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Biogeochemical properties and diagenetic changes during the past 3.6 Ma recorded by FTIR spectroscopy in the sediment record of Lake El'gygytgyn, Far East Russian Arctic

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Abstract

A number of studies have shown that Fourier transform infrared spectroscopy (FTIRS) can be applied to quantitatively assess lacustrine sediment constituents. In this study, we developed calibration models based on FTIRS for the quantitative determination of biogenic silica (BSi; $n = 420$; gradient: 0.9–56.5%), total organic carbon (TOC; $n = 309$; gradient: 0.02–2.89%), and total inorganic carbon (TIC; $n = 153$; gradient: 0.01–1.46%) in a 318 m long sediment record with a basal age of 3.6 Ma from Lake El'gygytgyn, Far East Russian Arctic. The developed partial least squares regression (PLSR) models yield high cross-validated (CV) $R_{CV}^2 = 0.85–0.91$ and low root mean square error of cross-validation (RMSECV) (2.1–4.3% of the gradient for the different properties). The FTIRS-inferred concentrations of BSi, TOC, and TIC provide an initial insight into the climatic and environmental evolution at Lake El'gygytgyn throughout the late Pliocene and Quaternary showing a considerably high bioproductivity in the lake ecosystem between $\sim 3.27–3.54$ Ma during the early Pliocene warm period. Moreover, we found that the recorded FTIR spectra contain information on sample burial depth as a result of diagenetic changes (dehydration/dehydroxylation) of certain mineral phases. Despite the indicated post-depositional processes, the calibration models yield good statistical performances showing that general FTIRS models can be developed for several hundred meters long records extending several million years back in time. Our results highlight FTIRS to be a rapid, cost-effective alternative to conventional methods for quantification of biogeochemical properties.

1 Introduction

The understanding of past environmental changes is of particular importance to facilitate the prediction of the magnitude and the regional implications of future environmental changes, especially in view of an anthropogenic-forced global warming (IPCC, 2007). Lake sediment records are valuable archives preserving these changes.

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variations in sediment composition arising from climatic, environmental or diagenetic changes bias the robustness of IR calibrations.

In this study, FTIRS is applied to a 318 m long sediment record from Lake El'gygytyn, Far East Russian Arctic (67° 30' N, 172° 5' E) (Fig. 1), which was recovered during an ICDP (International Continental Scientific Drilling Program) funded deep drilling campaign in 2009 (ICDP site 5011-1) (Melles et al., 2011). With its continuous formation and basal age of 3.6 Ma (Melles et al., 2012; Nowaczyk et al., 2012), the record of Lake El'gygytyn for the first time provides high-resolution insights into the climatic and environmental evolution of the Arctic during the Quaternary and late Pliocene.

Within the framework of this study, we aim to test for the first time the applicability of IR based calibration models for BSi, TOC, and TIC using a sediment record extending several million years back in time. This test will shed light on the impact of potential diagenetically triggered changes in sediment composition on FTIR calibration models. Moreover, this study aims at providing initial insights into the climatic and environmental evolution of the Arctic from the Pliocene to the present as recorded by bioproductivity indicators in the sediment record of Lake El'gygytyn.

2 Material and methods

2.1 Core recovery

Drilling operations were performed, from the lake ice cover, by Drilling, Observation and Sampling of the Earth's Continental Crust (DOSECC) Inc. using a GLAD-800 drilling system (Global Lake Drilling 800 m) in spring 2009. The lake sediments were sampled by three holes (A, B, and C) at ICDP site 5011-1, forming a core composite that penetrates down to the underlying impact breccia at 318 m below lake floor (m b.l.f.) (Fig. 1).

The sample site is situated in the deepest part of the lake.

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FTIRS measurements were performed on 380 samples covering the entire compos-
 5 and 16.6 m long cores were recovered in 1998 and 2003, respectively (Juschus et al.,
 2005; Melles et al., 2007).

2.2 Analytical methods

Conventionally measured concentrations of biogeochemical properties (BSi, TOC, TIC)
 were used as reference data for the development of our calibration models. All sedi-
 10 ment samples were freeze-dried and ground to a particle size < 63µm using either
 a swing mill (samples from ICDP site 5011-1) or a planetary mill (samples from PG1351
 and Lz1024). TC and TIC in samples from site 5011-1 were determined by suspension
 method using a DIMATOC[®] 100 liquid analyser (Dimatec Corp.). TOC was then calcu-
 15 lated by subtracting TIC from TC. The TOC content in samples from core PG1351
 was analysed with a Metalyt-CS-1000-S (ELTRA Corp.) after sample pretreatment with
 HCL (10 %) at a temperature of 80 °C to remove carbonate. Concentrations of BSi in all
 sediment cores were obtained by applying the wet chemical leaching method according
 to Müller and Schneider (1993).

