Universally Applicable Model for the Quantitative Determination of Lake Sediment Composition Using Fourier Transform Infrared Spectroscopy

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ABSTRACT: Fourier transform infrared spectroscopy (FTIRS) can provide detailed information on organic and minerogenic constituents of sediment records. Based on a large number of sediment samples of varying age (0−340 000 yrs) and from very diverse lake settings in Antarctica, Argentina, Canada, Macedonia/Albania, Siberia, and Sweden, we have developed universally applicable calibration models for the quantitative determination of biogenic silica (BSi; $n = 816$), total inorganic carbon (TIC; $n = 879$), and total organic carbon (TOC; $n = 3164$) using FTIRS. These models are based on the differential absorbance of infrared radiation at specific wavelengths with varying concentrations of individual parameters, due to molecular vibrations associated with each parameter. The calibration models have low prediction errors and the predicted values are highly correlated with conventionally measured values ($R = 0.94−0.99$). Robustness tests indicate the accuracy of the newly developed FTIRS calibration models is similar to that of conventional geochemical analyses. Consequently FTIRS offers a useful and rapid alternative to conventional analyses for the quantitative determination of BSi, TIC, and TOC. The rapidity, cost-effectiveness, and small sample size required enables FTIRS determination of geochemical properties to be undertaken at higher resolutions than would otherwise be possible with the same resource allocation, thus providing crucial sedimentological information for climatic and environmental reconstructions.
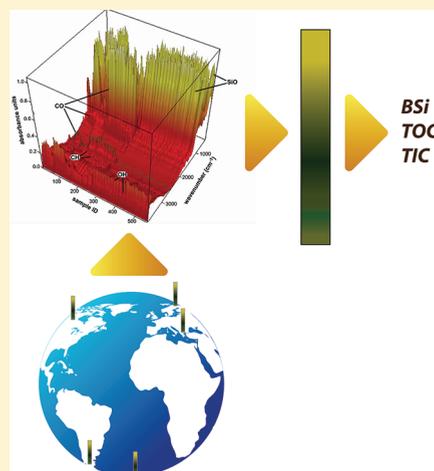
INTRODUCTION

Multiproxy approaches are often required for comprehensive paleolimnological reconstructions as information from an individual proxy indicator can be supported by a suite of other indicators thus reducing potential errors or ambiguities. Analyzing a suite of indicators is both time-consuming and expensive, particularly when assessing long sediment records.[1] In high-resolution studies, the amount of sample material available from each horizon can also be a limiting factor. Conventional measurements of biogeochemical constituents (including biogenic silica (BSi)) are laborious, time-consuming, and imprecise,[2] thus alternative approaches are required. X-ray fluorescence scanners and multisensor core loggers can provide highly resolved, qualitative and semiquantitative information on the inorganic geochemistry, mineralogy, and magnetic properties. Fourier transform infrared spectroscopy (FTIRS) analysis also offers a promising alternative to conventional techniques due to the wealth of information on minerogenic

and organic sediment constituents contained in FTIR spectra, the small sample size required, and the relative speed of analysis.[3−8]

The basic principles of FTIRS are that infrared radiation can excite molecular vibrations and, as a consequence of the quantum mechanical behavior, the radiation will be absorbed at specific energies, depending on the composition of the material examined. As most compounds display characteristic infrared spectra, changes in the organic and inorganic composition of sediments can be determined, including changes in carbohydrate, fatty acid, humic material, silicate, and carbonate concentrations.[3−5] This information is of particular interest for paleolimnological studies since sediment is commonly composed of a mixture of various

Table 1. Location and Environmental Characteristics of the Lakes Included in the FTIRS Models

