bands need to be excluded when the FTIR/LOI_{550°C} model is applied to carbonate-rich sediment. The statistical performance of the FTIR/LOI_{550°C} model, excluding carbonate-specific wave numbers was still good, showing an $R_{cv}^2 = 0.71^*$ and a RMSECV of 11% (Table 2). This specific model exhibits slightly reduced statistical performance than the model including all wave numbers. This is probably due to the fact that we excluded a wide range of wave numbers around the CaCO₃ peaks to make sure that no information on CaCO₃ interferes with the FTIR/LOI_{550°C} model. This means that information on organic and inorganic compounds important for the FTIR/LOI_{550°C} also was excluded. For example, stretching vibration of the –C=O group of fatty acids (1,715 cm⁻¹) absorbs in the same region as carbonates (1,800 cm⁻¹). The model, with the bands for carbonate excluded, should be used only when the FTIR/LOI_{550°C} model is applied to carbonate-rich sediment.

Fig. 1 **a** Examples of FTIR spectra from sediment samples with different concentrations of organic carbon, inorganic carbon and diatom BSi. Spectra are from Lake Badsjön and Lake C57. **b–d** Loading plots showing the FTIRS-spectral regions contributing to the PLS regression model for total organic carbon (TOC), total inorganic carbon (TIC) and biogenic silica (BSi, opal). Positive values indicate wave numbers positively correlated to the *Y* variable and negative values indicate wave numbers negatively correlated to the *Y* variable. Loadings refer to the weight vectors (w^*c) in the PLS model (component 1) (*y*-axis) and the corresponding spectral region (*x*-axis). Arrows indicate important regions for organic carbon (**b**), inorganic carbon (**c**) and silicates (**d**). **e** FTIR spectra from both benthic and planktonic diatoms using the FTIRS microscope technique. The diatoms come both from Siberian Lake El'gygytyn and Swedish Lake C98-54. The spectra quality from the microscope technique is poor below 1,000 cm^{-1} and above 3,000 cm^{-1} and should not be interpreted



Model performance and spectral information for the FTIRS–TIC model

To establish a FTIRS/TIC model, a Holocene sediment record from Lake Badsjön (Table 1), which contains sediment of both high and low carbonate content, was used. A 4-component PLS model showed a strong correlation between FTIR spectra and TIC concentration using all wavelengths and 55 samples from Lake Badsjön. The statistical performance of the model had an $R_{cv}^2 = 0.96$ and RMSECV = 0.5% (Table 2). High absorbance values for carbonate-rich sediment were centered around 700–725; 860–890; 1,300–1,560; 1,780–1,810 and 2,460–2,640 cm^{-1} (Fig. 1a), which corresponds well with strong positive loading values in the PLSC1 model for TIC (Fig. 1c) and the most important wave numbers for carbonate in sediment reported by Vogel et al. (2008). Carbonate in calcite minerals has in previous investigations shown important C–O molecular vibrations around 710, 875, 1,425, 1,460, 1,800 and 2,500 cm^{-1} (White 1974; Gaffey 1986; Mecozzi and Pietrantonio 2006). In a 4-component PLS model, in which only wave numbers from calcite minerals were included, the statistical performance remained high, with $R_{cv}^2 = 0.95$ and RMSEP = 0.5% (Table 2).

Model performance and spectral information for the FTIRS–BSi model

The 94-lake calibration set shows a statistically significant correlation between BSi concentration of lake sediment and the corresponding FTIR spectra. A 3-component PLS model gives an $R_{cv}^2 = 0.65$ and RMSECV = 7.1 (dw %) (Table 2).