Accumulation rates (AR_X) of BSi (AR_{BSi}), TOC (AR_{TOC}), and TIC (AR_{TIC}) in
 20 $g\text{ cm}^{-2}\text{ yr}^{-1}$ were calculated according to Eq. (1) (Bralower and Thierstein, 1987):

$$AR_X = SR \cdot (WBD - 1.025 \cdot \Phi) \cdot \%X \quad (1)$$

where SR is the sedimentation rate in cm yr^{-1} , WBD is the wet bulk density in g cm^{-3} ,
 25 Φ is the porosity, and %X is the concentration of the property of interest. Sedimentation
 rates were determined according to the age model of Nowaczyk et al. (2012) and WBD
 and Φ were reconstructed by their physical properties measured by a Geotek Multi-
 Sensor Core Logger (MSCL) according to Gebhardt et al. (2013). WBD and Φ were

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each model component. In this evaluation a calibration model based on 90 % of the available data was applied to the remaining 10 % to estimate its prediction ability. This procedure was then repeated a total of 10 times until the entire data set was predicted solely based on the corresponding spectral information. The resulting cross-validated coefficient of determination R_{cv}^2 and root mean square error of cross-validation (RM-SECV) were used to evaluate the internal model performance. The external validation was performed on 50 samples randomly chosen and equally distributed over the entire composite profile of ICDP site 5011-1. The coefficient of determination (R^2) between conventionally measured and FTIR-inferred concentrations of biogeochemical properties as well as the root mean square error of prediction (RMSEP) were considered to estimate the prediction ability of the developed calibration applied to samples not included in the calibration set.

We performed the multivariate data analyses using SIMCA-P 11.5 (Umetrics AB, SE-907 19 Umeå, Sweden). OPUS 5.5 (Bruker Optics Inc.) was used for the visualization of single FTIR spectra. For more information about the numerical analysis in this approach, see Vogel et al. (2008) and Rosén et al. (2010).

3 Results and discussion

3.1 Statistical performance of FTIRS models

All three models, the 2-component FTIRS-BSi-model, the 8-component FTIRS-TOC-model, and the 8-component FTIRS-TIC-model, are based on the spectral range from 450 to 3750 cm^{-1} and show a strong correlation between FTIRS-inferred and conventionally measured concentrations ($R_{cv}^2 = 0.86$ for BSi; $R_{cv}^2 = 0.91$ for TOC; $R_{cv}^2 = 0.82$ for TIC) (Table 1). Corresponding RMSECV are low: 2.4 % for BSi (4.3 % of the gradient), 0.09 % for TOC (3.1 % of the gradient), and 0.03 % for TIC (2.1 % of the gradient). The external validation showed good statistical performance. The R^2 values are 0.94 for BSi and 0.83 for TOC (Fig. 2), and the RMSEP values are 2.1 % for BSi (7.0 % of

the gradient) and 0.13 % for TOC (7.9 % of the gradient), which indicate both a high prediction ability of the general trend and high prediction accuracies with respect to the absolute values of the proxy of interest.

In comparison with the BSi and TOC models, the TIC-model has a slightly poorer statistical performance ($R^2 = 0.82$, RMSECV = 0.05 % (13.2 % of the gradient)) (Fig. 2). However, Rosén et al. (2010, 2011) have shown that a PLS model for TIC solely based on wavenumbers related to the C-O molecular vibrations of calcite (700–725, 860–890, 1300–1560, 1780–1810, 2460–2640 cm^{-1}) (Huang and Kerr, 1960; Mecozzi et al., 2001) can yield a high statistical performance as well. In this study, a 7-component TIC-model based on these selected wavenumbers shows an improved performance with an R_{cv}^2 of 0.85, an RMSECV of 0.03 % (2.1 % of the gradient), and for the external validation set, an R^2 of 0.89 (Fig. 2) and an RMSEP of 0.03 % (7.9 % of the gradient). This indicates that the TIC model using selected wavenumbers has higher prediction ability of the general trend as well as of the absolute values.