variable	Pingualuit	Hoare	Potrok Aike	Ohrid	El'gygytgyn	100-lake cal. set	Badsjön	Seukok-jaure	Vuolep Njakajaure	Makkasjön	Inre Harrsjön
country/region	Canada	Antarctic	Argentina	Macedonia	Siberia	Sweden	Sweden	Sweden	Sweden	Sweden	Sweden
latitude	61°17'N	77°38'S	51°58'S	41°01'N	67°30'N	67°07'–68°48'N	68°20'N	67°46'N	68°20'N	66°43'N,	68°21'N
longitude	73°41'W	162°53'E	70°22'W	20°43'E	172°05'E	23°52'–17°48'E	18°45'E	17°31'E	18°45'E	20°35'E	19°03'E
altitude (m a.s.l.)	494	73	100	693	492	170–1180	400	670	408	415	351
lake area (ha)	668	18	774	35 800	29 300	<20	0.4	11	13	3	2
catchment vegetation	arctic tundra/ permafrost	polar desert	cold-semi desert	mediterranean, anthropogenic	arctic tundra/ permafrost	boreal to alpine	subalpine birch forest	alpine	subalpine birch forest	boreal forest	permafrostmire/ subarctic
bedrock	precambrian granitic-gneissic	granites/ metasediments	volcanic rocks/ molasse-type sediments/ until	limestone/ metasediments/ ultramafics	volcanic rocks	mainly granite, gneiss	hard shales/ dolomite	granite/syenite	hard shales/ dolomite	granite	dolomite/sandstone
max. depth (m)	246	34	101	280	175	<16	2.3	6.1	13.7	15	5
sediment core length (m)	8.5	2.3	106	10.8	16.5	surface	3.5	1.8	3.2	1.2	0.25
approx. ages (years)	0–35 000	0–12 000	0–50 000	0–130 000	0–340 000	0–20	0–10 000	0–10 000	0–10 000	0–10 000	0–300

Table 2. Number of Surface Sediment Samples and Down-Core Samples Analyzed for Each Parameter, Including the Specific Sedimentary Sequences from Which the Down-Core Samples Were Collected

sample	BSi	TIC	TOC
number of Swedish lakes with surface samples	91		100
total number of downcore samples	725	879	3064
Lake Hoare	35	122	122
Laguna Potrok Aike	193	152	162
Pingualuit	30		222
Ohrid	200	504	504
El'gygytgyn	287		1793
Inre Harrsjön	21	99	99
Badsjön		51	
Seukokjaure	36		
Vuolep Njakajaure		50	
Makkasjön			62

organic and minerogenic compounds originating from aquatic organisms, chemical in-lake processes, and the erosion of soils in the catchment area of a lake. Absorbance peaks in FTIR spectra relate directly to the concentrations of specific components within the sediment, thus many organic and minerogenic constituents can be quantified using FTIRS. Two of the great advantages of FTIRS, compared to several other methods, are the small sample sizes (10 mg of dried sediment) and negligible pretreatment required. The potential, and possible applications, of FTIRS in paleolimnological work have previously been discussed.[6−8] These studies have shown that FTIRS quantifies selected constituents using either site-specific or regional calibration models.[7,8] It remains uncertain, however, if more universally applicable FTIRS calibration models can be developed and ubiquitously applied to lakes from distinctly different settings.

This study combines a large number of samples from lakes of varying sizes and settings distributed worldwide (Antarctica, Argentina, Canada, Macedonia/Albania, Siberia, Sweden) to assess if a universally applicable FTIRS calibration model can be developed for the rapid and simultaneous quantification of total organic carbon (TOC), total inorganic carbon (TIC), and BSi. Such calibration models would significantly reduce the amount of work required for paleoclimatic and paleoenvironmental reconstructions, as calibration to specific localities[8] will be less important.

■ MATERIAL AND METHODS

Site-Related Information. The major characteristics of the study lakes are summarized in Table 1. Lake sizes range from 1 to 35 800 ha, with maximum water depth of 1.5−280 m, and sediment ages of 0−340 000 yrs BP. Further site specific information has previously been published for Lake Hoare,[9] Laguna Potrok Aike,[10,11] Pingualuit,[1] Lake Ohrid,[12] El'gygytgyn,[13] Seukokjaure,[6] Inre Harrsjön,[14] and the surface samples from northern Sweden.[6]

Analytical Methods. The number of samples included from each sampling location varied by parameter (Table 2). Furthermore, the exact method employed for the conventional geochemical analyses of TIC and TOC also varied among the sampling programs, although all were recognized "Standard Methods". For example, a CNS elemental analyzer (EuroEA, Eurovector) was used for TOC measurements of samples from Pingualuit. In contrast, the TOC content of samples from Lake Hoare was determined with a

Metalyt CS 1000S (ELTRA Corp.) analyzer, after pretreatment with 10% HCl at 80 °C to remove carbonates, while the total carbon (TC) content was measured with an Elementar III (VARIO Corp.) analyzer. The TIC content was calculated by the difference between TC and TOC. Previous publications provided more information about analytical methods used (see above). At all locations, the leaching technique was used for the BSi measurements.[15]