Strong positive loading values in the PLSC1 model are shown in the region 1,050–1,250 cm^{-1} (Fig. 1d) and correspond well with the characteristic SiO absorbance maximum for BSi at 1,100 cm^{-1} (Moenke 1974; Gendron-Badou et al. 2003; Stehfest et al. 2005), and with loading values reported by Vogel et al. (2008). Sediment with no diatoms preserved shows low absorbance values between 1,050 and 1,250 cm^{-1} , while sediment with high diatom concentration shows high absorbance values in the same region (Fig. 1a). Further SiO molecular vibrations are responsible for most of the absorbance occurring between 400 and 1,000 cm^{-1} with characteristic peaks centered around 480, 540, 600, 650, 800,

920 cm^{-1} . Fossil marine diatom frustules have four characteristic bands. Two main bands at 1,100 and 471 cm^{-1} are attributed to triply-degenerated, stretching and bending, vibration modes of the $[\text{SiO}_4]$ tetrahedron, respectively (Gendron-Badou et al. 2003). The band at 800 cm^{-1} corresponds to an inter-tetrahedral Si–O–Si bending vibration mode, and the band near 945 cm^{-1} to a Si–OH mode present in marine-produced BSi (Rickert et al. 2002). However, strong negative loading values for all wave numbers between 400 and 1,000 cm^{-1} (Fig. 1d) indicate that these bands may not be specific to BSi produced in lakes, but also to other silicates. Other studies have used the bands around 470 and 3,615 cm^{-1} as an estimate for BSi (Mecozzi and Pietrantonio 2006). Our study indicates that the region centered around 3,600 cm^{-1} is not important for BSi because only moderate positive loading values were observed for that region and FTIR spectra from very minerogenic sediment show a clear absorbance peak centered on 3,600 cm^{-1} even though the sample has low BSi concentration (Fig. 1a,d). The results indicate that the region near 3,600 cm^{-1} should not be used to estimate BSi in lake sediment. This region is generally assigned to OH molecular vibrations (Farmer 1974; Kellner et al. 1998; Mecozzi and Pietrantonio 2006) and hydroxyl ions are common in both clay minerals and BSi.

