Climate change in southern South America during the last 51 ka based on geochemical analyses of Laguna Potrok Aike sediments

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Abstract

The climate archive Laguna Potrok Aike is located in a scarcely studied yet key area of the southern hemisphere. Recent studies on the role of the Southern Hemispheric Westerlies and the Southern Ocean circulation patterns in the global climate system stress the importance of this area. The Laguna Potrok Aike lacustrine sediment record covers the past 51 ka of environmental change. In order to capture the high variability in the climate system, high resolution analysis is particularly important. Therefore, aside from conventional methods and X-ray fluorescence scanning, infrared spectrometry, a relatively new method for analyzing sediment biogeochemistry, was applied. The Diffuse Reflectance Fourier Transform Infrared Spectrometry technique has proven to provide the most reliable calibration models for the analysis of the organic and carbonaceous fraction of the Laguna Potrok Aike sediments. For glacial sediments, paleoenvironmental reconstructions for Laguna Potrok Aike rely on proxies recording variations in organic versus clastic input to the lacustrine system. Increases in organic productivity (mainly aquatic moss growth and diatom blooms) may have been caused by ameliorations of the climatic conditions in the Laguna Potrok Aike area. At the same time, sediment availability for erosional processes would have been limited by the development of soils and vegetation cover. Intervals with more organic sediment compositions are often associated with periods of Antarctic warming (Antarctic A-events, the postglacial warming and the Younger Dryas chronozone). During intervals of highly clastic, coarse grained sediment we assume that lacking vegetation and erosion related to high waves and flash flood events increased sediment availability in the catchment and on the lake shore. The transport of this material to the lake center would have been facilitated by strong winds. The sediment is especially clastic and coarse grained during the presumably cold, arid and windy Oxygen Isotope Stage 2. Despite these conditions, the lake level must have remained relatively high during glacial conditions as inorganic carbonate is not precipitated until the end of the Late Glacial. Glacial high lake levels may be attributed to increased runoff over permafrost grounds, reduced evaporation due to colder temperatures and lacking influence of the Southern Hemispheric Westerlies. The southward shift of the Southern Hemispheric Westerlies over the latitudes of Laguna Potrok Aike is not assumed to have occurred prior to ca. 9.4 cal. ka BP; the onset of continuous inorganic carbonate precipitation. Throughout the Holocene the variability in the total inorganic carbon record shows the frequent lake level fluctuation probably related to shifts in the position of the Southern Hemispheric Westerlies.

Kurzfassung

Der Maarsee Laguna Potrok Aike liegt in einem kaum erforschten, aber für die Klimaforschung sehr wichtigen Gebiet der südlichen Hemisphäre. Die im Rahmen des PASADO-Projektes gewonnenen See-Sedimentkerne bieten ein lückenloses Klimaarchiv der letzten 51 ka. Um die hohe Variabilität des Klimasystems in diesem Zeitraum zu erfassen, sind hochauflösende Analysen besonders wichtig. Deshalb wurden zur Beschreibung der Geochemie, neben herkömmlichen Methoden, die deutlich schnelleren Verfahren des Röntgenfluoreszenz-Scannings und der Infrarot-Spektrometrie angewandt. Die in der Paleolimnologie bisher kaum genutzte Infrarot- Spektrometrie basiert auf der Tatsache, dass Infrarotstrahlung von unterschiedlichen minerogenen und organischen Substanzen jeweils bei spezifischen Wellenlängen absorbiert wird. Eine Vergleichsstudie ergab, dass die Diffuse Reflectance Fourier Transform IR Spectrometry (DRIFTS) Methode die zuverlässigsten Kalibrierungsmodelle zur Analyse der Organik- und Karbonat-Anteile liefert. Während des Glazials weisen Schwankungen der organischen und klastischen Sedimentanteile auf Veränderungen der Paläo-Umweltbedingungen um die Laguna Potrok Aike hin. Intervalle mit erhöhtem organischen Sedimentanteil hängen oft mit Erwärmungsperioden der Antarktis (die Jüngere Dryas, die postglaziale Erwärmung und die sogenannten antarktischen „A-Events“) zusammen. Der Anstieg von lakustriner Produktivität (hauptsächlich aquatische Moose und Algenblüten) könnte durch eine Verbesserung der klimatischen Bedingungen verursacht worden sein. Bodenbildung und Vegetationsbedeckung könnte gleichzeitig die Sedimentverfügbarkeit reduziert haben. Während des kalten, trockenen und windigen Sauerstoff-Isotopenstadiums 2 wurde vermehrt klastisches grobkörniges Material abgelagert. Für diese Intervalle wird angenommen, dass die Sedimentverfügbarkeit im Einzugsgebiet und am Seeufer erhöht war; möglicherweise infolge einer geringeren Vegetationsdichte und einer verstärkten Erosion durch erhöhten Wellengang und/oder aufgrund von Sturzfluten. Starke Winde könnten den Transport grobkörnigen Materials in das See Zentrum ermöglicht haben. Die glazialen Sedimentablagerungen sind weitgehend karbonatfrei, was auf einen relativ hohen Seespiegel hindeutet. Erhöhter Oberflächenabfluss über Permafrost-Böden, eine reduzierte Verdunstung durch die kälteren Temperaturen und der fehlende Einfluss der südhemisphärischen Westwinde könnten die Ursachen hierfür gewesen sein. Erst am Ende des Spätglazials deuten Karbonate im Sediment auf Niedrigwasserstände des Sees hin. Die kontinuierliche Karbonat-Ausfällung beginnt erst um ca. 9.4 cal. ka BP. Ab diesem Zeitpunkt hat vermutlich die Verstärkung der südhemisphärischen Westwinde aridere Bedingungen verursacht. Während des Holozäns deuten die Variationen des Karbonatanteils im Sediment auf Seespiegelschwankungen hin, die wahrscheinlich auf Veränderungen in der südhemisphärischen Westwindstärke zurückzuführen sind.

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Mein Dank gilt auch meinen Freunden und diversen Familienmitgliedern, meinem Onkel Horst für die schönen Jahre in der Katrepelerstraße und insbesondere meinen Eltern und meiner Schwester für ihre kontinuierliche Unterstützung bei all meinen Unterfangen.

Chapter 1:

Introduction

1. Laguna Potrok Aike - a key site

In order to accurately model global climate, paleoclimatic reconstructions from sparsely studied regions such as southern South America are necessary (Voelker, 2002; Neukom et al., 2011). The southern hemispheric mid-latitudes are of special importance due to their proximity of the climatically sensitive area of Antarctica and the Southern Ocean (Fig. 1.1; White and Peterson, 1996; Knorr and Lohmann, 2003). Currently an important role of the Southern Hemispheric Westerlies (SHW) in global climate change is being suggested by Andersen et al. (2009) and Toggweiler and Lea (2010). When the SHW are in a southerly position, aligned with the Antarctic Circumpolar Current, it is assumed that they draw more

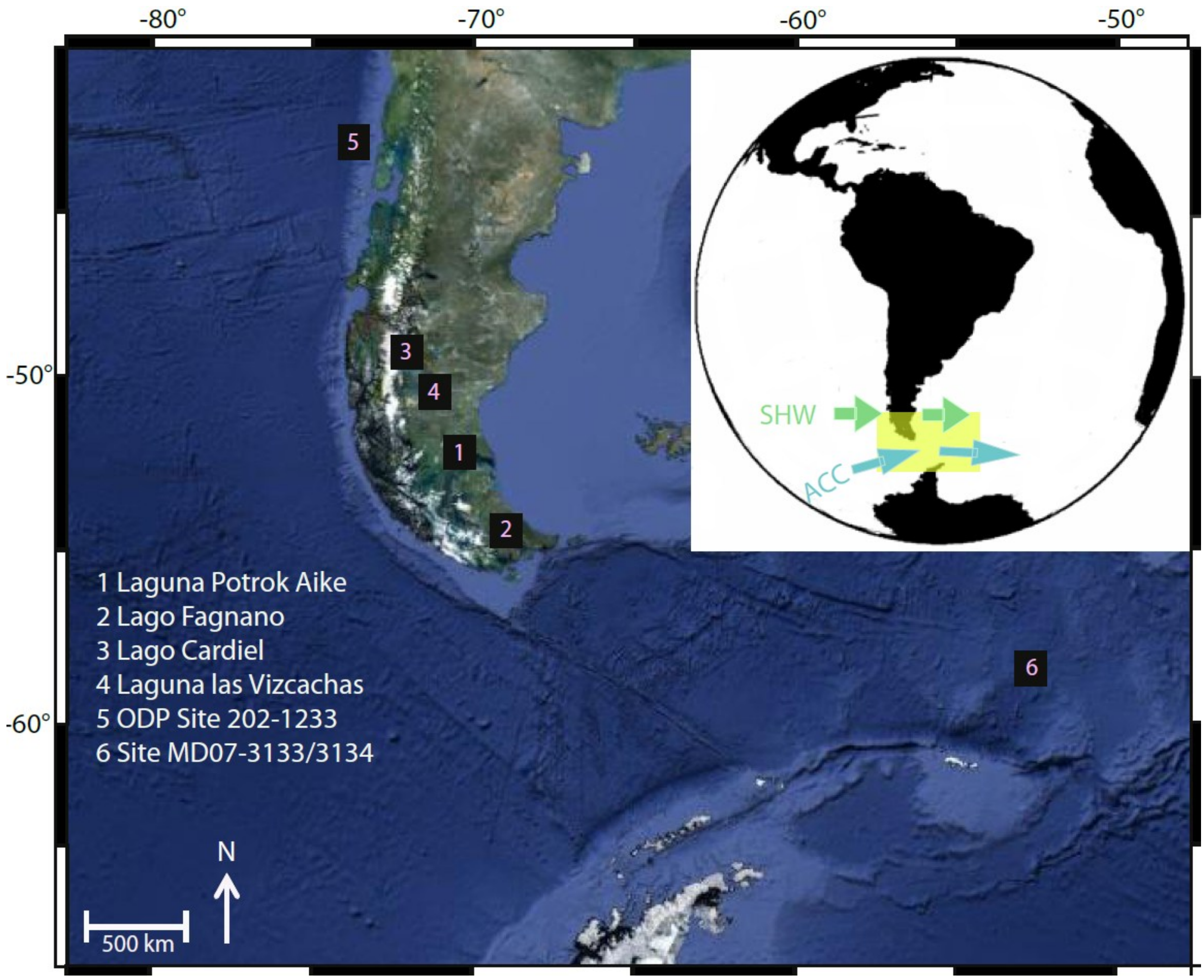

Fig. 1.1 Research area and selected lacustrine and marine climate archives. The location of the studied area is shown on the globe along with the present day position of the Southern Hemispheric Westerlies (SHW) and the Antarctic Circumpolar Current (ACC).

CO_2 rich deep water to the surface, causing an increase in atmospheric CO_2. An ongoing discussion deals with the cause for variations in atmospheric dust concentrations during glacial times (Weber et al. 2012). Fluctuations of dust input potentially have global climate implications, their cause however remains unclear. Prospero et al. (2002) identify Patagonia as a source area of dust and Basile et al. (1997) and Iriondo (2000) assume that the SHW act as a major dust transport mechanism. In the southern hemispheric mid-latitudes several marine sediment cores archive paleoclimatic variations, however often at lower temporal resolution (Fig. 1.1; Lamy and Kaiser, 2009; Weber et al. 2012). Since landmass is scarce, continental archives are rare in this region and do not offer continuous high resolution sediment records further back than the Holocene and the Late Glacial (Fig. 1.1; Gilli et al., 2005; Haberzettl et al., 2007; Fey et al. 2009; Moreno et al., 2009; Waldmann et al., 2009). The key location of Laguna Potrok Aike has attracted scientific attention to this climate archive (e.g. Zolitschka et al., 2006; Mayr et al., 2007a, b; 2009, Wille et al., 2007; Anselmetti et al., 2009; Kastner et al., 2010). In the framework of the "South Argentinean Lake Sediment Archives and Modelling" (SALSA) project a 19 m core, that continuously documents climatic and environmental variability during the last 16 ka, was recovered (Haberzettl et al., 2007). In order to extend this continuous high resolution climate record further back in time creating a continental counterpart of existing Southern Ocean marine records and Antarctic ice cores, the ICDP deep drilling campaign "Potrok Aike Maar Lake Sediment Archive Drilling Project" (PASADO) was initiated.