Prior to FTIRS analysis, samples were freeze-dried and ground. Samples from Sweden were ground by hand using an agate mortar and pestle. All the remaining samples were ground to <63 μm using either a planetary mill or a swing mill. Samples were then diluted and mixed with oven-dried (80 °C) potassium bromide (KBr; spectrograde, Fisher Scientific). The mass ratio between sediment and KBr (2%) was chosen to avoid very high absorbance (> 2), which results in low intensities of IR light reaching the detector thus producing noisy data and spectral distortions.[16] 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 and data were collected at every 2 cm^{-1} at a resolution of 4 cm^{-1} for wavenumbers between 3750 and 400 cm^{-1} (reciprocal centimeters) which is equal to wavelengths from 2666 to 25 000 nm, thus yielding 1735 data points per sample. To avoid variations 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.

Numerical Analyses. Multiple scatter correction (MSC) and baseline correction were used to linearize spectra and remove variation in spectra caused by noise.[6,17] Baseline correction performs a linear correction of the spectra so that two points (3750 and 2210−2200 cm^{-1}) equal zero. MSC removes spectral variation arising from different effective path lengths and particle sizes.[17] Partial least-squares regression (PLS) was used to develop quantitative calibration models between FTIR spectra of sediment and conventionally measured sediment properties.[18] Principal component analysis was used to assess variation in spectra intensity for specific wavenumbers. The predictive performance of the PLS calibration model was assessed by 10% cross-validation (CV). This means that the calibration model was developed using 90% of data of the calibration lakes with the remaining 10% of the lakes used to test the predictions. This process 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. SIMCA-P 11.5 (Umetrics AB, SE-907 19 Umeå, Sweden) was used for all multivariate data analyses. All primary sediment properties were square root transformed prior to analysis. For more detailed information see Rosén et al.[8] FTIRS calibrations for BSi and TOC were tested on sediments from Lake Pingualuit and the TIC calibration model was tested on Lake Hoare. The model results were compared to conventionally measured values to evaluate model performance.

RESULTS AND DISCUSSION

Spectral Information. The loading plots for BSi, TIC, and TOC show similar patterns to those reported in Rosén et al.[8] The FTIR spectra from sediment with different concentrations of BSi (Figure 1a) confirm the findings from the loading plot, namely that wavenumbers around 450, 800, and between 1050 and 1280 cm^{-1} are particularly important for the FTIRS-BSi model (Figure 2). Previous studies have shown two main bands at 1100 and
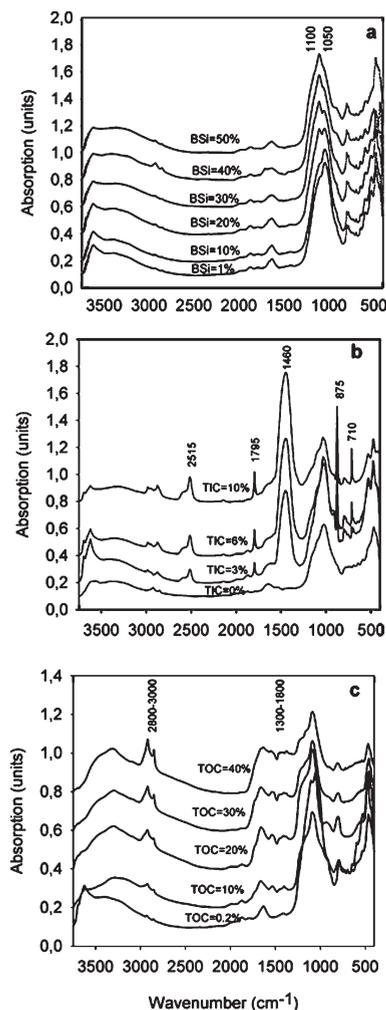

Figure 1. Examples of FTIR spectra from sediment samples with different concentrations of (a) biogenic silica (BSi) (Lake El'gygytgyn), (b) total inorganic carbon (TIC) (Lake Ohrid, Lake Hoare), and (c) total organic carbon (TOC) (Lake Makkasjön, Lake El'gygytgyn, Swedish surface sediment). For better visualization, spectra have been shifted vertically from their common baseline by adding a constant value to each spectra.

