

Independent measurement of biogenic silica in sediments by FTIR spectroscopy and PLS regression

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Abstract We present an independent calibration model for the determination of biogenic silica (BSi) in sediments, developed from analysis of synthetic sediment mixtures and application of Fourier transform infrared spectroscopy (FTIRS) and partial least squares regression (PLSR) modeling. In contrast to current FTIRS applications for quantifying BSi, this new calibration is independent from conventional wet-chemical techniques and their associated measurement uncertainties. This approach also removes the need for developing internal calibrations between the two methods for individual sediments records. For the independent calibration, we produced six series of different synthetic sediment mixtures using two purified diatom extracts, with one extract mixed with quartz sand, calcite, 60/40 quartz/calcite and two different natural sediments, and a second extract

mixed with one of the natural sediments. A total of 306 samples—51 samples per series—yielded BSi contents ranging from 0 to 100 %. The resulting PLSR calibration model between the FTIR spectral information and the defined BSi concentration of the synthetic sediment mixtures exhibits a strong cross-validated correlation ($R_{cv}^2 = 0.97$) and a low root-mean square error of cross-validation (RMSECV = 4.7 %). Application of the independent calibration to natural lacustrine and marine sediments yields robust BSi reconstructions. At present, the synthetic mixtures do not include the variation in organic matter that occurs in natural samples, which may explain the somewhat lower prediction accuracy of the calibration model for organic-rich samples.

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Introduction

Biogenic silica (BSi) accumulated in sediments of lacustrine and marine environments represents an important record of changes in past (bio-)productivity, which can occur in response to nutrient loading, landscape changes or climate changes on annual to glacial-interglacial timescales (Ragueneau et al. 2000; Conley and Schelske 2001). In these aquatic systems, BSi is formed by sedimentation of siliceous microfossils of sponges, silicoflagellates, chrysophytes, radiolarians or phytoliths, but mostly of frustules from diatoms, one of the main aquatic primary producers. The accumulation of BSi in sediments also plays an important role as a sink in the global biogeochemical cycling of silicon. The reliable quantification of BSi is key to understanding the role of lacustrine and marine sediments in the Si cycle, as well as the coupling between past productivity indicated by BSi and the carbon cycle (Ragueneau et al. 2000; Street-Perrott and Barker 2008 and references therein).

Fourier transform infrared spectroscopy (FTIRS) is an emerging analytical technique in biogeochemistry, which can be applied to quantify BSi. Conventionally, BSi has been measured using wet-chemical digestion techniques, which are time-consuming and subject to limitations in comparing results between laboratories. In contrast, FTIRS is a fast and cost-efficient technique with a straightforward measurement, which only requires small sample sizes (0.01 g). Furthermore, FTIRS can simultaneously provide quantitative data, not only for BSi, but also for, e.g. total organic carbon (TOC) and total inorganic carbon (TIC) (Vogel et al. 2008; Rosén et al. 2010, 2011), as well as qualitative information on changes in sediment composition (Rydberg et al. 2012).

In 1968, Chester and Elderfield demonstrated the first quantification of BSi in marine sediments by FTIRS, which was based on the intensity of a single absorption band specific for BSi. This approach was limited by the spectral overlapping of other sediment components with similar IR absorption features that complicate an accurate BSi determination. By using linear mixing models between FTIR spectra of different sediment components, Bertaux et al. (1998)

successfully estimated BSi in lacustrine sediments. The latter approach, however, requires an extensive a priori knowledge about the single components that make up the analyzed samples.

More recently, the use of partial least squares regression (PLSR) to quantify BSi from FTIR spectral information has been shown to produce accurate measurements in lake sediments (Vogel et al. 2008, 2010, 2013; Hahn et al. 2012; Brigham-Grette et al. 2013; Cunningham et al. 2013a, b; Meyer-Jacob et al. 2014) as well as in marine sediments (Sprenk et al. 2013). PLSR can be used to analyze data sets with strongly collinear, noisy, and numerous X-variables and is thus especially suitable for IR spectra. The method models the relationship between two matrices, which in this case are the FTIR spectral information of a sediment sample and the corresponding BSi concentration of the analyzed sample (Wold et al. 2001). These first applications of FTIRS and PLSR were developed for specific sediment records using internal downcore calibration models built on a subset of samples in which BSi was analyzed using conventional wet-chemical methods (Vogel et al. 2008). As a next step, Rosén et al. (2011) introduced the potential for a general calibration model that relies on globally distributed surface and downcore sediment samples. Initial applications of this model produced reliable results, demonstrating the possibility of a site-independent application of FTIRS and PLSR to quantify BSi.