3.2 Spectral information

Pronounced absorption bands in the loadings of the FTIRS models can be related to known absorption bands of organic and minerogenic compounds. For the BSi model the most important spectral regions positively correlated to the BSi concentration are situated between 790–860, 1060–1320 and 2750–3580 cm^{-1} (Fig. 3). Previous studies have shown that these regions can be attributed to absorptions caused by molecular vibrations of biogenic silica. Absorptions at around 1100 cm^{-1} are assigned to the stretching vibration mode of the $[\text{SiO}_4]$ tetrahedron, while the absorption band at around 800 cm^{-1} is caused by inter-tetrahedral Si-O-Si bending vibrations (Moenke, 1974b; Gendron-Badou et al., 2003). A FTIR spectrum of purified BSi from Lake El'gygytgyn sediment shows two additional absorption bands at around 471 and 945 cm^{-1} (Fig. 4), which are not pronounced in the loadings. The band at around 471 cm^{-1} is associated with the bending vibration mode of the $[\text{SiO}_4]$ tetrahedron and

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the band at around 945 cm^{-1} is related to Si-OH molecular vibrations (Rickert et al., 2002; Gendron-Badou et al., 2003). Instead, these spectral regions show a negative correlation to the BSi concentration due to fact that other silicates (e.g. feldspars, clay minerals) cause absorption in this part of the IR-spectrum as well (Farmer, 1974; Moenke, 1974b). This can result in an anti-correlation to the BSi content, because measurements of concentrations of biogeochemical properties reflect the relative proportion of biogeochemical and minerogenic compounds. The positive loading values in the spectral regions between 2750 and 3580 cm^{-1} can be linked to stretching vibrations of OH molecules (Moenke, 1974a), which are embedded in the molecular structure of BSi. The loadings of our BSi calibration model are consistent with the loading plots previously reported by Vogel et al. (2008) and Rosén et al. (2010, 2011).

The most important absorption band in the loadings of the TOC model is situated between 1050 and 1275 cm^{-1} (Fig. 3). Absorption of IR radiation in this region can be linked to known absorption bands of organic compounds. For instance, absorptions between 1040 and 1070 cm^{-1} are ascribed to C-O stretching vibrations of carbohydrates or polysaccharides (Calace et al., 1999; Chapman et al., 2001; Cocozza et al., 2003). Absorptions at around 1125 cm^{-1} are due to C-O-C stretching vibrations of complex carbohydrates, and absorption between 1230 and 1265 cm^{-1} are attributed to C-O stretching vibrations of ethers or carboxyl groups (Cocozza et al., 2003; Mecozzi and Pietrantonio, 2006). However, the similarity of the loading plots of TOC and BSi indicates an interdependency between both proxies. Sediment samples of Lake El'gygytgyn used for the calibration models are in general characterized by low TOC concentrations (mean: 0.41 %) and high BSi concentrations (mean: 12.1 %). It is likely that the positive loading values from 1050 to 1275 cm^{-1} are therefore attributed to Si-O molecular vibrations of BSi rather than to vibrations caused by organic matter. Positive loading values between 2800 and 3000 cm^{-1} with distinct peaks at 2850 and 2920 cm^{-1} can be attributed to stretching vibrations of C-H molecules in -CH, -CH₂ and -CH₃ groups of aliphatic and protein chains (Chapman et al., 2001; Cocozza et al., 2003; Mecozzi and Pietrantonio, 2006). Absorption in this part of the IR spectrum is

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characteristic of organic matter, since an overlap with specific absorption bands of BSi can be excluded. The positive values between 2560 and 3575 cm^{-1} as well as at around 3700 cm^{-1} are related to absorptions caused by hydroxide groups, which are common in organic matter. However, because the influence of BSi on the calibration model for TOC is likely, it is difficult to determine how much of the absorption is caused by hydroxide contained in organic matter (direct relationship) and how much of the absorption results from hydroxide groups associated with BSi (indirect relationship).