471 cm^{-1} are attributed to stretching and bending vibration modes of the SiO$_4$ tetrahedron, respectively.[20] The band at 800 cm^{-1} corresponds to an intertetrahedral Si−O−Si bending vibration mode. The band near 945 cm^{-1} corresponds to a Si−OH mode.[19] This band is not pronounced in our FTIRS-BSi model, possibly due to internal condensation reactions during silica maturation in surface sediments and formation of Si−O−Si linkages[19] which can cause changes in the intensity ratio of Si−O−Si/Si−OH. The region around 3600 should not be used for BSi estimates as samples with confirmed low BSi concentration show higher absorbance than samples high in BSi (Figure 1). A previous study[6] showed good model performance when only wavenumbers from 1050 to 1250 were included. However, as the internal structure of BSi can vary with age during crystallization and form (e.g., opal-CT), it is probably advisable to also include bands around 450 and 800 cm^{-1} in the model. This could be particularly important when FTIRS calibrations are used to assess BSi in long sediment cores where diagenetic modification of BSi is likely to increase with depth.

The loading plot indicates that wavenumbers in the ranges 700−725, 860−890, 1300−1560, 1780−1810, and 2460−2640 cm^{-1}
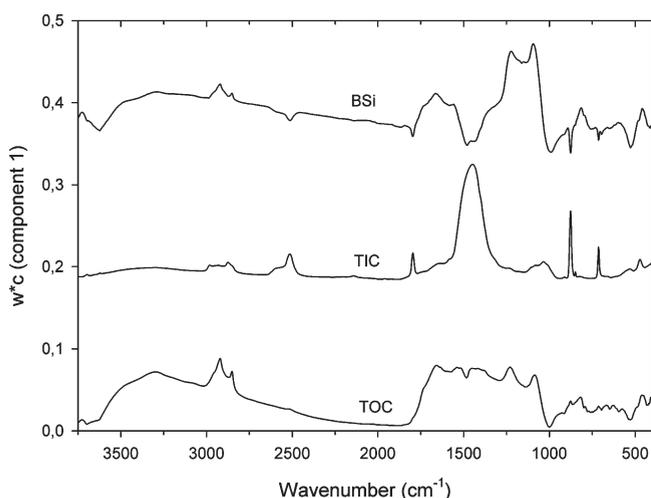
Figure 2. Loading plots showing the relative contribution of different wavenumbers to the PLS regression models for total organic carbon (TOC), total inorganic carbon (TIC), and biogenic silica (BSi). High values indicate wavenumbers are positively correlated to the Y variable and low values indicate wavenumbers are 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).

are particularly important for the FTIRS-TIC model (Figure 2). These wavenumbers correspond well to infrared bands of calcite and other carbonate minerals centered around 710, 875, 1425, 1460, 1800, and 2500 cm^{-1}.[5,21] Depending on the crystal chemistry and structure of the carbonate mineral, these wavenumbers can show slight deviations. The FTIR spectra from sediment with different concentrations of TIC confirm the findings from the loading plot (Figure 1).

The loading plots demonstrate that wavenumbers between 1050 and 1750 and 2800 and 3000 cm^{-1} are especially important for the FTIRS-TOC model (Figure 2). These spectral regions include the C−O vibrations of carbohydrates (1000−1200 cm^{-1})[5] as well as the characteristic amide I and amide II vibrations of proteins and −C−O stretching vibrations of carboxyl groups (1400−1700 cm^{-1}) which are commonly derived from humic substances.[5] Finally, absorbance in the region 2800−3000 cm^{-1} is associated with the C−H vibrations of −CH$_3$, −CH$_2$, and −CH groups of aliphatic molecules.[5]

Statistical Performance of the FTIRS-BSi Model. A 4-component PLS model using wavenumbers 400−3750 cm^{-1} has a $R_{cv} = 0.93$ and a RMSECV of 3.4% (6.2% of the gradient, gradient 0−55%, $n = 816$) (Table 3, Figure 3). Based on the loading plot (Figure 2) and known absorption bands for BSi, a model including the wavenumbers 435−480, 790−830, and 1050−1280 cm^{-1} was developed.[8,19,20] The 6-component PLS model has a $R_{cv} = 0.93$