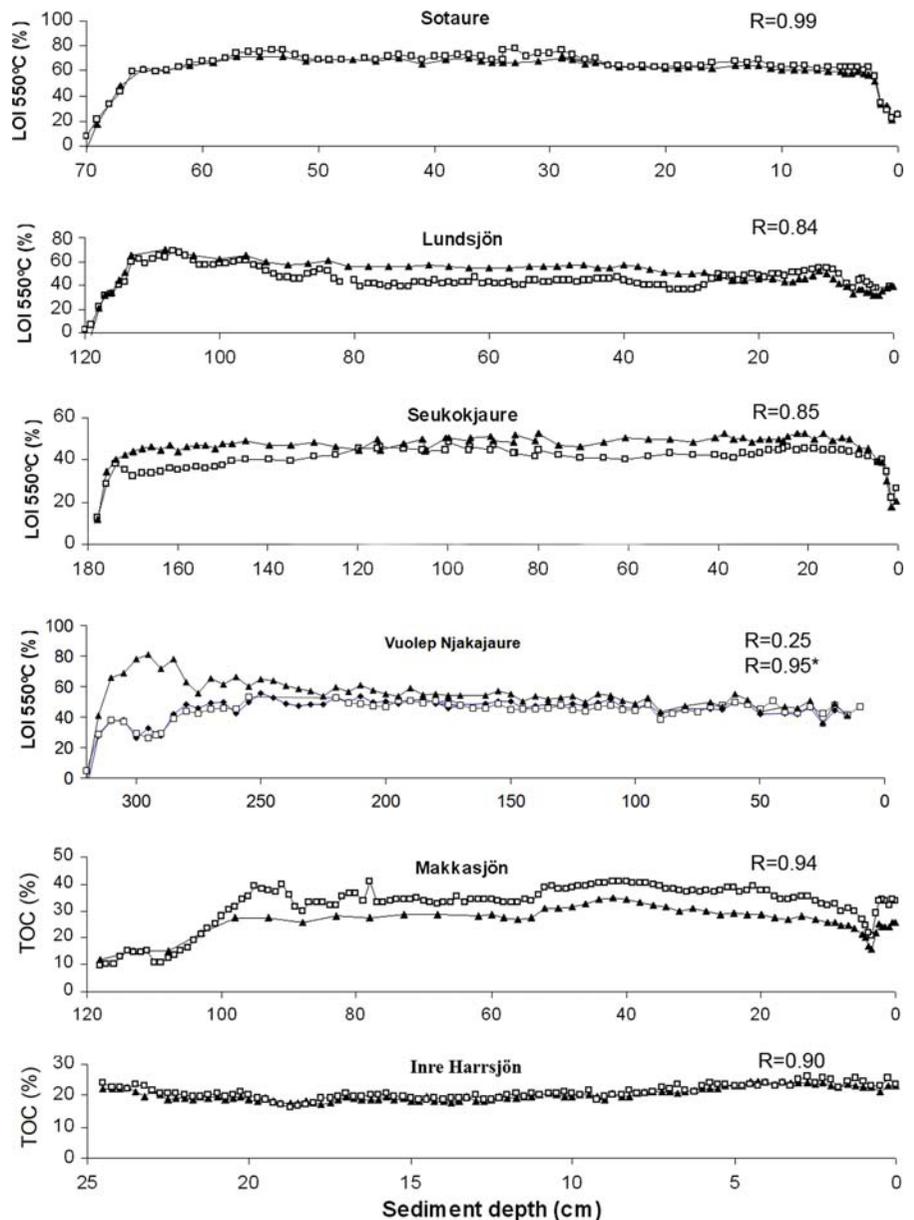
Our measurements are supported by direct FTIRS measurements using the microspectroscopy technique on individual diatom valves, which clearly showed that diatoms (BSi) absorb in the region 1,050–1,250 cm^{-1} . Spectra were very similar for both benthic (*Navicula* sp.) and planktonic species (*Cyclotella* sp.) (Fig. 1e). Based on these findings, a more specific FTIRS/BSi model was also developed in which only the band 1,050–1,250 cm^{-1} was included. The model showed similar statistical performance and a 1-component PLS model gave an $R_{cv}^2 = 0.64$ and RMSECV = 7.9 (dw %) (Table 2). The reason why the statistical performance did not improve when only the 1,050–1,250 cm^{-1} region was included in the model is probably due to the fact that BSi values are expressed as percent of total sediment dry weight. Therefore the information about other organic and inorganic compounds in the sediment can contribute to the model. Also, other organic and inorganic compounds absorbing in other regions can be correlated to BSi and improve the model.

Application of the FTIRS models to Swedish, Siberian and Macedonian sediments

The correlation between FTIRS-inferred $LOI_{550^{\circ}C}$ and conventionally measured $LOI_{550^{\circ}C}$ or TOC % varied between $r = 0.84$ (Lundsjön) and 0.99 (Inre Harrsjön) (Fig. 2). When the model was applied to carbonate sediment from Vuolep Njakajaure, the correlation was only $r = 0.25$. This is probably due to the fact that sediments from all calibration lakes have very low carbonate content. Carbonates show

very distinct absorbance peaks in the mid-infrared region. Since $-C-O$ molecular vibration can occur in both organic and inorganic carbon, carbonate-specific wave numbers should be excluded when TOC is inferred in carbonate-rich sediment. When the model that includes only carbonate-specific wave numbers was applied to Vuolep Njakajaure, the correlation between FTIRS-inferred $LOI_{550^{\circ}C}$ and conventionally measured $LOI_{550^{\circ}C}$ increased from $r = 0.25$ to $r = 0.95$. The FTIRS/ $LOI_{550^{\circ}C}$ model was not applicable to Lake El'gygytgyn and Lake Ohrid since