Currently, FTIRS calibrations for BSi rely on the determination of BSi using wet-chemical digestion techniques, and thus inherently depend on the accuracy and uncertainties of those techniques. Based on an inter-laboratory comparison, Conley (1998) showed that results from these wet-chemical digestion techniques can vary significantly between laboratories. These uncertainties can arise from, e.g. variable execution, such as the concentration of the digestion solution or the slope determination, contaminated water systems, and lack of an absolute accuracy because there are no BSi standards. The aim of this study was thus to develop an independent calibration for the quantification of BSi in marine and lacustrine sediments by means of FTIR spectroscopy and PLS regression. We calibrated FTIR spectral information of different synthetic sediment mixtures against their defined BSi content. By using samples of known BSi concentrations, the BSi quantification will no longer

depend on wet-chemical reference methods and their underlying measurement uncertainty. This approach may further create a universally applicable calibration model to infer BSi in sediments, removing the need to develop time-consuming and expensive site-specific internal calibrations.

Materials and methods

Synthetic sediment mixtures

Synthetic sediments were produced using purified diatom frustules, pure quartz sand (Sigma-Aldrich, Chemie GmbH, Germany), pure calcite (Merck KGaA, Germany), a mixture of quartz sand and calcite, and sediments from Badsjön (Sweden) and Lake Towuti (Indonesia). Sediment from Badsjön contains * 5.1 % TOC and * 2.4 % TIC, whereas sediment from Lake Towuti contains * 0.9 % TOC, * 0.8 % TIC (siderite), and its mineral fraction mainly consists of mineral phases present in ultramafic rocks (olivine, pyroxene, magnetite, chromite, serpentine) and respective weathering products (Fe-oxides, smectite, kaolinite). Diatom frustules were extracted from lake diatomite sediment sequences of Lake Yoa (Chad) and Kieselgur Grube Klieken (Germany). Diatomites from Lake Yoa and Kieselgur Grube Klieken were treated with 35 % hydrogen peroxide solution at a temperature of 50 °C for 18 h to remove organic matter. Diatom frustules were then extracted by density separation using a solution of sodium metatungstate monohydrate. Because biogenic silica has a relatively broad density range of 1.9–2.3 g/cm³, four steps of density separation with sodium metatungstate monohydrate solution densities of 2.40, 2.35, 2.30, and 2.25 g/cm³ were necessary. The resulting diatom frustule extracts were rinsed five times with deionised water, freeze-dried, and homogenized individually using a mortar and pestle. Extracts from Lake Yoa, available in larger quantities after density separation, and Kieselgur Grube Klieken were not mixed.

We produced six different synthetic sediment mixture series, each consisting of 51 samples for a total of 306 samples for the calibration set. These mixtures were produced as follows. Lake sediments, quartz sand, and calcite were each first homogenized and ground using a planetary mill. To achieve a BSi gradient from 0 to 100 % in 2 % steps, pure diatom extracts from Lake Yoa were then added at defined

weight ratios to each of the following: diatom-free sediment from Lake Towuti, quartz sand, calcite, and a 60/40 mixture of quartz sand and calcite. The fifth series was a mixture of sediment from Badsjön that was treated similarly; however, because of its natural BSi content of 22 %, the defined BSi concentration ranges between 22 and 100 % in steps of * 1.5 %. Finally, a synthetic mixture series similar to that for Lake Yoa sediment was made from pure diatom extracts from Kieselgur Grube Klieken and the Lake Towuti sediment. All BSi concentrations are expressed as percentage by weight.

FTIR spectroscopy

Prior to FTIR analysis, 0.011 g of each sample was mixed with 0.5 g of oven-dried spectroscopic-grade potassium bromide (KBr) (Uvasol[®], Merck Corp.) and subsequently homogenized using a mortar and pestle. A Bruker Vertex 70 equipped with a MCT (Mercury–Cadmium–Telluride) detector, a KBr beam splitter, and a HTS-XT accessory unit (multi-sampler) was used for the measurement. Each sample was scanned 128 times at a resolution of 4 cm^{−1} (reciprocal centimeters) for a wavenumber range from 3,750 to 450 cm^{−1}, in diffuse reflectance mode. Prior to the analyses, the samples were stored in a desiccator for at least 12 h to ensure a low and comparable moisture content in all analyzed samples. The FTIR analysis was performed in a temperature-controlled laboratory (25 ± 0.2 °C), in which the samples were stored at least 12 h prior to the measurement, to achieve constant measuring conditions.