2. The PASADO project

During the ICDP deep drilling campaign PASADO in austral spring 2008, 533 m of lacustrine sediments were recovered from the deepest part of Laguna Potrok Aike. 7 holes were drilled at 2 sites down to a maximum depth of 101.5 m below lake floor (Fig. 1.2). After completion of non-destructive core analyses a composite profile with the length of 106 m was established from cores of site 2 according to macroscopic sedimentary structures and Multi-Sensor Core Logger (MSCL) and X-ray fluorescence (XRF) profiles (Ohlendorf et al., 2011). For age-depth modeling redeposited sediment was identified by visual inspection and removed from the composite profile resulting in an event-corrected composite profile of 45.80 m. A consistent mixed-effect regression age-depth model based on 58 radiocarbon dates measured on organic macro remains results in a basal age of 51.2 ka cal. BP. The chronology was validated with geomagnetic relative paleointensity data and tephra correlation (Kliem et al., submitted). Preliminary results of core catcher analysis have been published by Recasens et al. (2012). The results presented in this study are the first results of the entire high resolution record published thanks to the application of rapid measurement techniques.

3. State of the art - infrared spectrometry

Rapid and cost-efficient analysis techniques are especially important for the analysis of long sediment sequences from deep drilling campaigns. Several core scanning and logging techniques have become standard practice in order to rapidly analyze these long records at

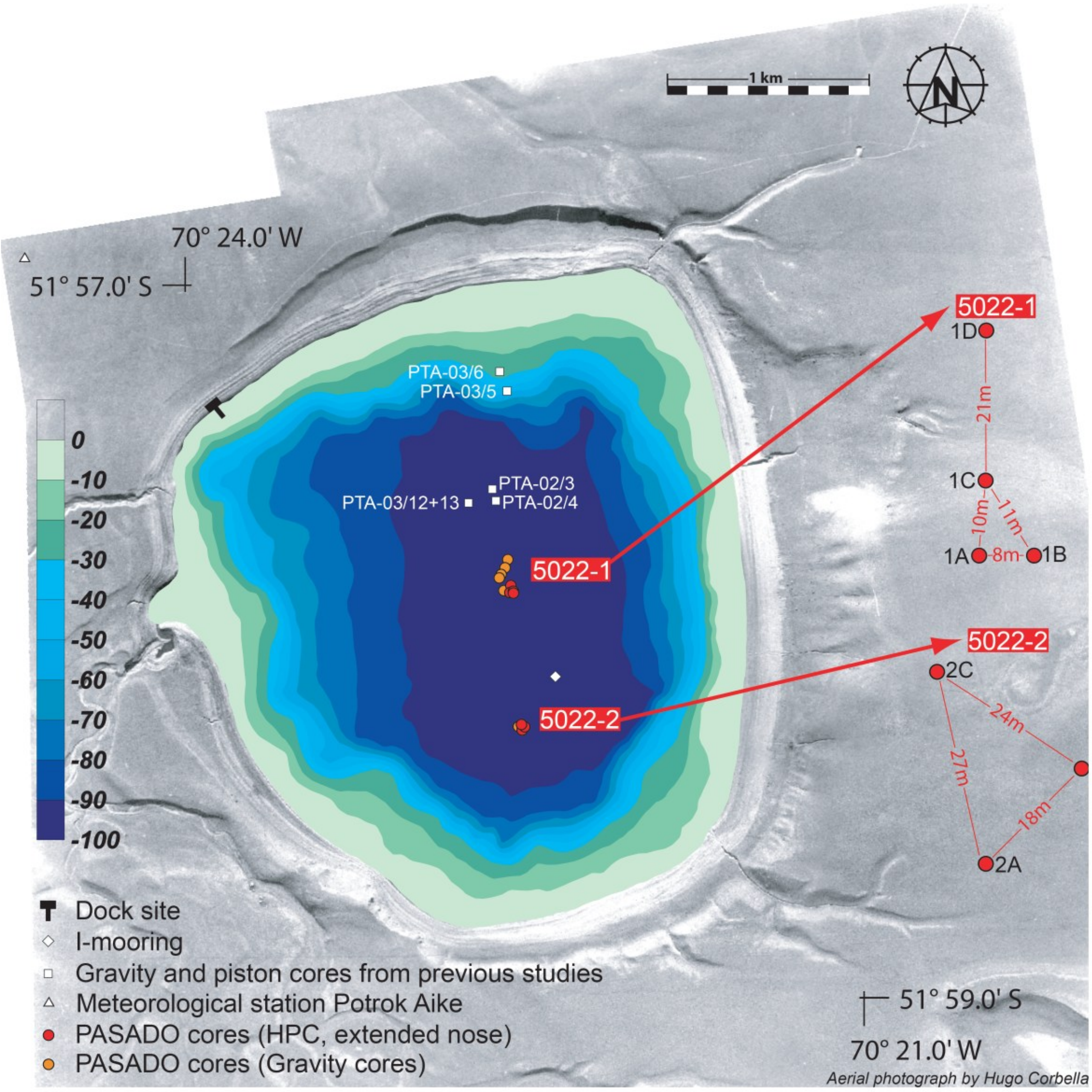

Fig. 1.2 Map showing the the position of the drill sites on the bathymetric map of Laguna Potrok Aike. Depth intervals given in m below lake surface.

high resolution (Zolitschka et al. 2001). However, the analysis of biogenic silica and total organic and inorganic carbon via IR spectrometry, a rapid cost efficient alternative to time consuming conventional measurements, is just recently emerging in paleolimnology (Rosen at al., 2010;2011; Vogel et al., 2010). Depending on their structural and atomic composition, molecules absorb IR radiation at different wavelengths. Organic and inorganic compounds in lake sediments therefore have unique infrared spectra (Kellner et al. 1998). However, IR analyses rely on calibration models between the spectra and the conventionally measured sediment properties as spectra of lake sediments are too complex to be interpreted directly (McCarty et al., 2002). Up till now it has been necessary to develop internal models for each coring site - a step that made the application of IR technology futile on short cores. Laguna Potrok Aike sediment contributed to a world-wide calibration dataset which allows to develop robust and universally applicable calibration models (Rosen et al., 2011). This study was an important milestone in the development of the IR technique as a standard tool in paleolimnology. Demonstrating that the relationship between compound-specific molecular vibrations and compound concentrations remains unchanged, irrespective of the lake's setting or age, enhanced the credibility of the method.

4. Objectives and outline

The methodological aim of this study is to explore the application of IR technologies to lacustrine studies. In chapter 2 we compare different IR techniques in order to find the most accurate and efficient tool for the specific requirements of lake sediment analysis. Having selected the best tool we apply IR technique to the long PASADO sediment record in chapter 3. The goal is to obtain a high resolution record of variations in organic and carbonaceous sediment content over the past 51 ka. The geochemical data obtained via XRF scanning is analyzed in chapter 4 to obtain further insight into the clastic sediment component. From this high resolution biogeochemical record we aim to make inferences concerning the paleoenvironment. These reconstructions are placed in the context of established regional paleoclimatic archives in an attempt to provide evidence for the development of ideas concerning the dust fluxes and the role of the SHW in the global climate system.

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Chapter 2:

Comparative study of infrared techniques for fast biogeochemical sediment analyses

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Abstract

Analysis of sediment samples in the visible to mid infrared (IR) region requires small amounts of sample material and enables rapid and cost efficient geochemical analysis of mineral and organic sediment components. Here we use geochemical properties (total organic and inorganic carbon, biogenic silica, total nitrogen) from the ICDP deep drilling project PASADO to compare three different IR spectroscopy techniques: Diffuse Reflectance Fourier Transform IR Spectrometry (DRIFTS), Attenuated Total Reflectance Fourier Transform IR Spectroscopy (ATR-FTIRS) and Visible Near IR Spectroscopy (VNIRS). ATR-FTIRS and VNIRS are more rapid techniques compared to DRIFTS. Results show that calibration models developed using DRIFTS are most robust (correlation coefficient: R =0.92 for TIC, R=0.84 for BSi, R=0.97 for TOC, R=0.95 for TN). However, good statistical performance was also obtained by using ATR-FTIRS and VNIRS. When time and costs are limiting factors, these tools may be given preference for rapid biogeochemical screening.

Keywords: Diffuse Reflectance Fourier Transform Infrared Spectrometry (DRIFTS); Visible Near Infrared Spectroscopy (VNIRS); total inorganic carbon (TIC); total organic carbon (TOC).

Introduction

Large efforts are being made to recover long paleorecords from a diversity of natural archives. Especially for documenting abrupt climate variations, high resolution studies are of essential importance. For reliable interpretations, it is necessary to apply a multiproxy approach for climate reconstruction. However, multiproxy studies on long sediment cores at high resolution are time consuming and expensive. Analyses of geochemical parameters require sample pretreatments, relatively large sample sizes and various analytical techniques. The analysis of sediment samples in the visible to mid-IR region offers a potential solution. Small amounts (0.01-0.1g dry weight) of sample material are analyzed for different geochemical properties simultaneously in a rapid and cost efficient manner. Due to differences in their chemical structure and composition molecules and minerals exposed to visible to mid-IR radiation display characteristic vibrations that correspond to specific absorption bands which in turn relate to certain sediment characteristics. This comparative study of IR techniques was carried out in the framework of the Potrok Aike Maar Lake Sediment Archive Drilling Project (PASADO), one of the first ICDP projects where IR spectroscopy is used as an analytical tool. Laguna Potrok Aike is a 100 m deep maar lake located in the dry steppe of the Pali Aike Volcanic Field in southern Patagonia (Fig. A1; Zolitschka et al., 2006). DRIFTS has been successfully applied for the assessment of total organic carbon (TOC), total inorganic carbon (TIC), biogenic silica (BSi) and total nitrogen (TN) at various lacustrine sites (Vogel et al., 2008; Rosén et al., 2010). DRIFTS has the disadvantage of including a time-consuming step

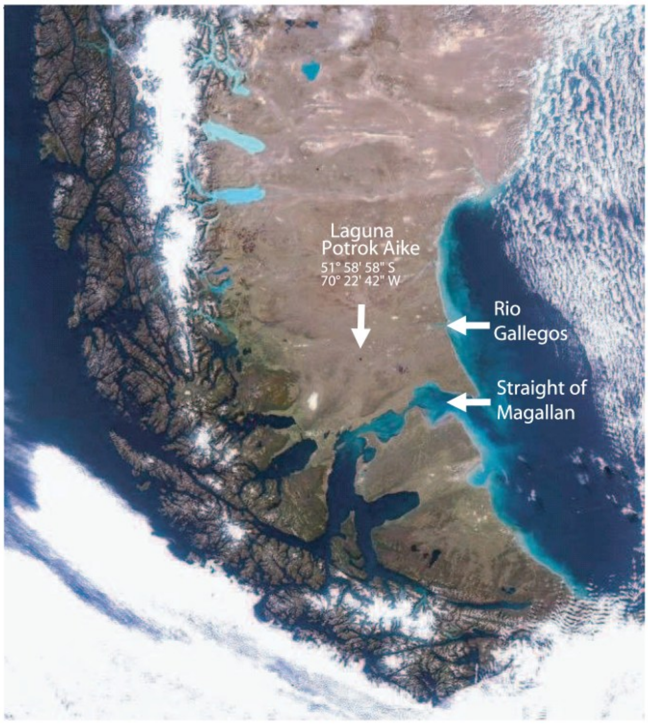

Fig. A1 Map showing the location of Laguna Potrok Aike in southern Argentina where sediment samples have to be diluted with spectrally inactive potassium bromide (KBr) (Du and Zhou, 2008). This is necessary because the intensity of absorption bands increases proportionally with sample thickness causing spectral distortions (Reeves, 2003). Dilution with KBr is not necessary if shorter wavelengths are used where bands are weaker due to the low intensity of vibrations (Colthup et al., 1990). VNIRS, avoiding the step of KBr dilution, has successfully been applied to measure various constituents of lake sediments including TC, TN and the number of diatoms (Malley et al., 1999). Still another option is limiting the path length of the IR beam into the sample. For ATR-FTIRS only evanescent waves interact with the sample, resulting in an attenuated signal. ATR-DRIFTS has been used in soil sciences (Linker et al., 2006) and for marine sediment cores (Mecozzi et al., 2006). However, to our knowledge, this is the first study to assess if ATR-DRIFTS can be used in a quantitative way to assess sediment properties in lake sediments. Diagenetic effects as well as overlapping and scattering effects have been found to distort spectra of minerogenic, volcanic and coarse-grained material (Gaffey, 1986). Therefore, we test the applicability of IR techniques to Laguna Potrok Aike sediment samples which is a prerequisite for this study. The main aim is to find the most accurate and efficient IR technique for the analysis of biogeochemical properties in this and other long lacustrine sediment archives.