Distinctive positive absorption peaks in the loadings of the TIC calibration model at around 715, 875, 1795, 2515 cm^{-1} as well as the broad absorption band at around 1460 cm^{-1} (Fig. 3) correspond well with known absorption bands caused by molecular vibrations of carbonates (Huang and Kerr, 1960; Mecozzi et al., 2001). Furthermore, FTIRS model developments by Vogel et al. (2008) and Rosén et al. (2010, 2011) as well as FTIR spectra of carbonate-rich sediments (Rosén et al., 2010) have shown that these spectral regions are the most important for carbonates. The negative loading values between 1025 and 1270 cm^{-1} as well as the negative values between 2630 and 3730 cm^{-1} can partly be explained by an indirect relationship between the occurrence of TIC and BSi. The appearance of carbonates in the analysed samples is almost exclusively restricted to the lowermost part of the sediment record and accompanied by low BSi concentrations, which result in a negative correlation of spectral regions related to molecular vibrations of BSi to the TIC content.

3.3 Indications for diagenetic changes

A 9-component calibration model relating spectral information to the sample burial depth ($n = 329$, 450–3750 cm^{-1}) shows a significant correlation between the FTIR-inferred and measured depth ($R_{cv}^2 = 0.85$, RMSECV = 29.3 m (9.4 % of the gradient), $R^2 = 0.85$, and RMSEP = 35.8 m (11.7 % of the gradient)) (Fig. 5a). This indicates that IR spectra of sediment samples contain information on burial depth/age and thus likely on changes in sediment composition after deposition. The loading plot of the developed model shows strong similarities to the loading plot of the calibration model

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increasing trend from the bottom to the top of the sediment profile. The lowest concentrations of BSi and TOC occur in sediments from the basal part of the record, which were deposited prior to 3.54 Ma and, somewhat less pronounced, between 3.54 and ~ 3.27 Ma. Sediments of the marine isotope stage (MIS) 11 interglacial (~ 400 ka) contain the highest BSi concentrations, while the most recent of the analysed samples (145 ka) shows the highest TOC concentration.

The inferred concentrations of TIC vary between 0 and 1.45 % (mean: 0.08 %) (Fig. 6). Samples deposited between ~ 3.27–3.54 Ma contain low concentrations of carbonate up to 0.3 %, whereas sediments formed within the first ~ 50 kyr after the lake formation show the highest concentrations of TIC up to 1.5 %. Samples covering the last ~ 3.27 Myr (mean: 0.05 %), in contrast, are supposed to be free of carbonate, due to the RMSECV and RMSEP of 0.03 % and the limit of detection of approximately 0.05 % for the conventional method on which the calibration model for TIC is based. The only exception is one sample at around 223 ka, which has a TIC content of 0.50 %.

Two different carbonate mineral phases, calcite and siderite, were determined in the analysed samples from their wavenumber-specific IR absorbance. Calcite ($\text{Ca}[\text{CO}_3]$) shows distinct absorption peaks at 712, 876, 1435, 1812, and 2545 cm^{-1} , while siderite ($\text{Fe}[\text{CO}_3]$) has specific peaks at 737, 866, 1422, and 1818 cm^{-1} (Huang and Kerr, 1960). Whilst calcite was determined in the basal sediments, siderite was detected in the ~ 223 ka old sample from the upper part of the sediment profile. The occurrence of both mineral phases has been confirmed by XRD and thermomagnetic measurements, respectively. The occurrence of carbonate in the basal sediments might be connected to the origin of the lake depression created by a meteorite impact 3.58 ± 0.04 Ma ago (Layer, 2000). The impact may have induced hydrothermal activity, which is common after impact events where the melted/heated target material acting as heat source interacts with near-surface H_2O (Naumov, 2002). Amongst others, calcite can be precipitated in such a hydrothermal system (Osinski et al., 2005). This process is also indicated by the existence of calcite veins in the underlying impact breccia (U. Raschke, personal communication, 2012).

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et al., 2011). The termination of the productivity maximum at Lake El'gygytgyn between 3.25–3.29 Ma is consistent with the onset of ice sheet expansion and cooling of coastal waters in Antarctica at about 3.3 Ma (McKay et al., 2012) and with decreasing $p\text{CO}_2$ concentrations from 3.2 Ma on (Seki et al., 2010). Pollen-based temperature and precipitation reconstructions from the El'gygytgyn sediment record suggest temperatures of 7–8°C and precipitation values of around 400 mm yr⁻¹ higher than today for the period between 3.6 and 3.4 Ma. Further, this period is characterized by a significantly larger size of the dominant planktonic diatom (*Pliocaenicus* sp.) compared to any other interval in the sediment record, indicating increased nutrient availability and reduced seasonal ice cover (Brigham-Grette et al., 2013).