Numerical analysis

Linear baseline correction was applied to normalize the recorded FTIR spectra and to remove baseline shifts and tilts by setting two points of the recorded spectrum to zero (3,750 and 2,210–2,200 cm^{−1}). We used PLSR (Wold et al. 2001 and references therein) to develop calibration models between the FTIR spectral information and the corresponding BSi concentrations. Models are based on the wavelength range between 3,750 and 450 cm^{−1} and BSi concentrations were square-root transformed for numerical analysis. Cross-validated (CV) coefficient of determination (R_{cv}^2) and root mean square error of cross-validation (RMSECV) (in % BSi) resulting from seven-fold

cross-validation were used to evaluate the internal model performance. The seven CV groups are based on quantiles of the BSi concentration. Loadings expressed as weight vectors ($w \cdot c$) of the first PLS component that explains most of the correlation between the x-variables (FTIR spectral information) and the y-variable (BSi concentration) were used to identify the contribution of each wavenumber to the PLSR model. Positive weight vectors indicate wavenumbers positively correlated to the BSi content and negative weight vectors indicate wavenumbers negatively correlated to BSi concentration.

An external validation of the independent calibration was performed on 816 globally distributed, lacustrine and marine, natural sediment samples included in the calibration model presented by Rosén et al. (2011), as well as on 246 downcore marine samples from the Scotia Sea (Sprenk et al. 2013) and 183 downcore samples from Lake El'gygytgyn, NE Siberia (Meyer-Jacob et al. 2014), for which wet-chemical BSi measurements were available. The coefficient of determination (R^2) between the wet-chemically measured and the independent FTIR-inferred BSi concentrations as well as the root mean square error of prediction (RMSEP) (in % BSi) resulting from the external validation were considered to estimate the prediction ability of the developed calibration model. The performance of the independent calibration was further verified by its application to a 16.6-m-long lacustrine sediment sequence from Lake El'gygytgyn (core Lz1024; 67°30.13' N; 172°06.46' E; $n = 1,657$ samples) and to a 58.2-m-long marine sediment sequence from the Scotia Sea (core MD07-3134; 59°25' S, 41°28' W; $n = 575$ samples). The independent FTIR-inferred concentrations were then compared to the BSi concentrations inferred from the internal FTIR downcore calibrations based on wet-chemically measured BSi reference values for the respective record (Sprenk et al. 2013; Meyer-Jacob et al. 2014). For more information about the numerical analysis, see Vogel et al. (2008) and Rosén et al. (2010).

We used principal component analysis (PCA) to test the compatibility between the synthetic sediment mixtures and the natural sediment samples contained in the global model. To determine whether there are analogs in both datasets, a PCA was performed based on the spectral information between 3,750 and 450 cm^{-1} of the synthetic sediment mixtures, where

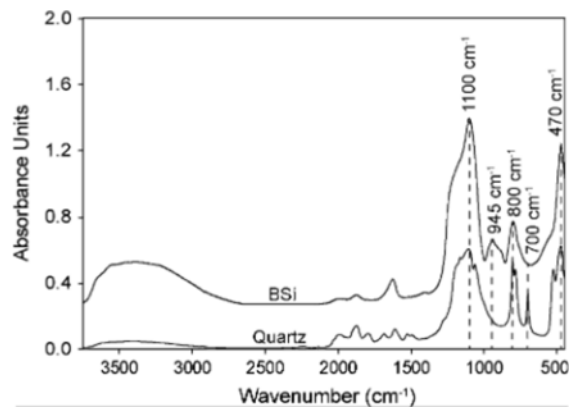


Fig. 1 FTIR spectra of biogenic silica (BSi) from Kieselgur Grube Klieken (Germany) and of pure quartz sand (Sigma-Aldrich, Chemie GmbH, Germany), showing characteristic IR absorption peaks around 1,100, 945, 800, and 470 cm^{-1} for BSi and around 1,100, 800, 700, and 470 cm^{-1} for quartz. FTIR spectra are stacked for better visualization

samples of the global model were treated as passive samples. SIMCA 13.0 (Umetrics AB, Umeå, Sweden) was used for PLS modeling and IBM SPSS Statistics 20 (IBM Corporation, NY, USA) for PC analysis.