2. Methods

2.1. Conventional measurements

199 core catcher samples from varying lithologies were used for calibration of the 101.5 m long PASADO record drilled in 2008 and from a 1 m long surface core recovered in 2002. Prior to conventional measurements, samples were freeze-dried and ground using mortar and pestle. The concentrations of TIC, TOC and TN were determined by an elemental analyzer (EuroEA, Eurovector). The manufacturer indicates an effective measurement range from 0.1-100 %. The precision of the measurement technique in our lab can be evaluated using the relative standard deviation of blank measurements which was 4% for nitrogen and 3 % for carbon. Biogenic silica was measured using the wet-chemical leaching method of Müller and Schneider (1993). The opaline material is leached by 1 M sodium hydroxide (NaOH) heated to 85°C, colored using molybdate and detected using a photometer. As biogenic silica completely dissolves very rapidly at the beginning of the leaching process it can be

Table 1 Statistical performance of calibration models for the estimation of geochemical properties of Laguna Potrok Aike sediments from DRIFTS, ATR-FTIRS and VNIRS spectra.

Statistics DRIFTS	TIC (%)	BSi (%)	TOC (%)	TN (%)
PLS components[e]	6	8	11	5
Samples (n)	199	173	199	199
Minimum	0,00	0,30	0,00	0,00
Maximum	3,62	9,10	7,62	0,55
Gradient	3,62	8,80	7,62	0,55
Mean	0,43	2,51	1,13	0,13
RMSECV[b]	0,27	0,76	0,25	0,03
RMSECV (% gradient)[c]	7,4	8,6	3,3	4,6
R^2_{CV} [a]	0,80	0,64	0,82	0,86
R[d]	0,94	0,84	0,95	0,95
Statistics ATR-FTIRS	**TIC (%)**	**BSi (%)**	**TOC (%)**	**TN (%)**
PLS components[e]	9	8	9	9
Samples (n)	199	173	199	199
Minimum	0,01	0,30	0,01	0,01
Maximum	3,62	9,10	7,62	0,55
Gradient	3,61	8,80	7,61	0,54
Mean	0,43	2,51	1,13	0,13
RMSECV[b]	0,23	0,76	0,33	0,03
RMSECV (% gradient)[c]	6,4	8,6	4,4	4,8
R^2_{CV} [a]	0,83	0,45	0,79	0,85
R[d]	0,94	0,84	0,95	0,95
Statistics VNIRS	**TIC (%)**	**BSi (%)**	**TOC (%)**	**TN (%)**
PLS components[e]	9	8	9	9
Samples (n)	199	173	199	199
Minimum	0,00	0,30	0,00	0,00
Maximum	3,62	9,10	7,62	0,55
Gradient	3,62	8,80	7,62	0,55
Mean	0,43	2,51	1,13	0,13
RMSECV[b]	0,30	0,78	0,24	0,03
RMSECV (% gradient)[c]	8,3	8,9	3,2	4,7
R^2_{CV} [a]	0,69	0,42	0,85	0,82
R[d]	0,94	0,84	0,95	0,95

[a] The coefficient of determination of cross validation (R^2_{CV}) assesses how a model made of a rotating 90% of the samples will work on an independent data set (the remaining 10% of the data).

[b] The RMSECV (root mean square error of cross validation) assesses the prediction error of the cross validation.

[c] Expressing the RMSECV as percentage of the calibration set gradient (RMSECV % gradient) gives a better insight on model performance.

[d] The model is used to predict the geochemical properties of the sediments from which it was constructed. The correlation coefficient (R) compares the inferred values with the results of conventional measurements.

[e] The number of components necessary for the best PLS model performance indicates the complexity of the model.

distinguished from minerogenic silica using the method of DeMaster (1981). In our lab, the relative standard deviation of blank measurements was 3.5%. Müller and Schneider (1993) report a degree of uncertainty around 0.4 wt % SiO_2 for samples, such as Laguna Potrok Aike sediments, with relatively low (10-2 wt %) opal content. Due to the strong base used for the measurement biases towards higher values may occur for measurements of samples with low BSi concentrations (Gehlen and van Raaphorst, 1993; Conley, 1998).

2.2. Infrared spectroscopy

The pre-treatment for all samples consisted of freeze-drying and grinding. For best results 5 ml stainless steel cylinders and one ball (Ø 1 cm) were used to grind approximately 3 g of sediment at 30 Hz with the "MM301 swing mill" (Retsch Inc, Germany). 120 s of grinding were necessary to assure that all particles were smaller than 63 µm. For the DRIFTS measurements, 11 (±0.1) mg of the sample was mixed with 500 (±0.5) mg of KBr. The hygroscopic KBr was dried prior to use in an oven at 105°C. Measurements took place in a temperature controlled laboratory (25°C) in which the samples were stored previously for more than five hours to equilibrate. The FTIR spectrometer "Bruker IFS 66v/S" (Bruker Optics GmbH, Germany) equipped with a diffuse reflectance accessory (Harrick Inc., USA) was used for analysis. Samples were measured with 64 scans under a vacuum of 4 mbar using a carrousel. The wavenumber range was from 400 to 3750 cm^{-1}, a data point was recorded every 1.9 cm^{-1}. FTIRS-ATR spectra were obtained from approximately 0.01 g of sample material using an "Alpha FT-IR spectrometer" with an Platinum-ATR accessory (Bruker Optics, Germany) which exerts a pressure of 389 bar. Data was collected at a resolution of 4 cm^{-1} with 40 scans in the wavenumber range between 400 and 3750 cm^{-1}. For the VNIRS measurements, approximately 0.1 g (0.5 ml) of sample material was analyzed with the diffuse reflectance technique using the "NIRSSystems 6500" instrument (FOSS NIRSystems Inc., USA). Measurements were obtained every 2 nm in the wavelength region between 400 and 2500 nm.

2.3. Numerical analyses

To minimize deviations in spectra that are due to varying measurement conditions in mid-IR spectra, wavenumbers without chemical information (3750-3800 and 2200-2210 cm^{-1}) were set to 0. VNIRS spectra do not contain specific wavenumbers suitable for baseline correction. The spectral region between 1800 and 2500 cm^{-1} was removed from ATR-FTIRS spectra because it is influenced by the diamond that forms the internal reflection surface. Multiple scatter correction (MSC) was used to remove noise-related deviations from all spectra (Geladi et al., 1985). Spectra of lake sediments are complex and cannot be directly interpreted in absolute quantities (Nguyen et al., 1991). Therefore, partial least square (PLS) regression, one of the most common techniques to extract information from visible to mid-IR data analysis (McCarty et al., 2002), is used to find correlations between spectra and conventionally measured sediment properties (Geladi and Kowalski, 1986). For normalization, all variables were centred to zero mean by subtracting their averages. In addition, the conventional measurements were scaled with their variance in order to give each y variable equal importance. This was not necessary for the x variables (wavelengths) since the axes already had the same length. Cross validation assesses repeatedly how a model made of a rotating 90% of the samples will work on an independent data set (the remaining 10% of the data). Therefore, this process can be used to determine the optimal number of components for the models. The statistical performance of these models was evaluated according to Rosen et al. (2010); Table 1). The software used for all analyses was SIMCA-P (Umetrics AB, SE 901 91 Umeå, Sweden).

3. Results and discussion

3.1. Model performance

Performances of all three techniques are comparable (Table 1; Fig. A2). Minor shortcomings are observed when reconstructing TOC using ATR-FTIRS and TIC using VNIRS. BSi would be the most interesting parameter to obtain because conventional measurements are time consuming and contain large errors (Conley, 1998). However, BSi models are generally less reliable probably due to large errors of conventional measurements. The performance of VNIRS and ATR-FTIRS BSi models are especially poor. This can be considered as a major drawback for these methods.

3.2. Loading plot analysis

Loading plot analysis of the first component is the most common tool for model performance evaluation (Vogel et al., 2008; Rosén et al., 2010). Models that rely on direct relationships between the component of interest and the spectra can be considered more reliable. Indirect relationships are explained by correlations between chemical properties. Simultaneous

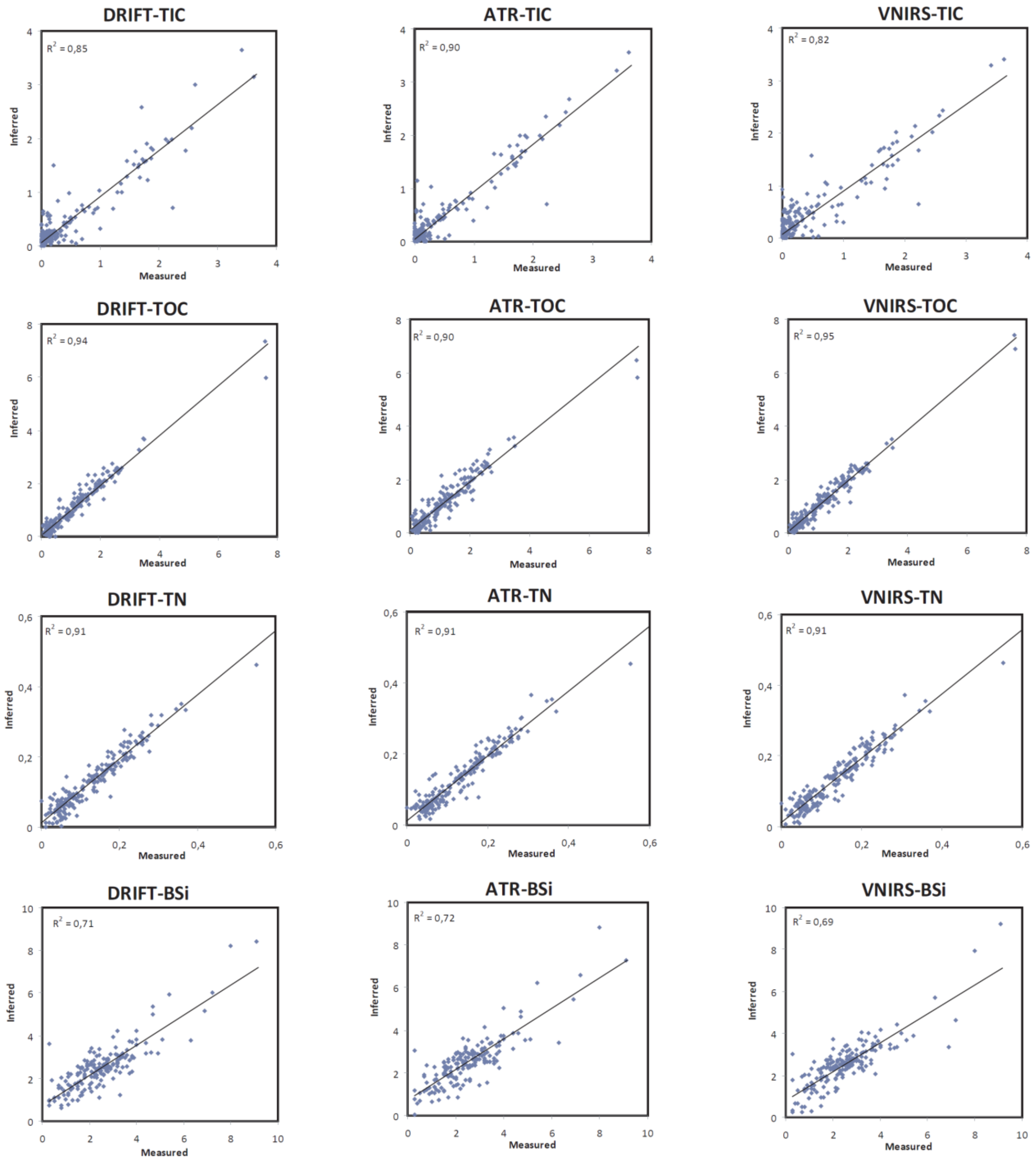

Fig. A2 Scatter plots of conventionally-measured (x-axis in %) versus DRIFTS, ATR-FTIRS and VNIRS inferred TOC, TIC, TN, and BSi concentrations (y-axis) for core catcher sediment samples from Laguna Potrok Aike

deposition of BSi, TOC and TIC is common (Koschel et al.,1987) and has also been observed in Laguna Potrok Aike (Haberzettl et al., 2005). Therefore, there are direct relationships between the wavelengths related to BSi (480, 540, 600, 650, 800, 920, 945 and 1050-1250 cm^{-1}; Moenke, 1974; Rosén et al., 2010), organic substances (1400-1750 cm^{-1}; Mecozzi et al., 2006), OH groups in organic and minerogenic components (2590-3630 cm^{-1}; Moenke, 1974), CH groups in organic compounds (2850-2920 cm^{-1}; Farmer, 1974) and calcite (710, 880, 1470, 1800 and 2520 cm^{-1}; White 1974; Gaffey 1986; Mecozzi and Pietrantonio 2006). Wavelengths due to mineral absorption (a large part of the spectral region 500-1050 cm^{-1}; Farmer, 1974) show negative correlations to TIC, TOC and BSi (Fig. 1). On the other hand, features in loading plots that cannot be explained by direct or indirect relationships between spectra and sediment composition are an indication of poor model performance. This is the case around 1000 cm^{-1} for ATR-FTIRS and in the 1800-2500 cm^{-1} region for DRIFTS spectra (Fig. 1). The region 2000-2500 cm^{-1} does not contain information relevant for sediment analysis and can therefore be excluded from the models. A detailed interpretation of loading plots from VNIRS is difficult due to the broad and overlapping spectral bands that prohibit the attribution of specific wavenumbers to certain constituents.