During the late Pliocene and Quaternary – ~ 3.27 Ma to present – accumulation rates of BSi and TOC are considerably lower. The decreased fluxes indicate a deterioration of environmental and climatic conditions in the Siberian Arctic impeding bioproductivity. Variations in the accumulation rates are comparatively small during the past 3.27 Myr and probably an effect of large scale glacial-interglacial climate change. During these large scale cycles, bioproductivity at Lake El'gygytgyn is primarily controlled by the duration of lake ice cover. Warm periods are characterised by high aquatic primary production and a mixing of the entire water body due to the summer melt of the ice cover, while during cold periods the bioproductivity is limited due to the year-round ice cover causing a stratification of the water column with anoxic bottom waters (Melles et al., 2007). However, the dataset does not reflect the entire glacial-interglacial pattern due to the low sample resolution.

4 Conclusions

The results of our study demonstrate that robust FTIRS calibration models can be developed for the quantitative assessment of biogeochemical properties in very long (> 300m) sediment records extending several million years back in time. The developed models relating FTIR spectral information to conventional measurements for

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TOC, TIC and BSi for the 3.6 Ma old sediment record of Lake El'gygytgyn show a good statistical performance. Furthermore, our results suggest that FTIRS provides information about the sample burial depth and therefore about post-depositional changes in sediment composition. For the sediment record of Lake El'gygytgyn, our findings indicate a dehydration/dehydroxylation of certain mineral phases with increasing burial depth/age. It remains uncertain which components are affected by these processes, but future analyses comparing IR information of single sediment components of different age might answer this question. The fact that robust FTIRS models can be developed despite the indicated diagenetic changes in the sediment column suggests that the technique is not limited to young, unconsolidated sediments. However, an internal calibration might be needed to provide results of high accuracy for sediment succession affected by diagenesis.

Our study demonstrates that FTIRS is a fast and cost-effective analytical alternative to conventional methods for the quantitative estimation of biogeochemical properties like BSi, TOC, or TIC. Its successful application to a record extending several million years back in time corroborates the potential of the technique for other lake deep drilling projects dealing with long sediment successions potentially affected by diagenetic processes.

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Table 1. Statistical performance of developed calibration models using wavenumbers from 450–3750 cm⁻¹ (all WN) and selected wavenumbers (selected WN) for biogenic silica (BSi), total organic carbon (TOC), and total inorganic carbon (TIC) based on sediments from Lake El'gygytyn.

Statistics		BSi (%) all WN	TOC (%) all WN	TIC (%)	
				all WN	selected WN
Calibration set	PLS components	2	8	8	7
	Samples (<i>n</i>)	420	309	153	153
	Min	0.9	0.02	0.01	0.01
	Max	56.5	2.89	1.46	1.46
	Gradient	55.6	2.87	1.45	1.45
	Mean	12.1	0.41	0.12	0.12
	Included wavenumbers (cm ⁻¹)	450–3750	450–3750	450–3750	700–725; 860–890; 1300–1560; 1780–1810; 2460–2640
Internal validation	R^2_{cv}	0.86	0.91	0.82	0.85
	RMSECV	2.4	0.09	0.03	0.03
	RMSECV (% gradient)	4.3	3.1	2.1	2.1
	Min	1.2	0.04		0.02
External validation set	Max	36.9	1.68		0.40
	Gradient	35.7	1.64		0.38
	Mean	10.1	0.37		0.09
	R^2	0.94	0.83	0.82	0.89
External validation	RMSEP	2.1	0.13	0.05	0.03
	RMSEP (% gradient)	7.0	7.9	13.2	7.9