Results

Spectral information

FTIR spectra of diatom extracts from Lake Yoa and Kieselgur Grube Klieken show the four main absorption bands of BSi (Fig. 1). These absorption peaks are centered around 470 cm^{-1} , caused by asymmetric bending vibrations of the $[\text{SiO}_4]$ tetrahedron (Gendron-Badou et al. 2003); around 800 cm^{-1} , associated with symmetric Si–O–Si stretching vibrations; around 945 cm^{-1} , assigned to Si–OH molecular vibrations; and around 1,100 cm^{-1} , related to the asymmetric stretching vibration mode of the $[\text{SiO}_4]$ tetrahedron (Schmidt et al. 2001; Patwardhan et al. 2006). FTIR spectra of samples with increasing BSi concentrations from the synthetic sediment mixture series between Kieselgur Grube Klieken diatom extracts and Lake Towuti sediments highlight the correlation of these spectral regions to the BSi content (Fig. 2). Hydroxyl molecules embedded in the molecular structure of BSi absorb IR radiation between 3,600 and 2,800 cm^{-1} (Moenke 1974), whereas the absorption band at around

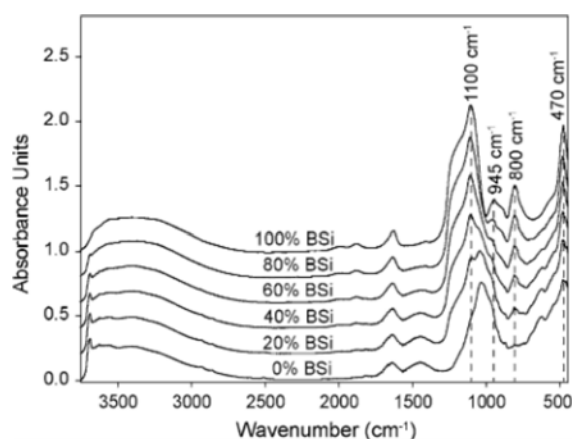


Fig. 2 FTIR spectra of samples with increasing biogenic silica (BSi) concentrations from the synthetic sediment mixture series between Kieselgur Grube Klieken diatom extracts and Lake Towuti sediments. FTIR spectra are stacked for better visualization

$1,630\text{ cm}^{-1}$ is linked to H–O–H bending vibrations within water molecules (Gendron-Badou et al. 2003; Pironon et al. 2003) that are adsorbed to the sample material and KBr. The differentiation of amorphous (BSi) and crystalline (quartz) phases of SiO_2 in FTIR spectra is facilitated by an additional distinct absorption peak of quartz at around 695 cm^{-1} related to symmetric bending vibrations of the $[\text{SiO}_4]$ tetrahedron (Hlavay et al. 1978) (Fig. 1).

Statistical performance

The calibration between FTIR spectral information and known BSi concentrations based on the 306 samples of the independent calibration set (0–100 % BSi) resulted in a five-component PLS model with an R^2_{cv} of 0.97 and an RMSECV of 4.7 % (4.7 % of the gradient) (Table 1; Fig. 3). The calibration model was externally validated by applying it to all available natural sediment samples with wet-chemically measured BSi reference values, giving an R^2 of 0.87 and an RMSEP of 5.9 % (9.5 % of the gradient) (Table 1; Fig. 4a). We applied the independent calibration to different sample subsets to further assess the model performance. The resulting R^2 and RMSEP are 0.91 and 6.7 % (12.2 % of the gradient) for downcore lacustrine sediment samples from Lake El'gygytgyn (core Lz1024; $n = 205$; 2–28 % BSi), and 0.71 and 9.3 % (15.7 % of the

Table 1 Statistical performance of the independent calibration PLS model for biogenic silica (BSi) based on synthetic sediment mixtures

Model	Independent calibration
PLS components	5
Samples (n)	306
Min (BSi %)	0
Max (BSi %)	100
Mean (BSi %)	51.8
SD (BSi %)	28.8
R^2_{cv}	0.97
RMSECV	4.7
RMSECV (% gradient)	4.7
R^{2a}	0.87
RMSEP ^a	5.9
RMSEP (% gradient) ^a	9.5

^a Resulting from the model application to 1,245 natural sediment samples

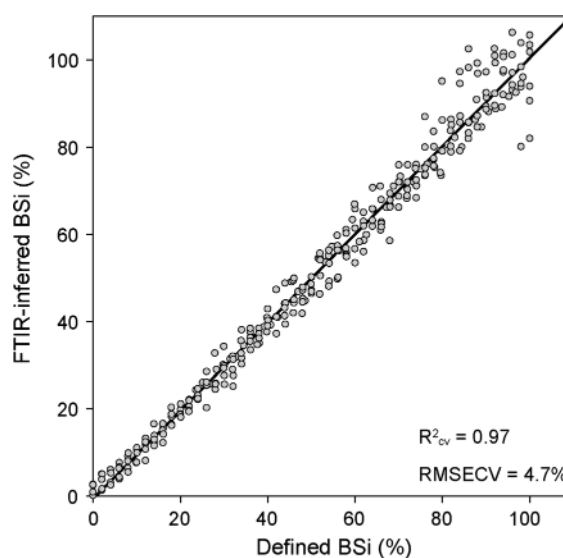


Fig. 3 Defined biogenic silica (BSi) concentrations of the synthetic sediment mixtures (*x*-axis) versus independent FTIR-inferred concentrations (*y*-axis) of BSi with the cross-validated coefficient of determination (R^2_{cv}) and root mean square error of cross-validation (RMSECV) resulting from the internal validation of the independent calibration