3.2.1. Indirect and direct relationships between mid-IR spectra and BSi contents

In the 1050-1250 cm^{-1} region the spectrum of an individual diatom valve shows high absorption (Rosén et al., 2010). The loading plots of the DRIFTS model support that this is most important region for BSi (Fig. 1). The models based on ATR-FTIRS spectra only partly rely on this wavenumber region (1180-1410 cm^{-1}). The loading plots show further regions (460, 480, 540, 600, 650, 800, 920 945 and 1100 cm^{-1}; Fig. 1) of slightly positive loadings which can be attributed to BSi (Lecomte, 1949; Moenke, 1974; Mecozzi and Pietrantonio, 2006).

3.2.2. Indirect and direct relationships between mid-IR spectra and TIC contents

Most inorganic carbon in Laguna Potrok Aike is present as calcite (Haberzettl et al., 2005). Absorbance from C-O vibrations in calcite is found in specific regions around 710, 880, 1470, 1800 and 2520 cm^{-1} (White, 1974; Gaffey, 1987; Mecozzi and Pietrantonio 2006). The loading plot shows that the absorbance bands at 710, 870 and 1400 cm^{-1} of ATR-FTIRS and 725, 890, 1490, 1850 and 2595 cm^{-1} of DRIFTS spectra are important for model performance. Calcite related peaks at wavenumbers of 1800 and 2520 cm^{-1} are in the region influenced by diamond absorption in the ATR-FTIRS spectra. Therefore, this region cannot be used for any interpretation of sediment properties (Fig. 1). The slight deviation of all observed peaks from those found in the literature may be due to grinding which has been known to cause structural damage to the mineralogy of carbonates and influences IR spectra (Milliman, 1974). Furthermore, differences in the internal calibration of instruments, chemical variations or

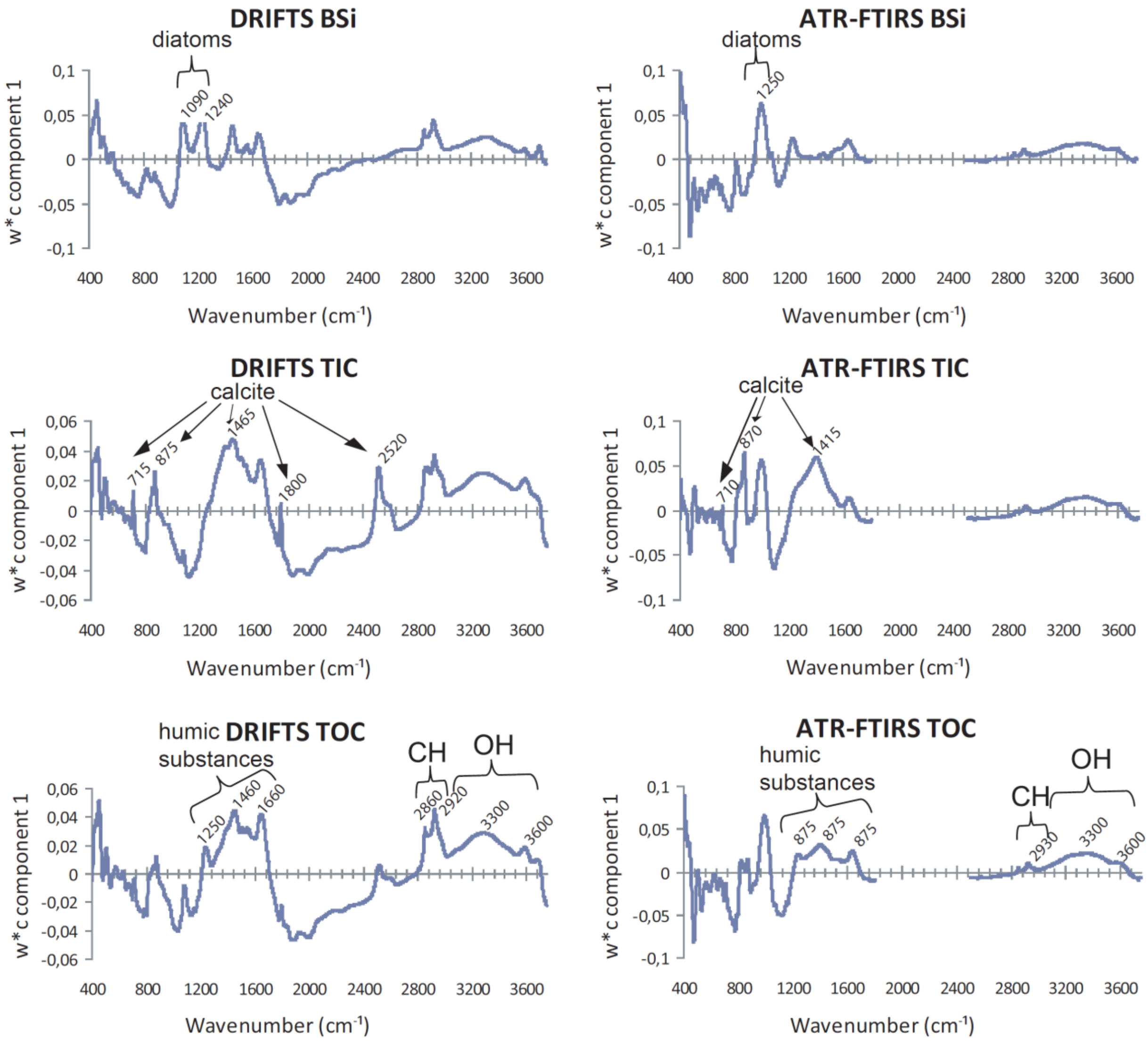

Fig. 1 Loading plots for each PLS component for DRIFTS and ATR-FTIRS methods express the contribution of each wavenumber to the explanation of varying constituent concentrations. The first loadings weight vectors (w*c) from the PLS regression decomposition are plotted against wavenumber. The figure documents the spectral regions important for predictive models. Positive loadings indicate wavelengths positively correlated and negative loadings indicate wavelengths negatively correlated to the respective property. The specific band assignments of the absorption of directly related sediment components are annotated.

minimal amounts of water in samples have been reported to cause variations in absorbance peaks (Gaffey, 1987; Reeves and Smith, 2009). Overlapping of bending aliphatic vibrations

(1100-1700 cm^{-1}) may be a confounding factor especially in the ATR-FTIRS model (Mecozzi and Pietrantonio, 2006).

3.2.3. Indirect and direct relationships between mid-IR spectra, TN and TOC contents

The models for TOC and TN, both present in organic compounds, have almost identical loading plots. In comparison to nitrogen, carbon is not only more common in sediments, but it is associated with a larger number of absorption bands in the mid-IR region. Thus, it can be assumed that it is mainly the carbon in organic components that is detected with nitrogen being strongly correlated. Spectral regions from 1220-1700, 2850-2950 and 3000-3700 cm^{-1} have positive loading values (Fig. 1). Humic substances absorb at bands in the region of 1100-1700 cm^{-1} (Mecozzi and Pietrantonio, 2006). In the region 2850- 2950 cm^{-1} C-H vibrations in $-CH_3$, $-CH_2$ and –CH groups of organic compounds have absorbance peaks (Farmer,1974; Kellner et al., 1998). Absorbance in the broad band 3000-3700 cm^{-1} can be attributed to OH vibrations in organic material (Farmer, 1974; Kellner et al., 1998).

3.3. Comparative study

3.3.1. Visible and near IR spectroscopy versus mid IR spectroscopy

The study shows that absorption bands (e.g. for BSi) vary between DRIFT and ATR techniques. This may be attributed to a different internal calibration of instruments (Gaffey, 1987; Reeves and Smith, 2009) and should be taken into consideration when comparing results. Previous studies document that mid-IR based calibrations outperform VNIR based calibrations for TN and TOC (McCarty and Reeves, 2006). VNIRS spectra consist of overlapping, broad and diffuse bands with very low structural selectivity. Bands cannot be precisely attributed because the same band may be related to several combinations of superimposed fundamental and overtone vibrations. The spectral basis of results obtained with VNIRS therefore remains unclear (Gaffey, 1986). FTIRS uses longer wavelengths which have the advantage that absorption is more intense and bands can be attributed to fundamental or ground vibrational transitions of both organic and inorganic compounds (Kellner et al., 1998). Mid-IR spectra therefore contain more details and are easier to interpret (Fig. A3). The mid-IR loading plots show that the PLS calibration model depends on specific wave numbers which compare well with published reference spectra. Furthermore, when using the mid-IR region, it is possible to delete wavenumbers not relevant for a specific sediment property. By deleting wavenumbers not important for BSi and TIC greatly improved the performance for these models using DRIFT.

3.3.2. Practical considerations when comparing the three techniques

VNIRS measurements take about 10 min/sample including grinding. A carousel increases the throughput considerably. ATR-FTIRS measurements take about 7 min/sample including grinding. It is so far not possible to use carousels for ATR-FTIRS measurements. DRIFTS measurements take about 13 min/sample including grinding and mixing with KBr. The use of a carousel can increase the speed considerably, if several trained persons work simultaneously. A disadvantage of VNIRS is that the required sediment amount is higher. However, the material may be reused for other analysis. DRIFTS requires laboratory personnel who can carefully mix the sediment with KBr using as precise as possible the given ratio between KBr and sediment. Since both KBr and sediment are hygroscopic, they should be stored with care to avoid distortion of the analyses by spectral absorption of water. Moreover, KBr mixing adds uncertainties due to user-to-user variations in sample preparation. It has been demonstrated in a variety of studies that the dilution with KBr is not always necessary when working with DRIFTS (Reeves, 2003). Unfortunately, trail runs with undiluted lake sediments resulted in spectra that were not interpretable according to the reference literature. This can be attributed to the intensity of absorption bands increasing proportionally with sample thickness causing spectral distortions to occur especially for certain components and compounds (such as humic acids) (Reeves, 2003). For ATR measurements, the penetration depth of the IR beam is only a few µm and decreases at shorter wavelengths. If the sample is not fine-grained and the contact between crystal and sample is insufficient, these wavelengths are not recorded correctly (Fig. A3). Furthermore, the amount of pressure applied to the samples influences the spectrum. This implies that variations in sample size as well as in density and structure of the samples can influence the spectra.