Table 3. Statistical Performance of the Calibration Models for Biogenic Silica (% BSi, Opal), Total Inorganic Carbon (% TIC), and Total Organic Carbon (% TOC) Using All Samples and Wavenumbers in the Calibration Set and Selected Samples and Wavenumbers Covering a Smaller Gradient

statistics	BSi			TIC (%)			TOC (%)		
PLS components	4	6	6	7	6	3	7	9	6
samples (n)	816	816	706^a	879	685	194	3164	3164	210
min	0	0	0	0	0	3	0	0	10
max	55	55	55	9.7	3.0	9.7	41	41	41
mean	9.0	10.6	10.7	1.9	0.4	8.2	2.7	2.7	24.5
SD	9.6	10.4	10.5	3.0	0.6	1.0	6.8	6.8	7.4
RMSECV	3.4	3.3	1.6	0.68	0.29	0.66	1.2	1.8	1.9
RMSECV (% gradient)	6.2	6.0	2.9	6.9	9.6	9.8	2.9	4.3	6.1
R_{cv}	0.93	0.93	0.94	0.97	0.89	0.92	0.98	0.97	0.96
wavenumbers included (cm^{-1})	400−3750	435−480; 790−830; 1050−1280	435−480; 790−830; 1050−1280	400−3750	700−725; 860−890; 1300−1560; 1780−1810; 2460−2640	700−725; 860−890; 1300−1560; 1780−1810; 2460−2640	400−3750	2800−3000	400−3750

^{a} Based on BSi estimates including all samples, an optimized BSi model was developed including only samples with a small difference between observed versus predicted values (<4%) in the full data set.
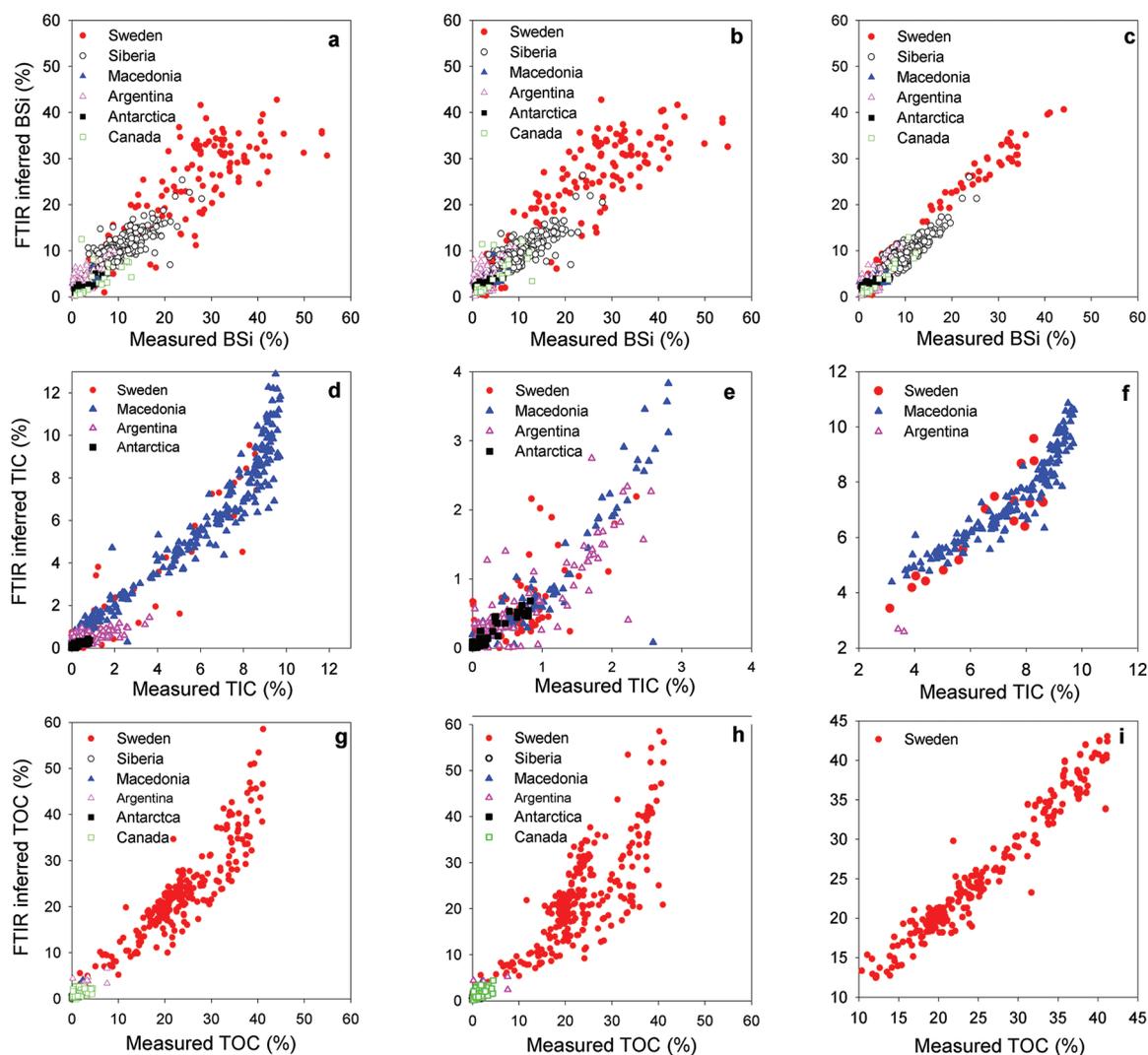