Fig. 2 Comparison between conventionally-measured (\square) and FTIRS-inferred loss-on-ignition (LOI_{550}) and total organic carbon (TOC) (\blacktriangle) in five Holocene sediment cores and one core covering the last ~ 300 years (Inre Harrsjön). The sediment from Vuolep Njakajaure contains a large percentage of $CaCO_3$ and is therefore an outlier in the 94-lake calibration set. We therefore present results from two FTIRS-models including all wave numbers (\blacktriangle) and a model excluding wave numbers for $CaCO_3$ (\blacklozenge). r is the correlation between conventionally-measured TOC and the FTIRS-inferred values using a model including all wave numbers and r^* the correlation to the FTIRS-inferred values using a model excluding wave numbers for $CaCO_3$



their sediments contain very low amounts of TOC (mean 0.5–1.2%), with values plotting at the lower end of the calibration set gradient (TOC range 1.2–35%), thus the FTIRS/LOI_{550°C} model was only tested on Swedish lakes. However, a previous study showed that an internal calibration model for TOC applied to Lake Ohrid and Lake El'gygytyn performed well (Vogel et al. 2008). In all calibration work, it is beneficial to have analogues in the calibration set for accurate and reliable estimates of samples (Birks 1998).

The FTIRS–TIC model was applied to sediment cores from Lake Vuolep Njakajaure and Lake Ohrid. The correlation between FTIRS-inferred TIC and conventionally measured TIC values was $r = 0.85$ for Vuolep Njakajaure and $r = 0.99$ for Lake Ohrid when all wavelengths were included (Fig. 3). When only wave numbers indicative of CaCO₃ were included in the model, the correlation was $r = 0.83$ for Vuolep Njakajaure and $r = 0.98$ for Lake Ohrid (Fig. 3). Vogel et al. (2008) presented an internal calibration for TIC from Lake Ohrid using FTIRS and the performance of their model was also very good, with an $r = 0.99$ between FTIRS-inferred TIC and TIC measured with conventional techniques. Although a strong PLS calibration model was produced for TIC, there was still a significant difference between inferred and measured values for sediment samples with high carbonate concentration from Vuolep

Njakajaure, and a general overestimation of low-TIC values in Lake Ohrid. One possible explanation is that the sediment was heterogeneous during periods of rapid change in TIC concentration and that values for FTIRS and LOI_{950°C} were not measured from the same sample. Another possible reason is that samples from Vuolep Njakajaure were ground by hand and that different particle sizes had an effect on the absorbance values in the mid-infrared region. The samples from Lake Ohrid were ground in a planetary mill to a particle size <63 μm, which might have yielded more consistent results. Future improvement of the FTIRS/TIC model might be achieved by including a larger set of lakes that display a broader range of TIC concentration, and by using samples carefully ground in a planetary mill. The FTIRS/TIC model was not applied to the other lakes due to very low concentrations of TIC in their sediment and therefore TIC was not measured conventionally.

The correlations between FTIRS-inferred BSi and conventionally measured BSi in down-core sediment samples from Sweden were $r = 0.68$ (Seukokjaure) and $r = 0.94$ (Inre Harrsjön) (Fig. 4). The FTIRS/BSi model also performed well for Macedonian Lake Ohrid ($r = 0.75$) and Siberian Lake El'gygytyn ($r = 0.86$) even though they are located far from the calibration lakes and are much larger and deeper (Table 1). The statistical performance of the results is very similar to the internal calibration