($n = 246$, 5–60 % BSi), 0.76 and 2.9 % (11.2 % of the gradient) for downcore lacustrine sediment samples from Lake El'gygytgyn (core Lz1024; $n = 205$; 2–28 % BSi), and 0.71 and 9.3 % (15.7 % of the

Fig. 4 Conventionally measured (*x*-axis) versus independent FTIR-inferred concentrations (*y*-axis) of biogenic silica (BSi) with the coefficient of determination (R^2) and root mean square error of prediction (RMSEP) resulting from the external validation of the independent calibration performed on (a) all available natural lacustrine and marine sediment samples, (b) downcore marine sediment samples from the Scotia Sea, (c) downcore lacustrine sediment samples from Lake El'gygytyn, and (d) surface sediment samples from northern Swedish lakes

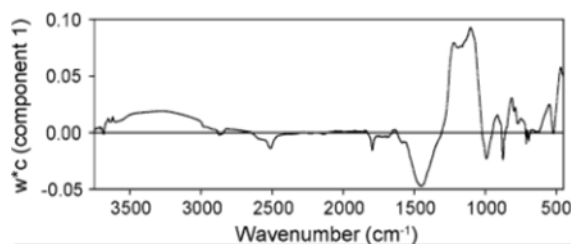
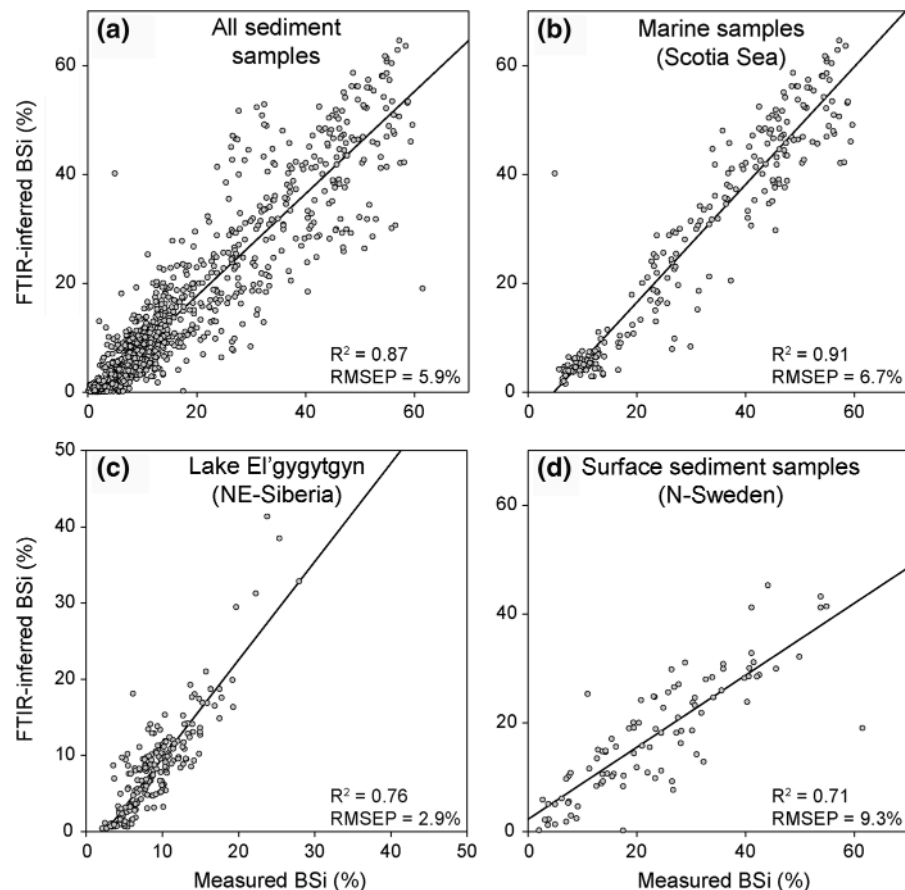