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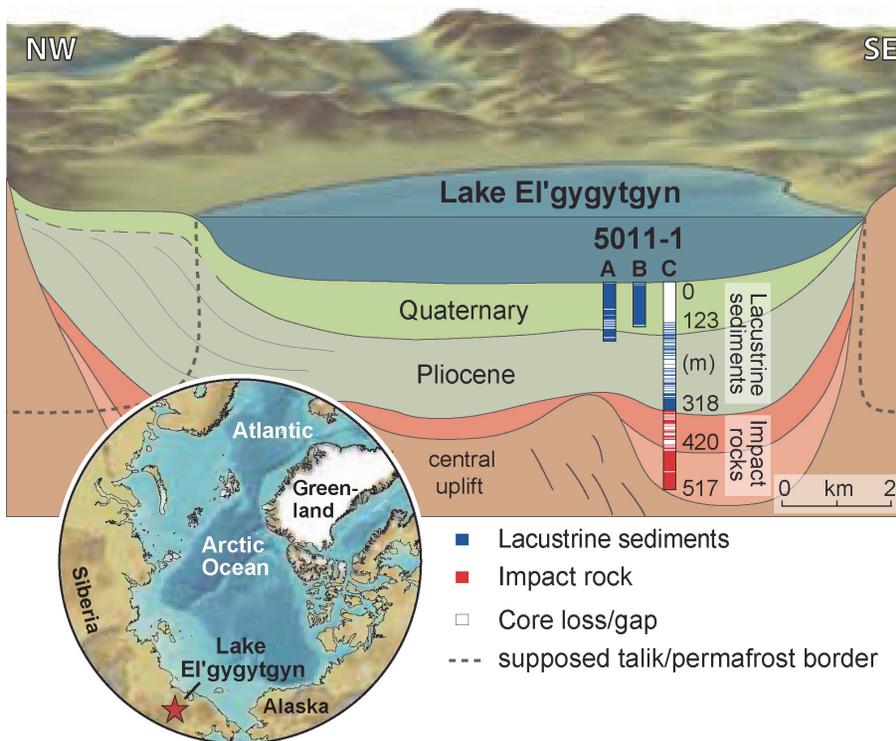



Fig. 1. Location of Lake El'gygytyn in North-Eastern Russia (inserted map) and schematic cross-section of the El'gygytyn basin stratigraphy showing the location of ICDP Site 5011-1 (from Melles et al., 2012).

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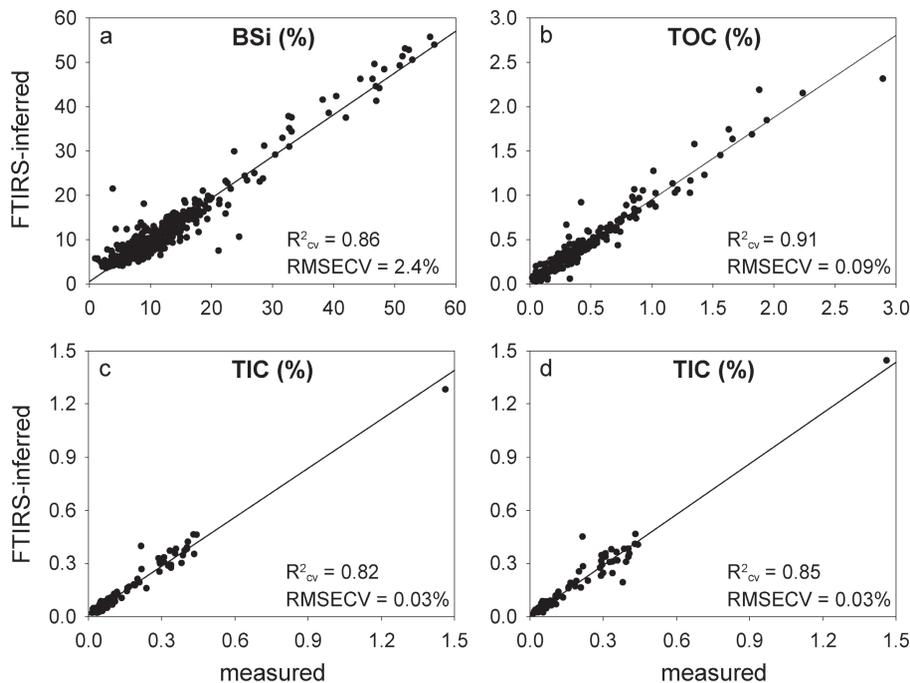


Fig. 2. Conventionally measured (x-axis) versus FTIRS-inferred concentrations (y-axis) of biogenic silica (BSi), total organic carbon (TOC), and total inorganic carbon (TIC) with the cross-validated coefficient of determination (R^2_{cv}) and root mean square error of cross-validation (RMSECV) resulting from the internal validation of the developed calibration models. **(a)** FTIRS-BSi calibration model using wavenumbers from 450 to 3750 cm^{-1} , **(b)** FTIRS-TOC calibration model using wavenumbers from 450–3750 cm^{-1} , **(c)** FTIRS-TIC calibration model including wavenumbers from 450–3750 cm^{-1} , and **(d)** FTIRS-TIC calibration model based on wavenumbers of known absorption bands of calcite (700–725, 860–890, 1300–1560, 1780–1810, 2460–2640 cm^{-1}).