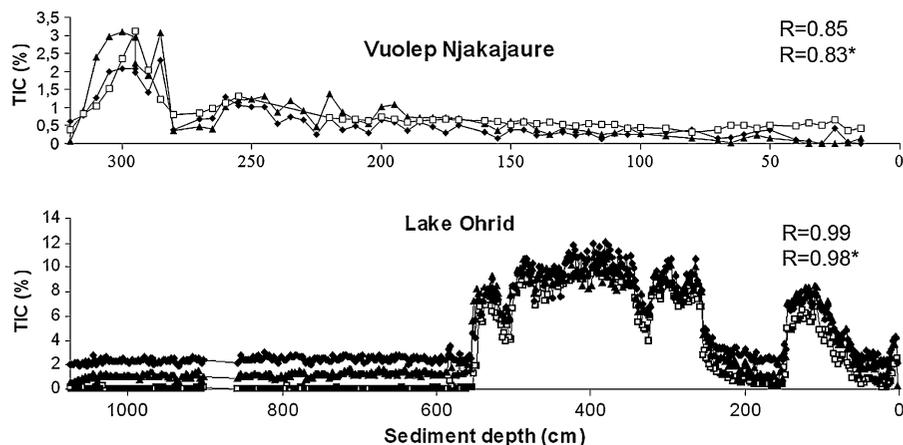


Fig. 3 Comparison between conventionally-measured (□) and FTIRS-inferred TIC in a Holocene sediment core from Vuolep Njakajaure, Sweden (9 kyrs) and Lake Ohrid, Macedonia covering the last ~40 kyrs. ▲ represent FTIRS-inferred TIC including all wave numbers and ◆ represent FTIRS-inferred

TIC including only wave numbers for CaCO₃. r is the correlation between conventionally-measured TIC and the FTIRS-inferred TIC using a model including all wave numbers and r^* the correlation to the FTIRS-inferred TIC using a model including only wave numbers for CaCO₃