3.4. Application of IR spectroscopy to coarse, mineral and volcanic material

The average grain size of Laguna Potrok Aike sediments is relatively coarse. In coarse-grained sediment, light can travel further before being reflected or scattered back at an air-crystal interface. Therefore, absorption is more intense (Gaffey, 1986). In the mid-IR region not only the intensity of the peaks can be influenced but also the position and shape of bands (Estep-Barnes, 1977; Fig. A4). Furthermore, grain size effects can cause pressure variations

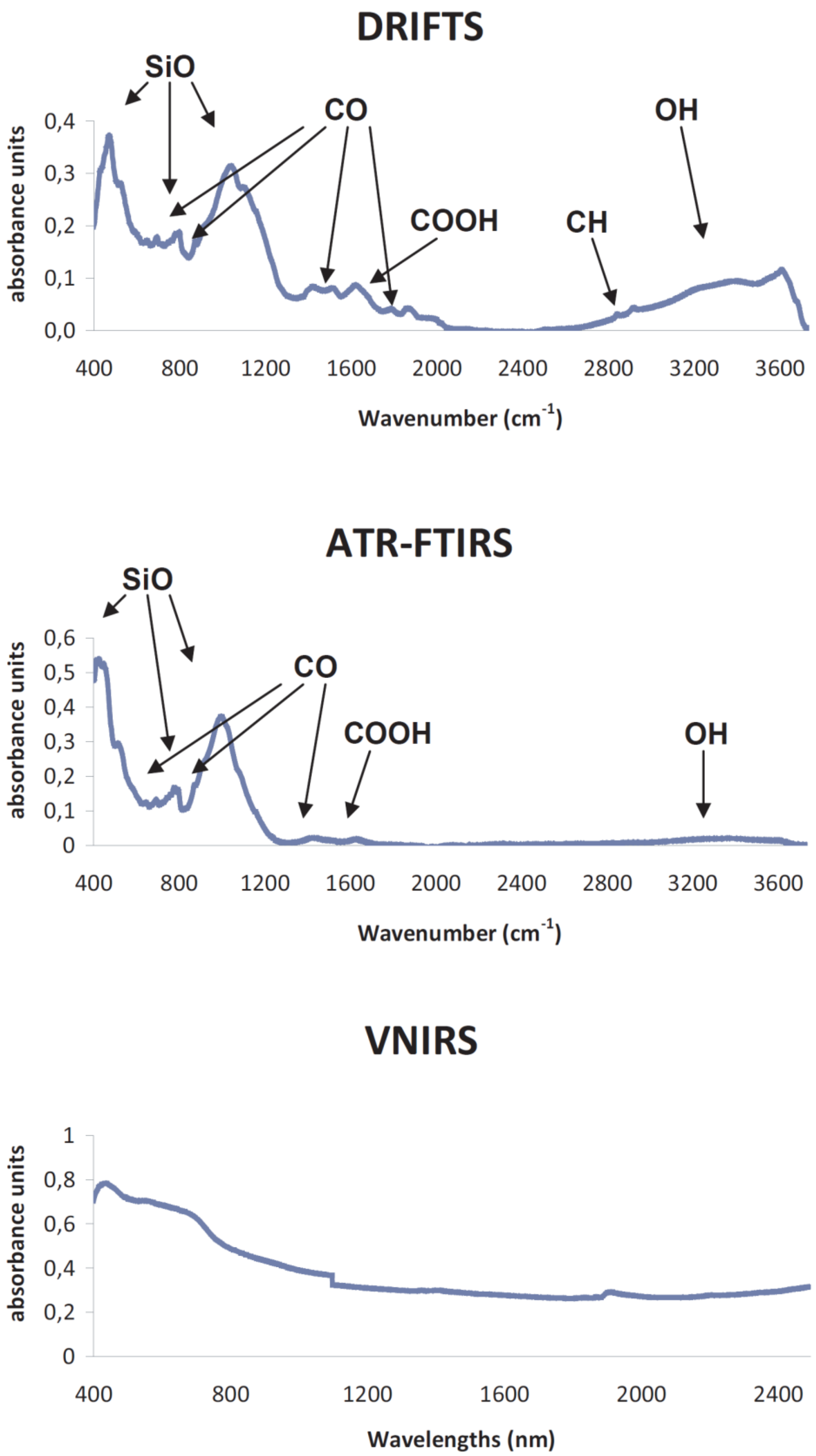

Fig. A3 Representative sediment spectra in the visible to near and mid-IR from Laguna Potrok Aike with intensity of the absorbed light expressed at different wavelengths. The mid-IR spectra are annotated with some sediment components and corresponding absorption peaks.

during ATR-FTIRS measurements. When using DRIFTS, there may be further effects related to the higher density of sand samples since the sample weight is kept constant. In this study, it was possible to include carefully ground coarse samples in the calibration set. Model performance of the visible to mid-IR techniques are dependent on accurate estimates using the conventional technique (Malley et al., 1999) and sediment samples with very low (<2% wt) opal, such as the Laguna Potrok Aike sediments, can be biased towards higher values (Müller and Schneider, 1993). This may be another explanation for the poor performance of BSi models. Moreover, in volcanic regions, the presence of tephra may be a confounding factor because it also contains amorphous silica and therefore has absorbance regions similar to those of BSi (Brito et al. 2004).

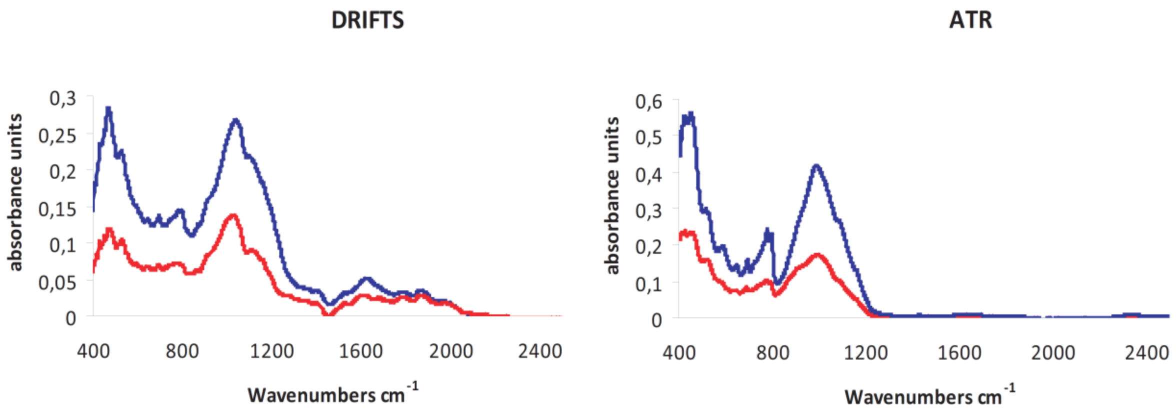

Fig. A4 Spectra of the same coarse grained sample measured with DRIFTS and ATR-FTIRS techniques before (red) and after (blue) grinding.

4. Conclusion

This comparative study shows that the statistical performance of the models for TIC, BSi, TOC and TN is acceptable for all three techniques. Most accurate results were achieved using DRIFTS technique. However, for rapid screening of sediment cores and for projects where costs and time are limiting factors, ATR-FTIRS and VNIRS can be used to assess major changes in sediment properties. VNIRS spectra have the disadvantage of relying entirely on multivariate statistics for their interpretation. Especially mid-IR techniques have various advantages over many conventional techniques of sediment analysis. In addition to a rapid and quantitative estimate of sediment properties, we can also assess the type of carbonates, silicates and assess qualitative differences in organic compounds. The DRIFT model developed in this study will be used in the PASADO project to assess geochemical properties with highest possible resolution along the entire >100 m long sedimentary record.

Acknowledgments

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Chapter 3:

Climate induced changes as registered in inorganic and organic sediment components from Laguna Potrok Aike (Argentina) during the past 51 ka

in review at: Quaternary Science Reviews

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Abstract

Total organic carbon, total inorganic carbon, biogenic silica content and total organic carbon/total nitrogen ratios of the Laguna Potrok Aike lacustrine sediment record are used to reconstruct the environmental history of south-east Patagonia during the past 51 ka in high resolution. High lake level conditions are assumed to have prevailed during the last glacial, as sediments are carbonate-free. Increased runoff linked to permafrost and reduced evaporation due to colder temperatures and reduced influence of Southern Hemispheric Westerlies may have caused these high lake levels with lake productivity being low and organic matter mainly of algal or cyanobacterial origin. Aquatic moss growth and diatom blooms occurred synchronous with southern hemispheric glacial warming events such as the Antarctic A-events, the postglacial warming following the Last Glacial Maximum and the Younger Dryas chronozone. During these times, a combination of warmer climatic conditions with thawing permafrost could have increased the allochthonous input of nutrients and in combination with warmer surface waters increased aquatic moss growth and diatom production. The Southern Hemispheric Westerlies were not observed to affect southern Patagonia during the last glacial. The Holocene presents a completely different lacustrine system because (a) permafrost no longer inhibits infiltration nor emits meltwater pulses and (b) the positioning of the Southern Hemispheric Westerlies over the investigated area gives rise to strong and dry winds. Under these conditions total organic carbon, total organic carbon/total nitrogen ratios and biogenic silica cease to be first order productivity indicators. On the one hand, the biogenic silica is influenced by dissolution of diatoms due to higher salinity and pH of the lake water under evaporative stress characterizing low lake levels. On the other hand, total organic carbon and total organic carbon/total nitrogen profiles are influenced by reworked macrophytes from freshly exposed lake level terraces during lowstands. Total inorganic carbon remains the most reliable proxy for climatic variations during the Holocene as high precipitation of carbonates can be linked to low lake levels and high autochthonous production. The onset of inorganic carbon precipitation has been associated with the southward shift of the Southern Hemispheric Westerlies over the latitudes of Laguna Potrok Aike. The refined age-depth model of this record suggests that this shift occurred around 9.4 cal. ka BP.

Key words:

carbonates, organic matter, biogenic silica, Diffuse Reflectance Fourier Transform Infrared Spectrometry (DRIFTS), lake level, primary productivity, Laguna Potrok Aike, Patagonia, Argentina, ICDP-project PASADO

1. Introduction

In order to answer questions about possible future climate changes and contribute to prediction efforts, we need to consider the long-term climate variability of the past. The southern mid-latitudes of South America are a key area that has been scarcely studied in the past, even though it is of importance due to its proximity to the climatically sensitive areas of Antarctica and the Southern Oceans (White and Peterson, 1996; Knorr and Lohmann, 2003). Laguna Potrok Aike is located on the only large continental land mass in the southern hemispheric mid-latitudes and contains one of the longest high resolution continental archives that continuously records climate and environmental changes in this area. During austral spring 2008, a 106 m composite profile of lacustrine sediments was recovered from the maar lake Laguna Potrok Aike in southern Patagonia, Argentina, in the framework of the ICDP project PASADO (Potrok Aike Maar Lake Sediment Archive Drilling Project). Haberzettl et al. (2005; 2007) have shown that the biogeochemical proxies TOC, TIC and C/N and BSi offer valuable information for paleoenvironmental reconstruction. However, analyses of these proxies are time consuming and expensive, especially when measuring long sedimentary archives at high resolution. In order to achieve high resolution analyses of the 106 m long PASADO record efficiently, we used the Diffuse Reflectance Fourier Transform Infrared Spectrometry (DRIFTS) technology (Vogel et al., 2008; Rosén et al., 2010; 2011; Hahn et al., 2011). Obtained proxies can be used to reconstruct lake level (TIC) and paleoproductivity (BSi, TOC) and the origin of organic matter (C/N ratio). By means of comparison with other southern hemispheric archives, we gain insights into inter-hemispheric climate coupling and regional differences in past climate changes e.g. moisture, temperature and wind speed during the past 51 ka. Altogether, this study aims at contributing to the understanding of the timing, frequency, and amplitude of rapid climate variability that characterizes the last glacial-interglacial transition and the last glacial period. In particular, the location of Laguna Potrok Aike permits a focus on shifts in the Southern Hemispheric Westerlies (SHW), which may be of importance for linking the climate on both hemispheres. It has been proposed that the ventilation of the deep Southern Ocean and thus the flux of CO_2 from the ocean into the atmosphere are controlled by strength and position of the SHW (Toggweiler and Lea, 2010). Anderson et al. (2009) suggest that the shift of the SHW caused CO_2 to increase at the onset of the Antarctic warming period at ca. 17 ka cal. BP. These recent studies have underlined the relevance of the southern hemisphere oceanic and atmospheric circulation to global climate changes.