Fig. 5 Loadings of the independent calibration for biogenic silica (BSi), showing the contribution of each wavenumber to the partial least squares regression (PLSR) model. The loadings are expressed as weight vectors ($w \cdot c$) of the first PLS model component (*x*-axis) and the corresponding spectral range (*y*-axis). Positive weight vectors indicate wavenumbers positively correlated to the BSi content and negative weight vectors indicate wavenumbers negatively correlated to BSi concentration

gradient) for surface samples from northern Swedish lakes ($n = 94$, 2–62 % BSi) (Fig. 4b–d). The loadings of the first PLSR component, which explain 56 % of

the variance in the FTIR spectra (*x*-variable) and 61 % of the variance in the BSi concentration (*y*-variable), are distinctly positively correlated to the BSi content in the spectral regions 3,674–2,985, 1,296–1,028, 945–891, 847–721, 607–532, and 513–450 cm^{-1} (Fig. 5). Pronounced negative correlations occur at 2,594–2,482, 1,807–1,780, 1,605–1,327, 1,018–962, 885–868, 714–710, and 696–692 cm^{-1} . A PCA of the IR spectral information of the synthetic sediment mixtures contained in the independent calibration shows that the first two principal components (PC) explain 78.2 % of the variance, with 49.5 % explained by PC1 and 28.7 % by PC2.

Discussion

The independent calibration based on the synthetic sediment mixtures with defined BSi content shows a strong correlation between known and FTIR-inferred

BSi concentrations as indicated by the high R^2_{cv} of 0.97 and low RMSECV of 4.7 % (4.7 % of the gradient) (Fig. 3). The strong correlation highlights the direct relationship between the BSi concentration of a sample and the amount of IR radiation absorbed by the sample. Spectral regions positively correlated to the BSi content correspond well with the absorption bands of BSi centered around 470, 800, 945, and 1,100 cm^{-1} . These spectral ranges, however, are not unique to BSi and are also, at least partly, associated with other sediment components such as clay minerals and quartz (Hlavay et al. 1978; Madejová and Komadel 2001). For example, the absorption peak around 800 cm^{-1} is also characteristic for quartz and therefore complicates a BSi quantification based on the intensity of this absorption band only (Chester and Elderfield 1968). PLS modeling, however, also considers spectral regions that are negatively correlated with the variable of interest, which compensates for spectral overlaps by other sediment components. Because the BSi concentration reflects the ratio between BSi and non-BSi in the sediment, spectral regions negatively correlated with the BSi concentration are associated with absorption features of all remaining components in the synthetic mixtures. For example, calcite is characterized by spectral absorption around 2,545, 1,812, 1,435, 876, and 712 cm^{-1} (Huang and Kerr 1960); the absorption band unique for quartz compared to BSi is situated around 695 cm^{-1} (Hlavay et al. 1978); and spectral features related to Si–O stretching vibrations of clay minerals are centered between 1,050 and 1,000 cm^{-1} (Madejová and Komadel 2001). As with wet-chemical digestion techniques, a differentiation between BSi and other forms of amorphous silica such as volcanic glasses, duripans or hydrothermal concretions (Conley and Schelske 2001) is not possible by FTIR spectroscopy because of their analog structure and composition and consequently similar IR signature. In general, these compounds do not significantly contribute to the composition of most marine and lacustrine sediment, but need to be considered if present in the catchment of a study site.

When applied to natural sediment samples, the independent calibration shows a strong correlation between FTIR-inferred and wet-chemically measured BSi concentrations ($R^2 = 0.87$) and a RMSEP of 5.9 % (9.5 % of the gradient), indicating a good

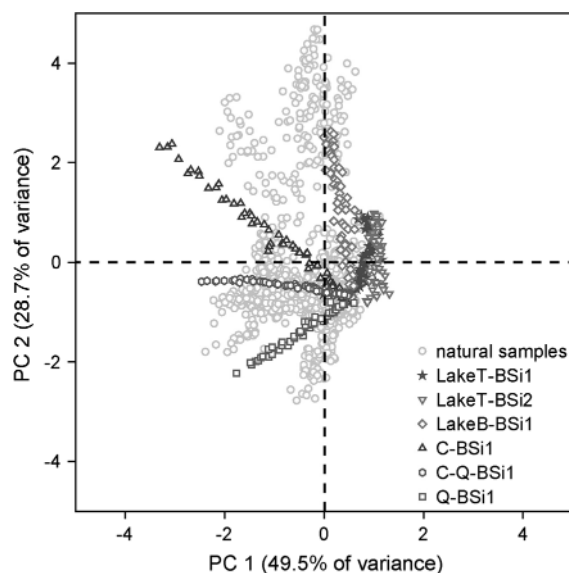


Fig. 6 Principal component analysis (PCA) of the FTIR spectral information performed on the synthetic sediment mixtures of the independent calibration. Natural sediment samples are plotted passively to underline the analogy of both sample sets. (BSi1 = diatom extract from Lake Yoa, BSi2 = diatom extract from Kieselgur Grube Klieken, LakeT = sediment from Lake Towuti, C = calcite, Q = quartz)