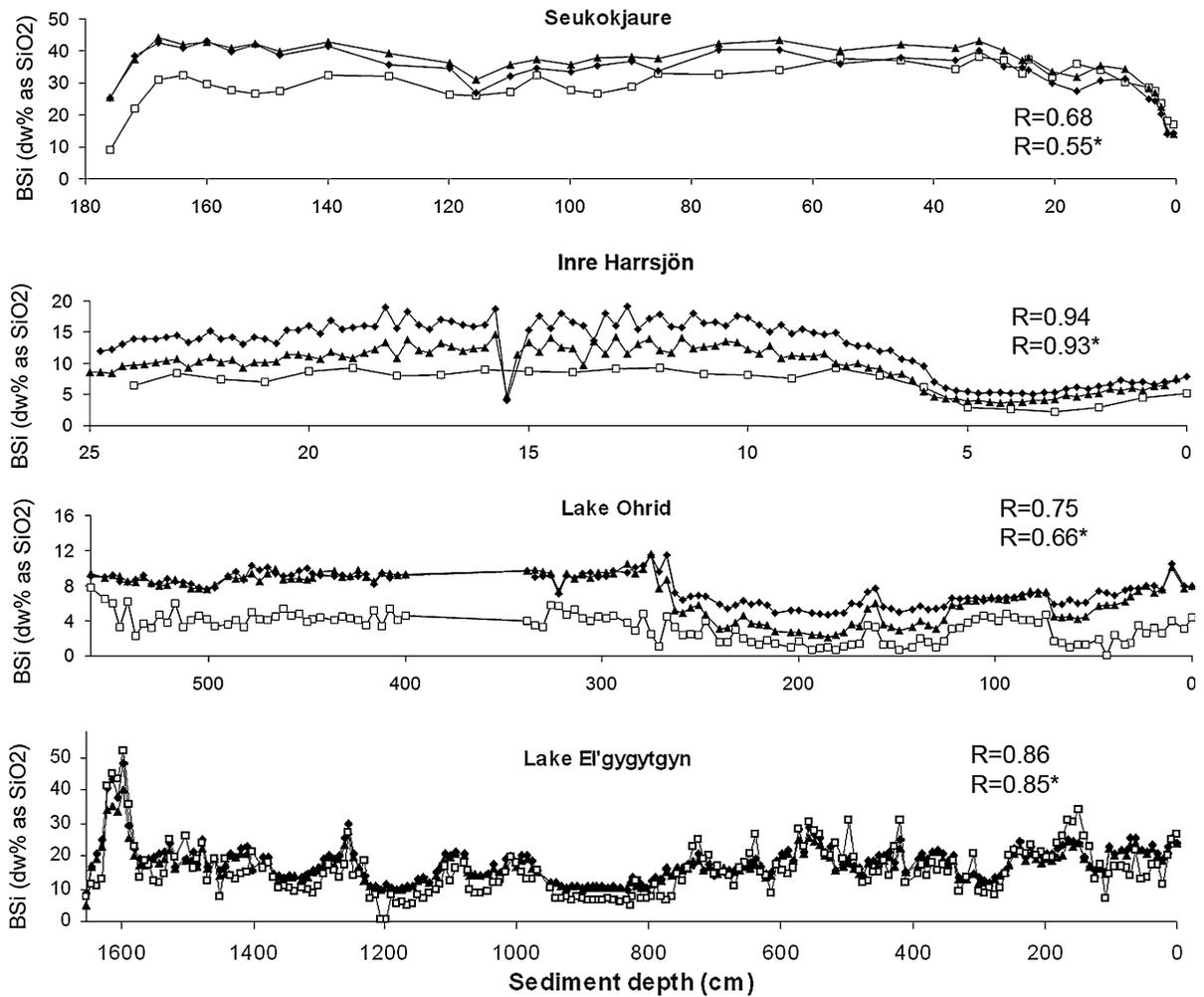


Fig. 4 Comparison between conventionally-measured (□) and FTIRS-inferred biogenic silica (BSi, opal) in a Holocene sediment core from Seukokjaure, Sweden, a core covering the last ~300 years (Inre Harrsjön), and Lake Ohrid, Macedonia covering the last ~40 kyrs and Lake El'gygytgyn, NE Siberia covering the last ~350 kyrs. ▲ represents FTIRS-inferred BSi

including all wave numbers and ◆ represents FTIRS-inferred BSi including only wave numbers for BSi (1,050–1,250 cm⁻¹). *r* is the correlation between conventionally-measured BSi and the FTIRS-inferred BSi using a model including all wave numbers and *r** the correlation to the FTIRS-inferred BSi using a model including only wave numbers for BSi

models for Lake El'gygytgyn and Lake Ohrid presented by Vogel et al. (2008). They report an *r* = 0.87 for Lake El'gygytgyn and an *r* = 0.79 for Lake Ohrid between FTIRS-inferred BSi and BSi measured with conventional techniques. Although the patterns obtained between FTIRS and conventional measurements are very similar, the FTIRS-modelled BSi is generally higher. Aquatic sediment and soils contain a broad range of material containing Si, which vary in their lability from readily dissolvable amorphous BSi to very stable,

highly-ordered crystalline structures (Conley et al. 2006). Both the FTIRS estimates and the values obtained by traditional wet chemical digestion of BSi contain uncertainties. The FTIRS estimates can be confounded by organic components absorbing in the same region as BSi. Wet chemical digestion methods that use weak base solutions to dissolve amorphous silica components of the sediment may fail to dissolve more refractory forms of amorphous silica (Saccone et al. 2007) that are detected by FTIRS.

Conclusions and future possibilities and limitations of the FTIRS technique

This paper shows that FTIRS can be used to make quantitative assessments of organic and inorganic carbon and BSi in lake sediment. A major step forward compared to the study by Vogel et al. (2008) is that a calibration model from small lakes in Sweden was applied to much larger lakes in Macedonia and Siberia and still produced reasonable results. For accurate quantitative determination of different sediment constituents, we need to have detailed knowledge about their FTIR spectra. This will enable development of robust and specific models for the compounds of interest. Statistical models include correlations between the spectra and compounds, but some compounds can have overlapping spectra. As a result, model performance can vary among lakes, depending on the mixture of components in the sediment. We therefore advise that quantitative estimation using FTIRS should be verified with conventional methods. Alternatively, an internal calibration model for each lake could be developed in which a large number of samples is analysed by both FTIRS and conventional methods for the component of interest. If good models can be developed, they can then be used to assess the component of interest in a high-resolution, rapid and cost-efficient way. Internal calibration is probably the best choice when several hundred meters of sediment are to be analysed at high resolution, such as the cases of Lakes El'gygytgyn and Ohrid (Vogel et al. 2008).

The FTIRS technique is used rarely in paleolimnological research. Results presented here and by Vogel et al. (2008), as well as the fact that the method is fast and cost-effective, requiring only small sediment samples, should encourage more paleolimnologists to use the method.

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