2. Study site

Laguna Potrok Aike (52°S, 70°W; 113 m a.s.l.) is a 770 ka old maar lake with a diameter of 3.5 km and a maximum depth of 100 m (Zolitschka et al., 2006). It is situated in the Pali Aike Volcanic Field in Southern Patagonia, 80 km NW of the Strait of Magellan and ca. 110 km WSW of the city of Rio Gallegos (Fig. 1). The catchment area covers more than 200 km^2, yet runoff only occurs episodically mainly after snowmelt. The annual precipitation at Laguna Potrok Aike is about 200 mm and the potential evaporation rate is in the range of 1000-1600 mm per year (Endlicher, 1993; Borrelli and Oliva, 2001; Ohlendorf et al., submitted). This cold and semi-arid desert (Soriano, 1983), is typified by a steppe-type vegetation. The main climatic component is the strong SHW that dominates the lake site especially during summer months.

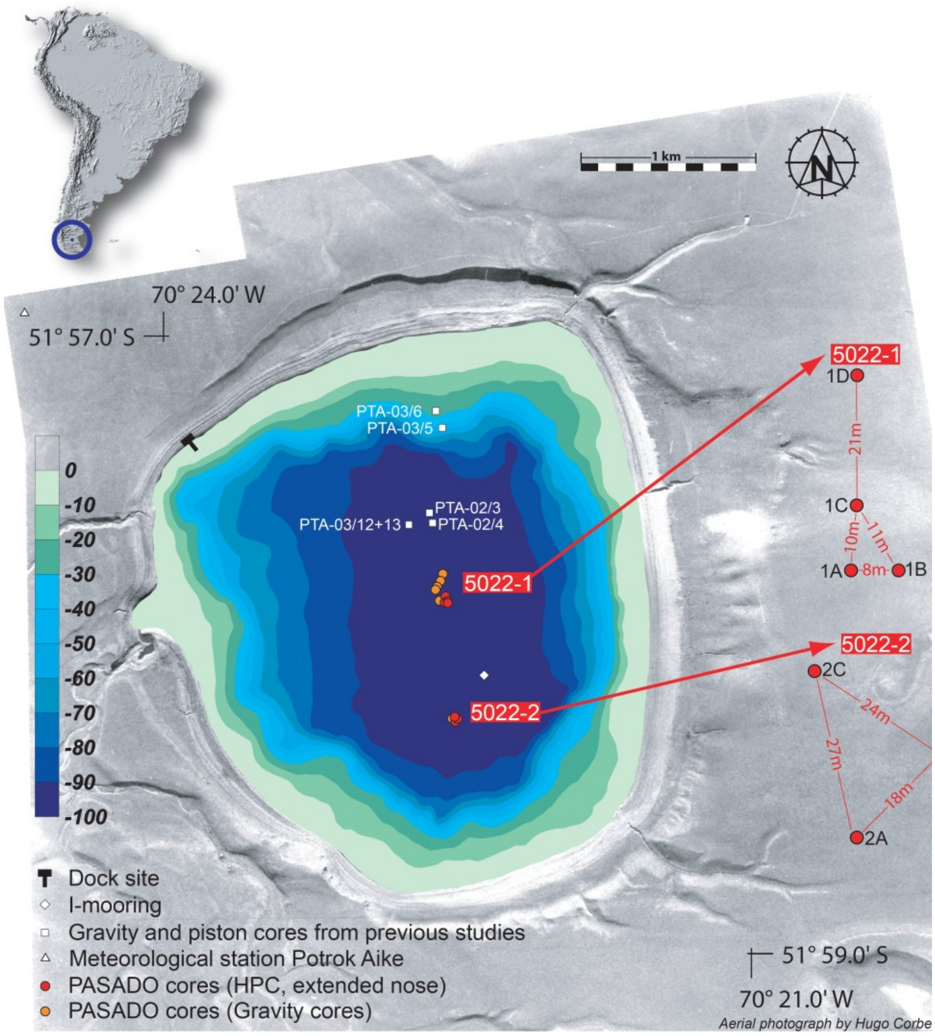


Fig. 1 Bathymetric map with coring sites of Laguna Potrok Aike and location in South America.

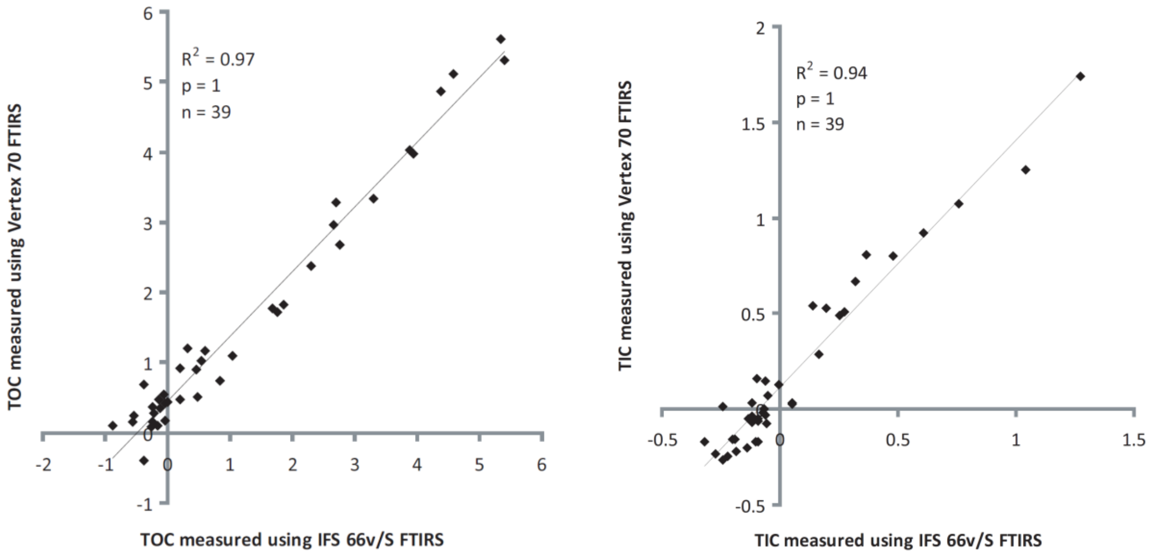
3. Materials and methods

3.1. Previous and concurrent work

Drilling operations were performed by DOSECC (Drilling, Observation and Sampling of the Earth's Continental Crust, Inc.) using the GLAD800 platform with mainly a Hydraulic Piston Coring system (HPC). At two drill sites seven overlapping cores were recovered (Fig. 1). After logging, cores were split, scanned and described lithologically. The latter was used to divide the record into lithographic units (A, B, C-1, C-2, C-3) by Kliem et al. (submitted, a). The lithololgy of unit A is described as consisting of pelagic laminated silts with a high content of calcite crystals. Pelagic laminated silts as well as thin fine sands and coarse silt layers with high amounts of aquatic mosses, a few fish bones and scattered calcite crystals dominate Unit B. Down core mass movements become thicker and more frequent. In unit C sediments are dominated by poorly laminated silts and fine sands. Logging data and lithological descriptions were used to construct a composite profile from the three parallel holes of site 2. This composite profile was subsampled in consecutive 2 cm intervals (Ohlendorf et al., 2011). Based upon visual inspection, samples were classified as tephra, remobilized and not remobilized material. Remobilized material and tephra layers were removed from the composite profile resulting in an event-corrected composite depth of 45.8 m cd-ec (meters composite depth-event corrected). For the Holocene and the Late Glacial record of Laguna Potrok Aike radiocarbon dating was done on the calcite fraction and different organic macro remains (Haberzettl et al., 2007). Prior to the Late Glacial, macro remains of aquatic mosses were the only material useful for radiocarbon dating. The developed age-depth model for the complete record is based on calibrated AMS ^{14}C dates using mixed regression modeling (Kliem et al., submitted, a).

3.2. Sedimentological analysis

The site 2 composite profile was subsampled at 2 cm spatial resolution. Gastropods and plant macro remains were removed from bulk material prior to analysis. The concentrations of total carbon (TC) and total nitrogen (TN) were determined on freeze-dried and ground samples using a CNS elemental analyzer (EuroEA, Eurovector). Samples for the measurement of TOC were pretreated with 3% and 20% HCl at a temperature of 80°C for several hours to remove carbonates and afterwards analyzed by the same device. Values for TIC concentrations resulted from the subtraction of TOC from TC values. C/N ratios were calculated by dividing the TOC content of a sub-sample by its TN content. For samples with very low TOC values of <0.3% we did not calculate C/N ratios due to high uncertainties in the estimates (Mayr et al., 2009). Organic macro remains in the sediment were detected visually. In 55 selected samples carbonates were identified using standard powder X-ray diffraction (XRD) analyses (Philips X'Pert Pro MD equipped with an X'Celerator Detector Array) and microscopic analysis of smear slides. In order to calculate dry densities for all samples, a known volume of ca. 10 g was weighed, freeze-dried and weighed again. To increase the spatial (temporal) resolution by a factor of 4 from 8-16 cm (80-160 years) achieved by the described conventional geochemical methods to a resolution of 2-4 cm (20-40 years) we applied the DRIFTS technique. Organic and inorganic compounds in lake sediments are “infrared (IR) active” in the mid-IR region. Differences in chemical composition and structure result in distinctive and complex signals, i.e. unique IR spectra that are used for the identification of different sediment properties (Osborne and Fearn, 1988; Kellner et al., 1998). Therefore, IR spectra are used to obtain information about the constituents of samples in many industrial and research applications (Workman et al., 2004). The DRIFTS technique has shown to be successful and promising for the assessment of TIC, TOC and BSi content in various lacustrine studies (Vogel et al., 2008; Rosén et al., 2010; 2011). The applicability of IR techniques to sediment samples from Laguna Potrok Aike was already confirmed (Hahn et al., 2011); DRIFTS was found to be the most accurate and efficient tool for high resolution analysis. For DRIFTS analyses of the top 1250 samples an IFS 66v/S FTIR spectrometer (BrukerOptik GmbH, Germany) equipped with a diffuse reflectance accessory (Harrick Inc., USA) was used. On the remaining 660 sediment samples a Vertex 70 FTIR Spectrometer (BrukerOptik GmbH, Germany) was used. To ensure comparability of data generated by using two different spectrometers, 39 samples were subdivided and measured with both devices. The R^2 between these measurements is 0.96 for BSi, 0.94 for TIC and 0.97 for TOC (Fig. 2). This small variation indicates that the two applied IR analyses provide almost identical results. Sample pretreatment, IR spectroscopy measurement conditions and processing procedures applied to the raw spectra are the same for all samples and described by Rosén et al. (2010; 2011) and Hahn et al. (2011). Using principal component analysis six outliers were detected and excluded. The occurrence of outliers can arise from the conventional TIC, TOC, C/N and BSi as well as from DRIFTS measurements. Potential reasons are sample contamination, large differences in sample composition (e.g. grain size effects), variability in sample pretreatment or measurement conditions. Partial least square regression (PLSR) is used to detect



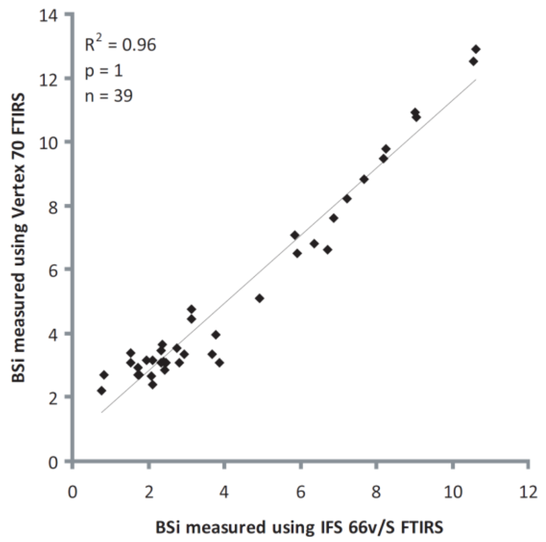


Fig. 2 Correlation of results obtained with the two devices used for DRIFTS analyses (IFS 66v/S FTIR spectrometer and Vertex 0 FTIR spectrometer).

relationships between the spectra and the conventionally measured sediment properties (Geladi and Kowalski, 1986). Calibration models are based on 479 samples from the composite profile, the core catchers and the short core for TIC and TOC and on 173 core catcher and short core samples for BSi. BSi was measured conventionally using the leaching method according to Müller and Schneider (1993). For further analytical details see Hahn et al. (2011). The calibration models of BSi and TIC are based on very distinct spectral regions which can be attributed to the absorption of BSi (1050-1320 cm^{-1}) and calcite (710, 880, 1470, 1800 and 2520 cm^{-1}; cf. Hahn et al., 2011 and references therein). Therefore, it was possible to improve these calibration models by developing models using only the relevant spectral regions. The software used for all statistical analyses was SIMCA-P (Umetrics AB, SE-901 91 Umeå, Sweden). For further details on numerical analyses and spectral interpretations see Hahn et al. (2011).