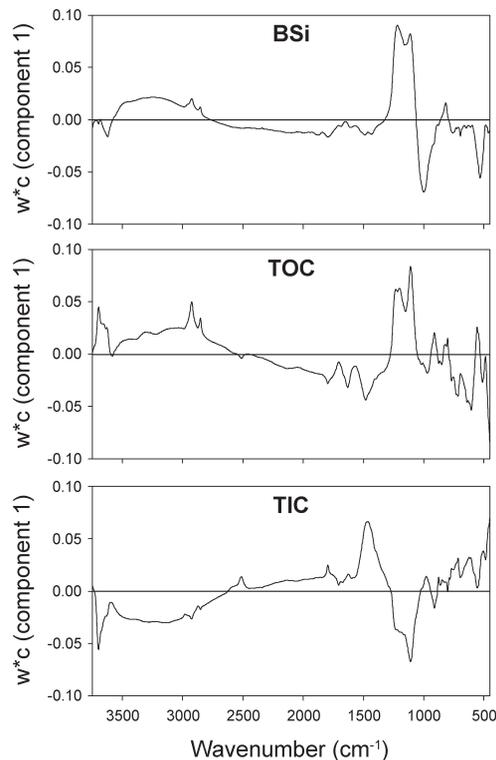


Fig. 3. Loadings of the developed FTIRS-calibration models for biogenic silica (BSi), total organic carbon (TOC), and total inorganic carbon (TIC) showing the contribution of each wavenumber to the partial least squares regression (PLSR) model. Positive values indicate wavenumbers positively correlated to the property of interest and negative values indicate wavenumbers negatively correlated to the property of interest. Loadings are expressed by weight vectors ($w \cdot c$) of the first PLSR model component (x-axis) and the corresponding spectral range (y-axis).

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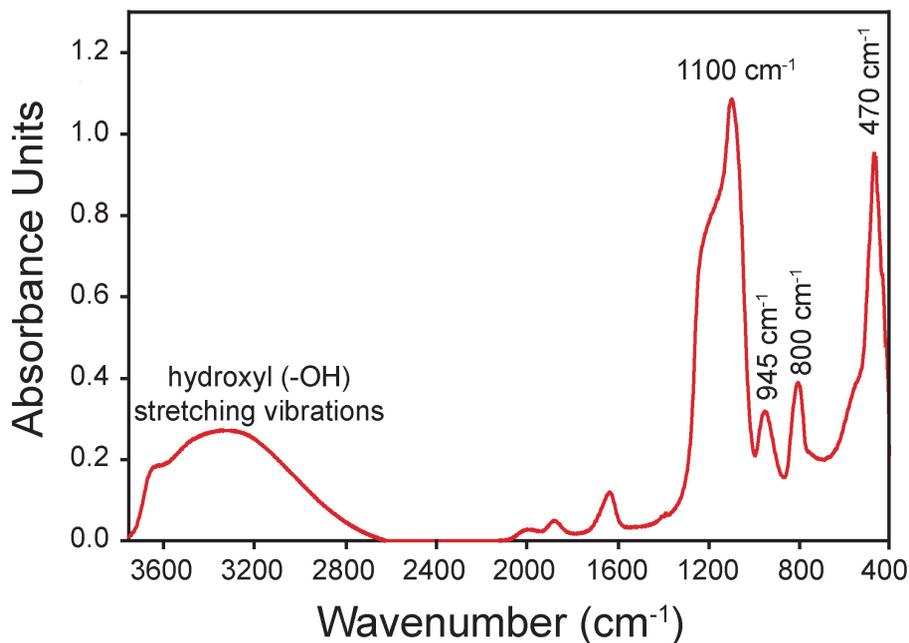


Fig. 4. FTIR spectrum of biogenic silica (BSi) from a sediment sample of Lake El'gygytyn purified according to Chaplignin et al. (2012) showing distinct absorption bands at around 1100 cm⁻¹ (Si-O stretching vibration), 945 cm⁻¹ (Si-OH stretching vibration), 800 cm⁻¹ (intertetrahedral Si-O-Si vibration), and 470 cm⁻¹ (Si-O bending vibration).