Figure 3. Scatter plots showing the relationships between conventionally measured and FTIRS inferred biogenic silica (BSi), total inorganic carbon (TIC), and total organic carbon (TOC) using sediment from c. 100 Swedish lakes, Lake El'gygytgyn (Siberia), Lake Ohrid (Albania/Macedonia), Laguna Potrok Aike (Argentina), Lake Hoare (Antarctica), and Lake Pingualuit (Canada). BSi models shown include (a) all wavenumbers ($400-3750$ cm^{-1}), (b) a model restricted to known absorption bands for BSi ($435-480$, $790-830$, $1050-1280$ cm^{-1}) and (c) an optimized model based on samples with a prediction error <4% from the model including all wavenumbers. TIC models shown include (d) all wavenumbers ($400-3750$ cm^{-1}), (e) a model restricted to known absorption bands for carbonates ($700-725$, $860-890$, $1300-1560$, $1780-1810$, $2460-2640$ cm^{-1}), and (f) an optimized model based on high TIC concentrations using all wavenumbers ($3-10\%$). TOC models shown include (g) all wavenumbers ($400-3750$ cm^{-1}), (h) a model restricted to known absorption bands for TOC ($2800-3000$ cm^{-1}), and (i) an optimized model based on high TOC concentration ($10-41\%$) using all wavenumbers. For statistical information see Table 3.