4. Results

4.1. Unit C: 45.8 to 15.2 m cd-ec

Unit C has been subdivided into C-1 (29.1 to 15.2 m cd-ec), C-2 (29.1 to 43.9 m cd-ec) and C-3 (43.9 to 45.8 m cd-ec). Throughout unit C C/N values range between 4 and 11, TOC values between 0 and 2% and BSi values between 0 and 8% (Fig. 3). The measurements of TN, for C/N calculations, as well as TIC contents are generally below 0.1%. The correlation (R^2= 0.41) between TOC and BSi content is weak (Fig. 4e). In unit C-3 BSi is below 1% and TOC values are so low (<0.3%) that C/N ratios are unreliable. In comparison to units C-1 and C-3, unit C-2 is characterized by an increase in C/N ratios (6-13), TOC (0-2%) and BSi (1-9%), particularly from 43.9 to 40.6 m cd-ec, from 36.8 to 34.6 m cd-ec and from 32 to 30.8 m cd-ec. In unit C-1 TOC content varies between 0 and 1%, BSi contents between 0 and 3% and C/N ratios between 4 and 12. Although there are no prominent variations in unit C-1, a higher variability for all proxies is detected at the lowermost part of the unit up to about 19 m cd-ec. In the uppermost part of C-1 (above ca. 19 m cd-ec) there is almost no variation; BSi, TOC and C/N values are constantly very low (Fig. 3).

4.2. Unit B: 9.1 to 15.2 m cd-ec

Throughout unit B there is a correlation between TOC and BSi contents (R^2= 0.67) and between TOC contents and C/N ratios (R^2=0.66) (Fig. 4c-d). At the base of unit B, TOC, C/N and BSi values increase to maximum values of 5% (TOC), 17 (C/N), and 17% (BSi). After a minor drop of all proxies at about 14.3 m cd-ec, values continue to rise until about 14 m cd-ec, where the highest values in the record of TOC (8%), C/N (18) and BSi (17%) are reached. From this level and upward, the uppermost part of this unit is dominated by a decrease of all values, which is intercepted by smaller peaks in all proxies coinciding with peaks in TIC at 13.6 m cd-ec, 13.3 m cd-ec and 13.1 m cd-ec, respectively (Fig. 3). Afterwards steady decreases to values typical for unit A (C/N ca. 9, TOC ca. 1% and BSi ca. 2%) are recorded. At the onset of higher TIC values above 11.5 m cd-ec, the correlation of BSi and TOC contents deteriorates. The correlation between TOC contents and C/N is maintained; in

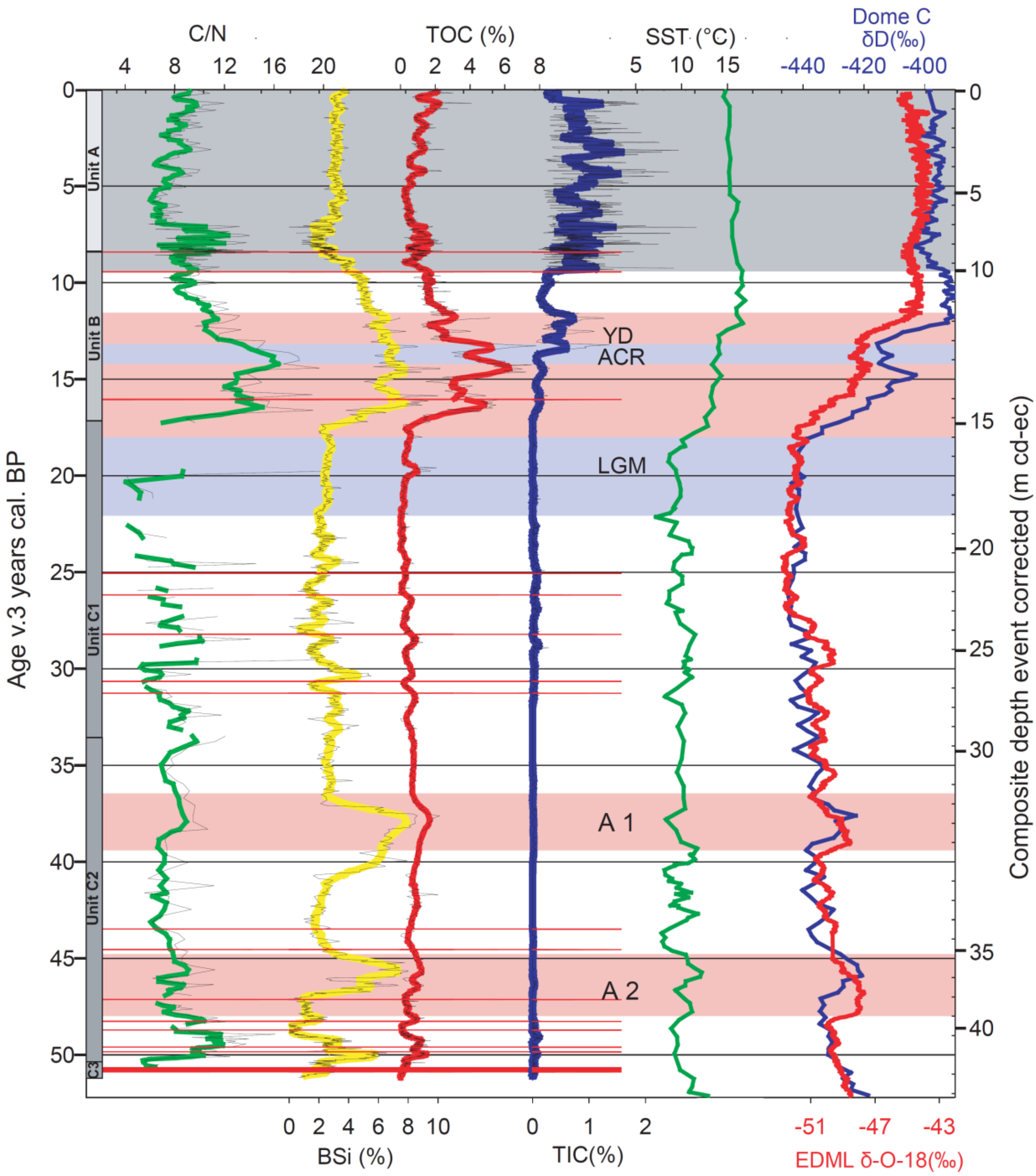


Fig. 3 Laguna Potrok Aike 3-5pt running means of event-corrected composite records of C/N, BSi, TOC, and TIC (thin black lines). C/N values of samples with TOC <0.3% were not calculated. These parameters are compared to Antarctic ice core temperature records; the Deuterium record from Dome C (blue; EPICA Community Members, 2004) and the oxygen isotope record from Dronning Maud Land (DML) ice-core (red; EPICA Community Members, 2006) and alkenone-based sea surface temperatures (SST) from ODP-site 1233 in the south-east Pacific (green; Kaiser et al., 2005). Age model v.3 and lithological units are according to Kliem et al. (submitted, a). The non-equidistant scaling of the depth axis to the right marks variations in sedimentation rate. Periods of prominent warming (red) and cooling (blue) such as the Antarctic A-events 1 and 2 (A1; A2), the Last Glacial Maximum (LGM), the Antarctic Cold Reversal (ACR) and the Younger Dryas (YD) are shaded in color. Gray shading marks the part of the record during which the SHW are positioned over Laguna Potrok Aike. Red lines mark the occurrence of a tephra layer of variable thickness.

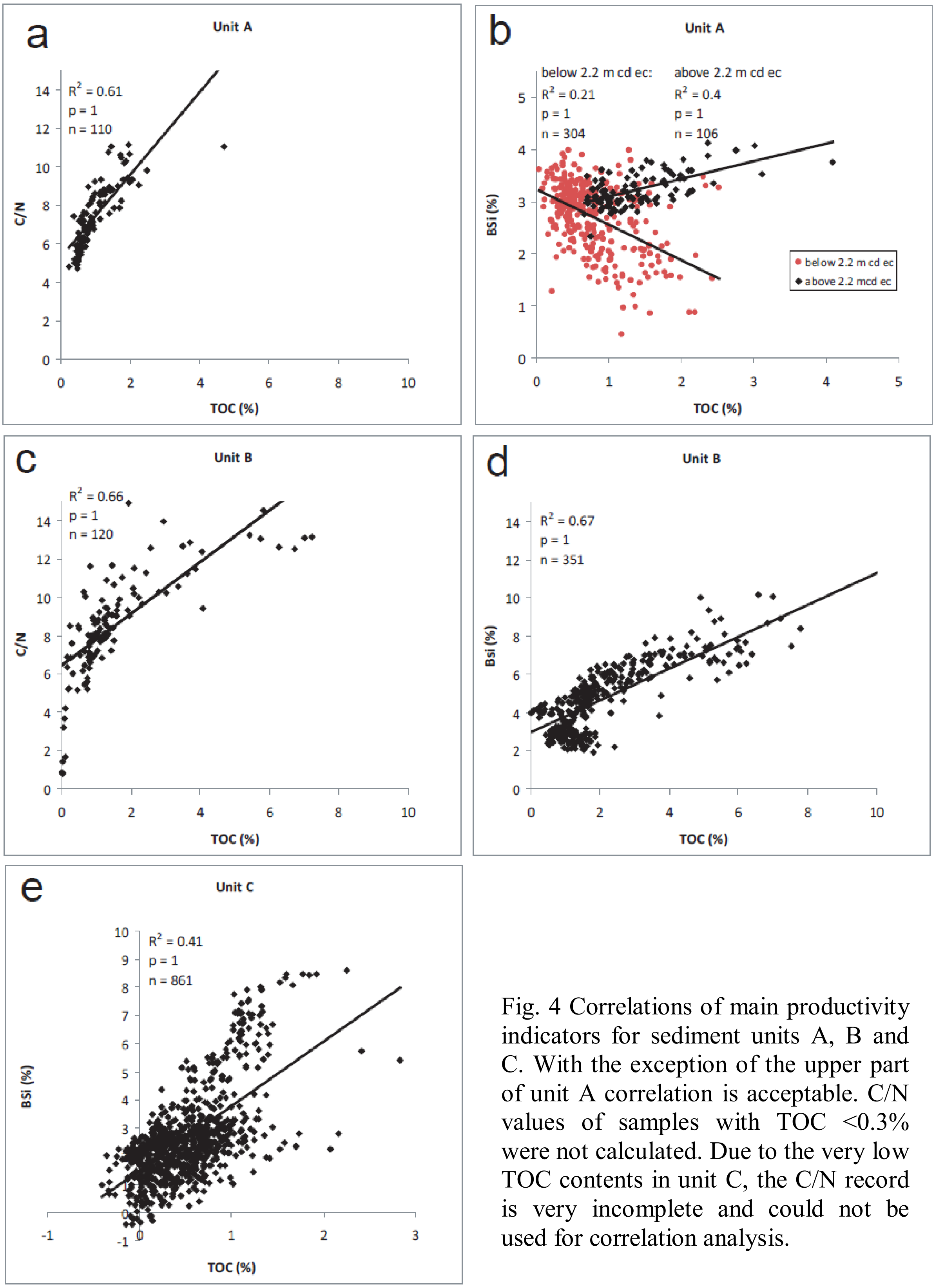


Fig. 4 Correlations of main productivity indicators for sediment units A, B and C. With the exception of the upper part of unit A correlation is acceptable. C/N values of samples with TOC <0.3% were not calculated. Due to the very low TOC contents in unit C, the C/N record is very incomplete and could not be used for correlation analysis.

addition, the TIC curve appears to covary with these two proxies. The BSi concentrations however vary in an antiphased pattern relative to the other parameters (Fig. 5).