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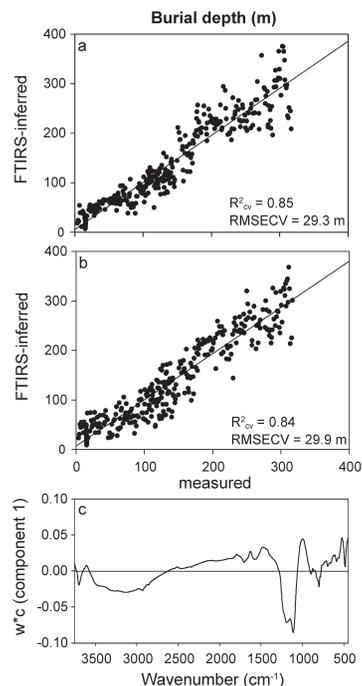


Fig. 5. (a,b) Conventionally measured (x-axis) versus FTIRS-inferred burial depth (y-axis) with the cross-validated coefficient of determination (R^2_{cv}) and root mean square error of cross-validation (RMSECV) resulting from the internal validation of the developed models (included wavenumbers: (a) 450–3750 cm⁻¹ and (b) 2600–3750 cm⁻¹). (c) Loadings of the developed FTIRS-burial depth calibration model showing the contribution of each wavenumber to the partial least squares regression (PLSR) model. Positive values indicate wavenumbers positively correlated to the property of interest and negative values indicate wavenumbers negatively correlated to the property of interest. Loadings are expressed by weight vectors ($w \cdot c$) of the first PLSR model component (x-axis) and the corresponding spectral range (y-axis).

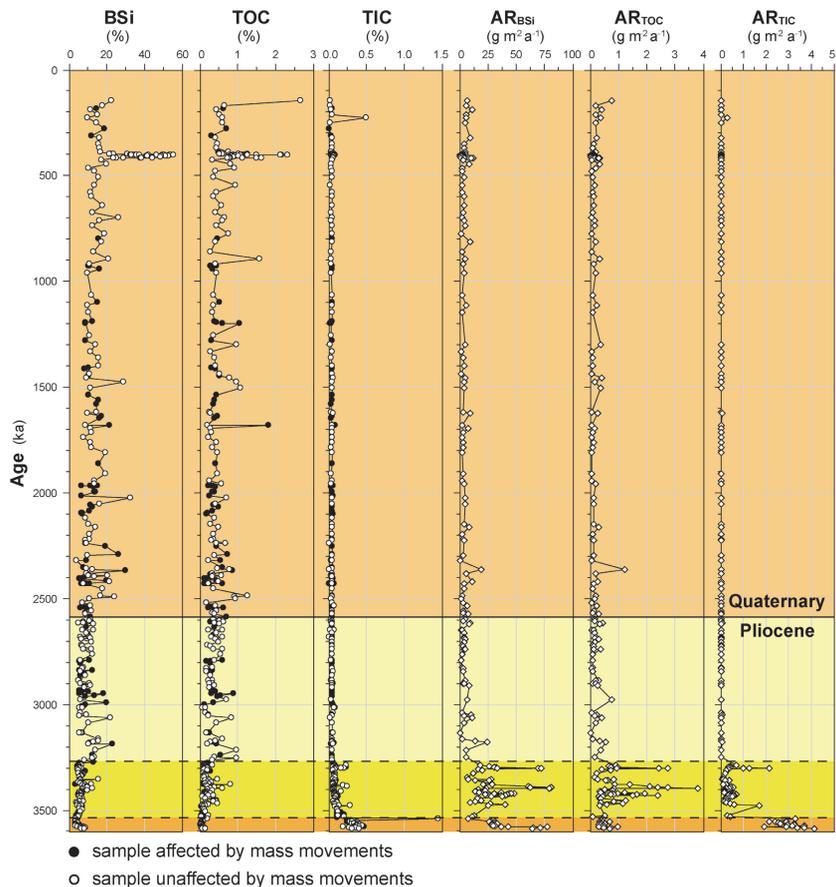


Fig. 6. Down-core plot of FTIRS-inferred concentrations and calculated accumulation rates (AR) of biogenic silica (BSi), total organic carbon (TOC), and total inorganic carbon (TIC) of the sediment profile of Lake El'gygytyn (ICDP site 5011-1). Samples affected by mass-movements were excluded from the calculation of accumulation rates.