and a RMSECV of 3.3%. The conventional leaching technique can contain large errors; for example, Conley[2] demonstrated that when 30 different laboratories used the leaching method to analyze a sample with high BSi concentration the estimates varied by $19-70\%$ ($x = 44.3 \pm 9.38$ (± 1 SD)). Because traditional measurements of BSi can contain large errors[2] we also developed a model only including samples which showed a good correlation between inferred and measured values. The selected samples have an error less than 4% between conventional analyses versus FTIR inferred BSi values. Out of 814 samples, 706 pass this criterion. This optimized 6-component PLS model has a $R_{cv} = 0.94$ and RMSECV of 1.6% (2.9% of the gradient).

Statistical Performance of the FTIRS-TIC Model. A 7-component PLS model using wavenumbers $400-3750$ cm^{-1} has a $R_{cv} = 0.97$ and a RMSECV of 0.68% (7% of the gradient, $n = 879$,

gradient $0-10\%$ TIC) (Table 3, Figure 3). Based on the positive loadings (Figure 2) and known C–O molecular vibrations present in carbonates, a specific model for TIC was developed, incorporating the following wavenumbers: $700-725$, $860-890$, $1300-1560$, $1780-1810$, $2460-2640$ cm^{-1}.[5,8,21] The statistical performance remained high with $R_{cv} = 0.97$ and a RMSECV of 0.72%. The FTIRS model overestimates TIC values for higher values. This could potentially result from spectral saturation causing non-linear relationships between peak absorption and TIC at high concentrations, which can cause problems for models covering a large gradient. This issue can be avoided by developing specific models for low and high concentrations. By using all wavenumbers and TIC range of $0-3\%$ the prediction error is reduced to 0.29% ($R_{cv} = 0.89$; $n = 685$). When the gradient is set to $3-10\%$, RMSECV is reduced to 0.66% ($R_{cv} = 0.92$; $n = 194$).
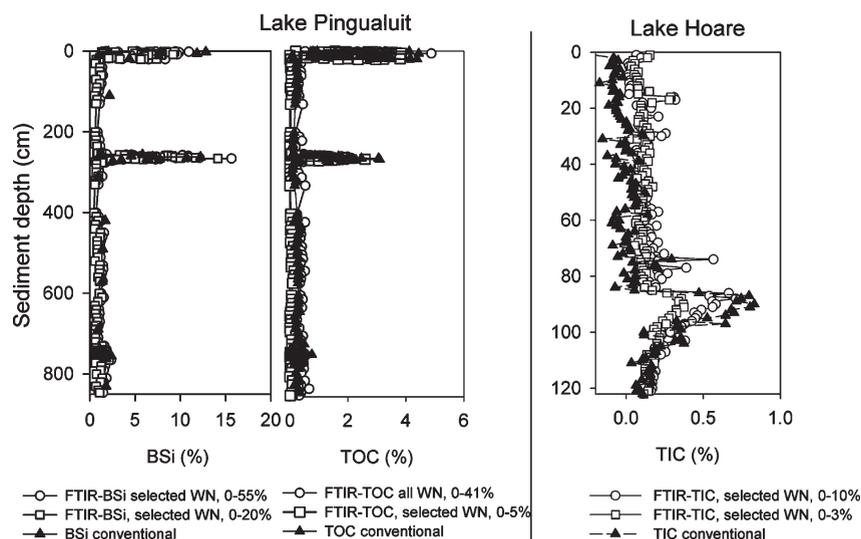
Figure 4. Comparisons between conventionally measured and FTIRS inferred biogenic silica (BSi) and total organic carbon (TOC) in the 8.4-m-long sediment core from Lake Pingualuit, Canada, covering the last c. 35 kyrs. The comparison for total inorganic carbon (TIC) is based on a Holocene sediment sequence from Lake Hoare, Antarctica. Selected wavenumbers refer to known absorption bands for BSi (435−480, 790−830, 1050−1280 cm^{-1}), carbonates (700−725, 860−890, 1300−1560, 1780−1810, 2460−2640 cm^{-1}), and organic carbon (2800−3000 cm^{-1}).

Statistical Performance of the FTIRS-TOC Model. A 6-component PLS model using wavenumbers 400−3750 cm^{-1} has a R_{cv} = 0.98 and a cross-validated root mean squared error of prediction (RMSECV) of 1.2% (2.9% of the gradient) (Table 3, Figure 3) (0−41%, n = 3164). Based on the positive loadings (Figure 2) and known C−H vibrations of −CH$_3$, −CH$_2$, and −CH groups of organic compounds, a specific model was developed based on the region 2800−3000 cm^{-1}. The statistical performance remained high with R_{cv} = 0.97 and RMSECV of 1.8%. Model performance was reduced at high TOC concentrations (10−41%, R_{cv} = 0.74). As with the TIC model, this is probably related to spectral saturation (see above). A specific model for high TOC values (10−41%) was therefore developed using all wavenumbers; the resulting model showed improved performance (R_{cv} = 0.96, RMSECV = 1.9% (6.1% of the gradient), n = 210). A model developed for TOC values between 0 and 5%, a common range for TOC in larger oligotrophic lakes, also had a reduced prediction error (RMSECV) of 0.28% (5.6% of the gradient, n = 2807). Loss-on-ignition at 550 °C (LOI-550 °C) is commonly used to estimate the organic carbon content in sediment.[22] One hundred samples were analyzed with both LOI 550 °C and TOC% using an elemental analyzer.[23] The correlation between LOI 550 °C and TOC% is lower (R = 0.89, n = 100, 0−41%) than the correlation between FTIRS-TOC and TOC% reported above. Consequently FTIRS may be a better method than LOI for rapid quantification of TOC.

Down-Core Application of FTIRS Models. The output from PLS models can be dependent on the gradient for the response variable (Y) as shown for the TIC and TOC models.[18] For optimal performance, a subset of samples covering the gradient of interest should be used.[24] One way to achieve this is by applying a flexible two-step approach to assess sediment properties with FTIRS. The first step uses the entire calibration set to cover the range of expected values. The second step is to use these initial results to refine the model to a narrower range. This should improve the model performance and reduce the prediction error. For example, if the initial results show a range of 5−10% in TOC, an optimized model for this range might include

samples from 0 to 15% rather than the 0−41% range that is used in the global model. The correlation coefficient for the model may decrease but, more importantly, the error of prediction will also decrease. If the model is applied to very different settings, however, there is still a risk that compounds in the sediment with very different molar absorption properties could cause interference thus resulting in a poor fit (large distance to model, DmodX). This can be avoided by developing a specific model, which only includes wavenumbers specific to the compound of interest, which is demonstrated for BSi, TIC, and TOC below.