prediction ability of the general trend and good prediction accuracy with respect to the absolute values. The overall good prediction ability of the independent calibration cannot, however, hide the fact that the FTIR-inferred BSi concentration for certain samples differs noticeably from the conventionally measured concentration (Fig. 4a). This deviation arises from two limitations: 1) measuring uncertainty of the conventional wet-chemical digestion method and 2) simplification of the sediment composition in the independent calibration. In a comparison among 30 laboratories using wet-chemical digestion techniques to quantify BSi, Conley (1998) showed that measured concentrations for the same sample could vary considerably. The percentage standard deviation of the mean ranged from 67.5 % for a sample with low BSi content (1.31 ± 0.88 %) to 21.2 % for a sample with high BSi content (44.3 ± 9.38 %).

The second limitation results from the nature of the synthetic sediment mixtures used in this study. Variations of BSi concentrations in natural sediments are commonly accompanied by changes in the general sediment composition, e.g. changes in the quality and

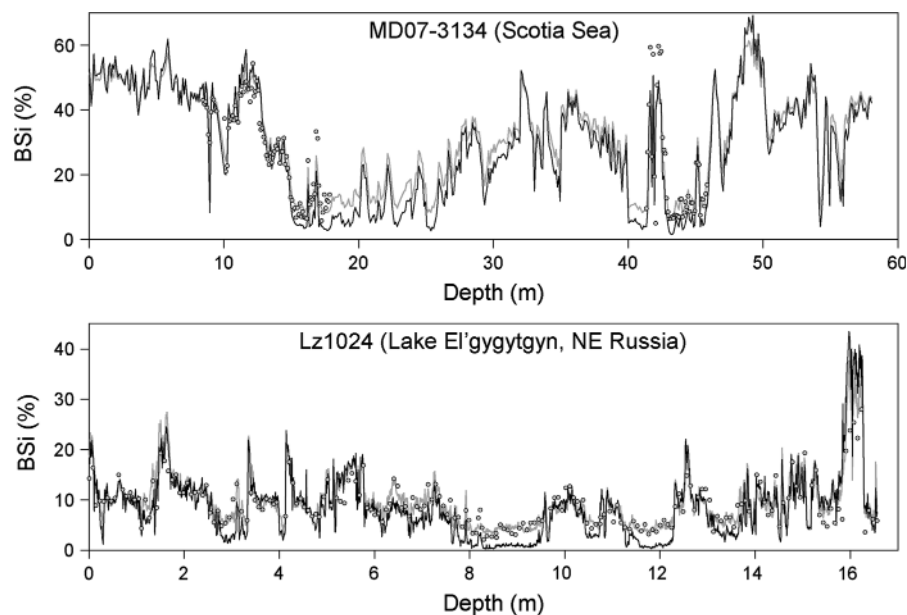
quantity of organic and inorganic matter. The independent calibration, however, is based on six synthetic sediment mixture series, each a two-component system, in which only the BSi content varies, whereas the composition of the second component remains unchanged. The distribution of the passively plotted natural sediment samples in the PCA biplot of the synthetic sediments shows that, overall, the variance in both sample sets is comparable (Fig. 6). For several natural samples, however, there is no direct analog in the independent calibration, indicated by their distance to the nearest synthetic sample. This lack of direct analogs at this stage potentially leads to less accurate BSi estimates by the independent calibration for some samples.

The independent calibration shows the highest accuracy for marine sediments from the Scotia Sea [$R^2 = 0.91$, RMSEP = 6.7 % (12.2 % of the gradient)] (Fig. 4b). Although simplified, these deep-sea samples can be seen as a two-component system that consists mainly of BSi and detrital material (Weber et al. 2012). Changes in their general sediment composition are driven mostly by changes in BSi concentration, rather than by other sediment components (Hüneke and Mulder 2011). Good, but somewhat lower model performance was also obtained for sediment samples from Lake El'gygytgyn [$R^2 = 0.76$, RMSEP = 2.9 % (11.2 % of the gradient)] (Fig. 4c) and for surface samples from northern Swedish lakes [$R^2 = 0.71$, RMSEP = 9.3 % (15.7 % of the gradient)] (Fig. 4d). The somewhat lower prediction accuracy for these lacustrine samples, in comparison to the marine samples, is likely a result of a more complex and lake-specific sediment composition, driven by somewhat more dynamic catchment and in-lake processes. The somewhat poorer performance for organic-rich samples from northern Swedish lakes [LOI up to 87 %; (Bigler and Hall 2002)] most likely arises from the lack of samples with higher organic matter content and low variability with respect to organic matter composition in the independent calibration. The independent calibration might be improved by using synthetic sediment mixtures that fulfill these composition criteria, which would overcome the above-mentioned limitations and improve the prediction accuracy for samples with higher organic matter concentrations. It is important to note that this evaluation of the independent calibration is based on results from conventional wet-chemical

techniques as reference values, and is thus not entirely adequate because of the uncertainty of the reference method itself; consequently, this evaluation likely underestimates the true model performance of the independent calibration. At present, there is no alternative to this approach because of the lack of a broad range of BSi standards.