The FTIRS calibration models for TOC and BSi were applied to an 8.4-m-long sediment core from the Arctic crater lake Pingualuit (Figure 4), which spans the last c. 35 kyrs. To test the robustness of our general model, samples from Lake Pingualuit were excluded from the calibration models. The correlation between conventionally measured BSi using the full gradient (0−55%) and the FTIRS model based on known absorption bands for BSi (Table 3) was R = 0.66 (n = 30, p < 0.005). Two outliers were identified; their exclusion increased the correlation to R = 0.88, similar to the FTIRS-BSi model performance reported above. If the gradient is reduced to 0−20%, the correlation remains the same (R = 0.88). The two outliers occurred 0.8 cm apart within the core and were situated at a sand layer with large difference in sediment composition (lower TOC, higher density, larger mean grain size, H. Guyard, personal communication). Because subsampling of FTIRS samples and the conventionally analyzed samples was undertaken on different occasions, it is likely that the measurements have not been performed using sediment with comparable sediment properties. This conclusion is supported by a similar mismatch for the FTIRS-TOC% and TOC% measured with the conventional technique within these two outliers. Using the full gradient for TOC and known absorption bands for organic carbon (Table 3), the correlation is R = 0.85 (n = 218, p < 0.005). When the gradient is reduced to 0−5%, the R value remains almost the same (R = 0.84).

Lake Pingualuit only contains very low concentrations of TIC and consequently detailed analyses using conventional methods

were not undertaken. The FTIRS-TIC model was therefore applied to the 1.2-m-long Holocene sediment core from Antarctic Lake Hoare, which contains low (<1%) but variable TIC concentrations. When the whole gradient (0−10%) is included, the model performs well with a correlation between conventionally measured and FTIR-inferred TIC of 0.86 (Figure 4, $n = 122$; $p < 0.005$). Similar results ($R = 0.85$, $p < 0.005$) are achieved when the calibration model is restricted to a smaller gradient (0−3%).

Implications and Future Directions. The results demonstrate that FTIRS can be used to simultaneously assess BSi, TIC, and TOC from lake sediments, including long sediment cores. Previous studies have relied on internal calibration to achieve optimal model performance.[7] By using samples from very diverse settings and of varying ages, this study significantly advances FTIRS calibration methods by developing universally applicable models for BSi, TOC, and TIC. Furthermore, the greater number of samples included within these newly developed calibration model has also resulted in improved statistical performance. The loading plots indicate that similar wavenumbers are important for the models as shown in previous studies,[7,8] demonstrating that the FTIRS calibration models are based on a robust relationship between compound-specific molecular vibrations and compound concentrations. There are, however, some indications of nonlinear relationships between compound-specific absorption and high concentrations of TIC and TOC. Future research will assess if nonlinear PLS methods can overcome these issues.

Our results demonstrate that FTIRS is a useful and rapid analytical alternative for quantitative inferences of BSi, TIC, and TOC in lake sediments using small sample quantities (10 mg). This technique could be beneficial for other lake deep drilling projects where long sediment successions need to be analyzed. The calibration models presented here are broadly applicable to many settings, thus greatly reducing the amount of work required to apply these method at new study sites. FTIRS also represents a valuable analytical tool for studies where only small sample quantities are available, such as high-resolution studies of varved sediments. Future research should also test if calibration models based on lacustrine sediments can be applied to marine sediment or whether specific models need to be developed for the marine realm. Considering that the technique is used in soil science for studies on molecular-level processes at mineral, organic, and bacterial surfaces that influence the biogeochemical cycles of elements,[25] there are potentially many more applications for FTIRS sediment studies which still need to be explored. In combination with X-ray fluorescence scanners and multisensor core loggers, FTIRS can provide highly resolved, qualitative and quantitative data on the geochemistry, mineralogy, magnetic, and biogeochemical properties of sediment samples. The models presented here can be used to provide crucial sedimentological information and consequently help to improve reconstructions of environmental variability using lake sediments.

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