Application of the independent calibration to full sediment sequences from the Scotia Sea and Lake El'gygytgyn, and their comparison to reconstructions based on internal calibrations using wet-chemically measured reference values for the respective records, show that results of the two approaches are highly correlated, with R^2 values of 0.98 and 0.92, respectively. Both models, i.e. the independent calibration based on synthetic sediment mixtures and the internal calibration built on a subset of samples from the sediment records themselves, describe the same trend throughout the sequences, but show differences with respect to absolute values (Fig. 7). For instance, the independent calibration indicates lower concentrations in samples at the lower end of the calibration range, compared to the inferred values based on the reference values from the wet-chemical leaching method. A likely explanation for this potential overestimation of low concentrations by the internal calibration approach is the fact that the underlying wet-chemical BSi measurements used for the calibration models were not corrected for possible dissolution of minerogenic silica from alumino-silicates during the leaching process (Kamatani and Oku 2000). This process is particularly relevant for samples with low BSi content, and correction for the minerogenic contribution to the leached silica requires determination of Al in the leachate and the sediment mineralogy by, e.g. X-ray diffraction analysis (Ohlendorf and Sturm 2008 and references therein). For Lake El'gygytgyn, the difference between BSi concentrations inferred using the two different FTIR calibration approaches is particularly pronounced at about 8 m (* 185,000 years BP) and 12 m (* 226,000 years BP) depth. For these sample levels, wet-chemical measurements, and consequently the calibration using these measurements as reference values, predict concentrations around 5 %, whereas the independent calibration indicates an almost complete absence of BSi. Total diatom counts for Lake El'gygytgyn also indicate that these periods are almost devoid of diatoms (Snyder et al. 2013) and thus corroborate

Fig. 7 Downcore plot of FTIR-inferred (line plots) and wet-chemically measured (grey circles) biogenic silica (BSi) concentrations for the sediment sequences from the Scotia Sea and Lake El'gygytgyn. FTIR-inferred concentrations are based on the independent calibration (black line) and internal calibrations based on wet-chemical measurements for the respective record (grey line) (Sprenk et al. 2013; Meyer-Jacob et al. 2014)



the more accurate BSi estimate from the independent calibration. Overall, good agreement between the two approaches highlights the robustness of BSi reconstructions based on FTIRS and PLS modeling.

Conclusions

We employed synthetic sediment mixtures to establish a calibration for determination of BSi in sediment samples using FTIRS, independent from conventional methods. The use of defined mixtures between BSi (diatom extracts) and natural sediments, quartz or calcite facilitates evaluation of the independent calibration, unbiased by measurement uncertainty associated with wet-chemical digestion methods. The obtained model shows strong statistical performance and its application to natural marine and lacustrine sediment samples provides reliable results (RMSEP = 5.9 %) with a high correlation between FTIR-inferred and conventionally measured BSi concentrations ($R^2 = 0.87$). Reconstructions based on the independent calibration and internal calibration models, which are based on reference values from wet-chemical methods, captured the same trend throughout two analyzed sediment sequences, but showed differences with respect to absolute values. Additional studies that include BSi standards are required to better understand

this methodological deviation and to allow more adequate evaluation of the independent calibration by comparing the method to known absolute values rather than results from wet-chemical measurements, which have their own uncertainty.

The independent calibration yields particularly good results for samples with comparatively simple sediment composition, in which changes are dominated by BSi variations. In the case of more complex sediment composition, for example, one that includes changes in the quantity and quality of organic matter, the calibration exhibits somewhat lower model performance because of the fact that the synthetic mixtures in the calibration do not fully cover the spectral variance measured in natural sediments. To overcome this limitation and improve the independent calibration, it will be important to add additional synthetic mixtures that reflect the full range of sediment matrices encountered in natural sediments. The most obvious component to include in the independent calibration mixtures would be organic matter, which in the natural samples used in this study ranged up to 87 %.

This study demonstrated that an independent calibration for FTIR-inferred BSi concentration can be developed and applied to any sediment sample. This approach avoids the additional measuring uncertainty introduced by wet-chemical reference methods. It also

eliminates the necessity to analyze a subset of samples for BSi using conventional wet-chemical methods and develop an internal calibration for each new project.

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