4.3. Unit A: 0 to 9.1 m cd-ec

In unit A the TIC, TOC and C/N results are consistent with results from previous cores (Fig. 5; Haberzettl et al., 2007). Throughout this unit, values vary between 0 and 2% TIC, 0 and 4% BSi, 0 and 4% TOC and 6 to 12 for C/N ratios. The measurements of TN, used for C/N calculations, are generally above 0.1%. The antiphasing of BSi to C/N, TOC and TIC, that commenced in the uppermost part of unit B, is withheld throughout unit A until 2.2 m cd-ec. For the top 2.2 m the BSi record is positively correlated to TOC (R^2=0.47) (Fig. 4b). The correlation between TOC and C/N profiles is maintained throughout unit A (R^2=0.61) and the TIC profile generally follows the trends of the other three parameters (Figs. 4a and 5).

5. Discussion

5.1. Lake level – the TIC record

The proxy TIC is well established as a lake level indicator for Laguna Potrok Aike (Haberzetttl et al., 2005, 2007; Oehlerich et al., submitted). The underlying assumption is that low lake levels with a reduced water volume promote supersaturation and thus carbonates precipitate (Haberzetttl et al., 2005, 2007). However, the relationship between the global mechanism (climatic change), the regional phenomenon (lake level oscillations) and carbonate precipitation registered by the proxy (TIC) may not be as straight forward as assumed. Especially since Laguna Potrok Aike is a groundwater-fed lake (Mayr et al., 2007a). Furthermore, pollen and diatom analyses (Wille et al., 2007) are not always concordant with climate reconstructions based on TIC. Nevertheless, there is strong evidence from dated lake level terraces, subsurface acoustic imaging and lake level modelling (Haberzettl et al., 2005; Anselmetti et al., 2009; Ohlendorf et al., submitted) supporting the idea that TIC is a qualitative paleo-lake level indicator of Laguna Potrok Aike. For the Holocene and Late Glacial record we are able to reproduce the TIC curve published by Haberzettl et al. (2007; Fig. 5) and support their interpretations. For the glacial record, however, we have to rely on other proxies as there is no carbonate precipitation at all. The lack of calcium precipitation during the Glacial is an indicator for high glacial lake levels.

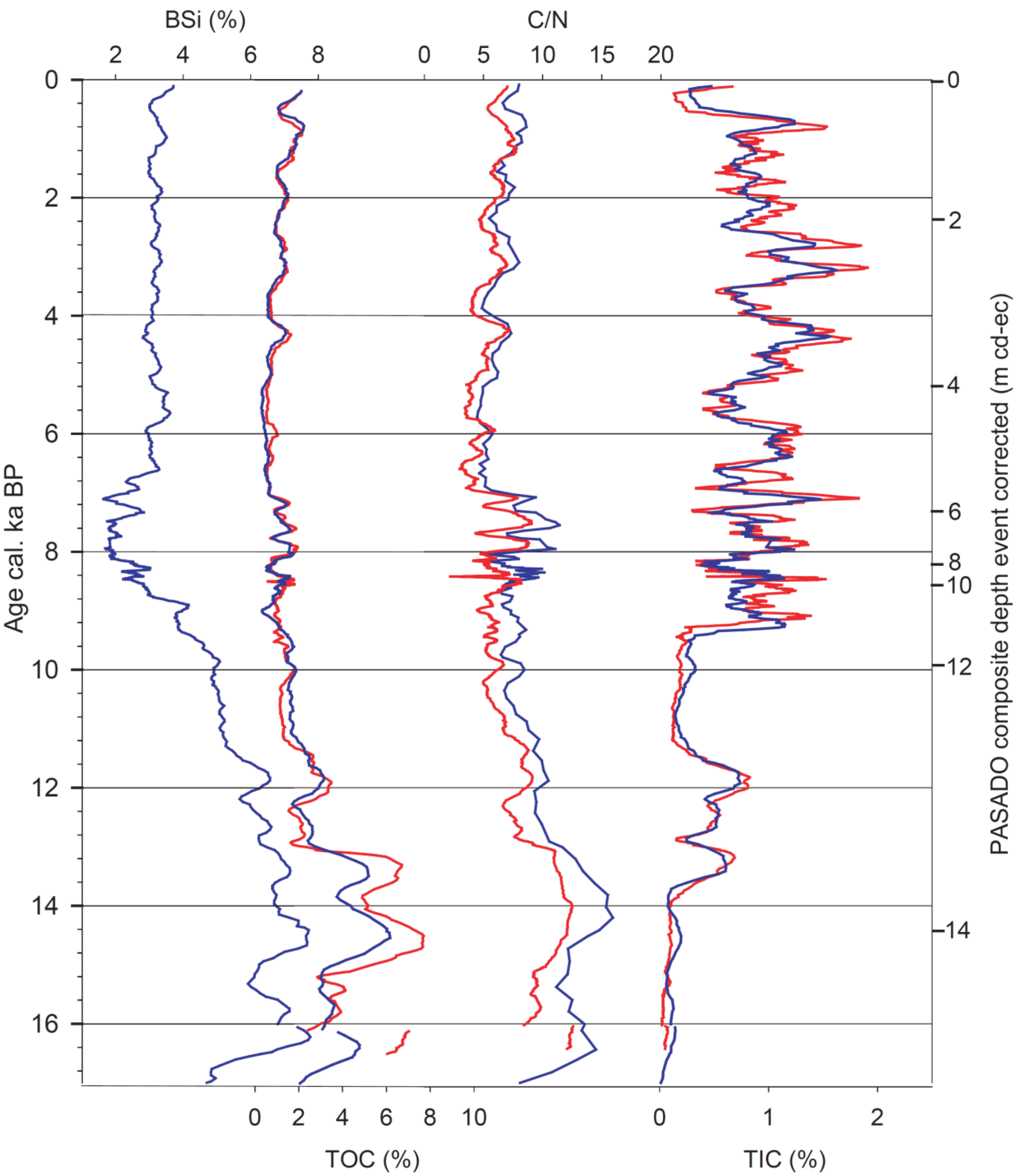


Fig. 5 Late Glacial and Holocene PASADO (blue) record of BSi, TOC, C/N and TIC compared to the SALSA (red: Haberzettl et al., 2007) TIC, TOC and C/N record plotted against event corrected composite depth and age according to the PASADO v.3 age model (Kliem et al., submitted, b). The non-equidistant scaling of the depth axis marks variations in sedimentation rate.

5.2. Paleoproductivity – the TOC, BSi, C/N record

5.2.1. Total Organic Carbon (TOC)

The TOC values from the deep basin of Laguna Potrok Aike are representative of the organic matter (OM) input (Kastner et al., 2010; Mayr et al., 2009) and have been used to infer lacustrine production increases during the glacial when lake level was assumed to be high (Haberzettl et al., 2005; 2007). However, during lake level lowstands reworked TOC is possibly resuspended by wave turbulences and carried into the system from the lake shores (Haberzettl et al., 2005; 2007; Fearnside, 2012). Therefore, in previous Laguna Potrok Aike studies TOC increases during the Holocene are interpreted as an indicator for wave action eroding previously deposited aquatic macrophytes from freshly exposed lake level terraces Haberzettl et al. (2005; 2007).

5.2.2. C/N ratios

C/N ratios give insight into the abundance of terrestrial and aquatic components of OM which reflect climate related changes in vegetation communities in and around a lake (Meyers and Lallier-Verges, 1999; Talbot and Laerdal, 2000). Previous studies at Laguna Potrok Aike by Mayr et al. (2009) show that C/N data is a reliable tool for the distinction of diatomaceous ooze, cyanobacteria and soils from vascular plants including aquatic (macrophytes and mosses) and terrestrial plants. Pelagic OM was found to be homogeneously distributed throughout the lake (Mayr et al, 2009; Kastner et al., 2010). We therefore refrain from interpreting C/N ratios as a shoreline proximity and thus lake level indicator, as suggested by Haberzettl et al. (2005). Instead, we refer to C/N data as a source of information about the origin of OM. A few hundred meters from the shore terrestrial OM input should be insignificant, especially considering the scarce vegetation in the catchment area and the absence of major fluvial tributaries. Submersed aquatic macrophytes growing in the photic zone along the shoreline of Laguna Potrok Aike have C/N values of 24 to 49 (Mayr et al., 2009). Therefore, they are considered to be the origin for elevated C/N ratios (Haberzettl al., 2005; 2007). Layers of aquatic mosses and dispersed macro remains are dominating constituents among the OM macro remains found in Laguna Potrok Aike. The fragile twigs of these mosses are mostly intact which indicates short distances of transportation. They have mostly been interpreted as not redeposited by Kliem et al. (submitted, a). The low C/N ratios of 4-10 in Laguna Potrok Aike sediments point to phytoplankton (mainly algae, but also cyanobacteria) as a main source of OM with the theoretical possibility of soil input (Haberzettl et al., 2007; Mayr et al, 2009; Massaferro et al., submitted). Similar low C/N values were also found in lake sediments from Lakes Baikal, El´gygytgyn and Ohrid (Watanabe et al., 2004; Melles et al., 2007; Vogel et al., 2010). However, such low C/N values have also been attributed to the presence of inorganic nitrogen in sediments with low OM content (Lehmann et al., 2002; Mueller, 1977). In order to estimate the inorganic nitrogen content we examine the correlation between TOC and TN contents. The high correlation coefficient ($R^2 = 0.9$) indicates that the larger fraction of nitrogen is organically bound. The regression line intercepts the y-axis at 0.03% TN (Fig. 6). This indicates that the percentage of not organically bound nitrogen is small and that 0.03% TN corresponds to the maximum amount of inorganic nitrogen to be expected in these sediments (Müller, 1977; Talbot, 2001; Veres et al., 2008). In combination with the BSi and TOC datasets, the Laguna Potrok Aike C/N record should therefore be a reliable tool for describing the source of OM.

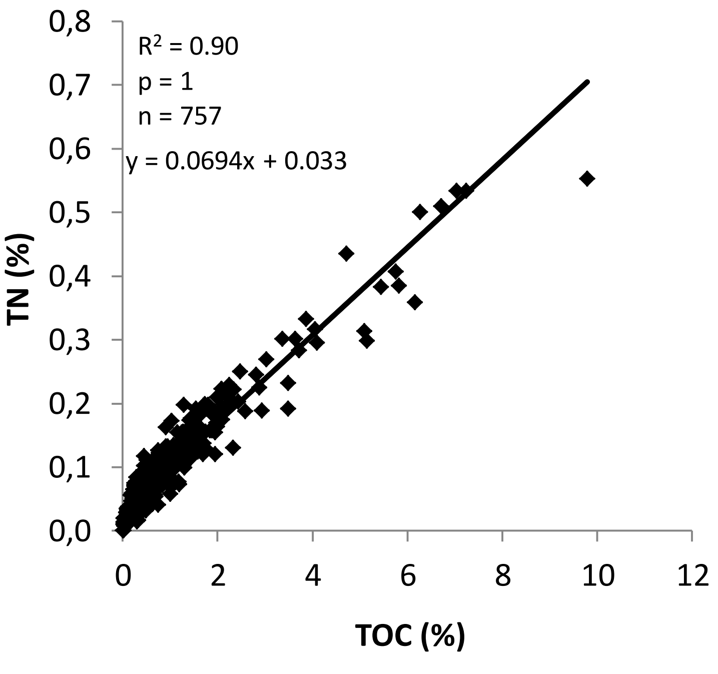


Fig. 6 Correlation between conventionally measured TOC and TN contents indicates that the nitrogen in the sediment is mainly organic.

5.2.3. Biogenic silica (BSi)

BSi is a bulk measure of siliceous microfossils (diatoms, phytoliths, crysophytes and sponge spicules) in sediments. Microscopical sediment analyses have documented the abundance of diatoms in the sediment (Recasens et al., 2012). Although phytoliths are common in the

Patagonia steppe (Wille et al., 2007) their influence is probably minimal due to the mid-basin core location and the reduced amount of surface water inflow. BSi has thus been used as a diatom productivity indicator for Laguna Potrok Aike gravity cores (Haberzettl et al., 2005; Kastner et al., 2010). Biogenic silica has been used for climatic interpretations in several long lacustrine records (Prokopenko et al., 2001; Melles et al., 2007). However, the originally produced BSi is often dissolved before and after deposition (Lisitzin, 1971; Hurd, 1973). Because of this potential for dissolution of variable amounts of silica, the assumption that BSi is a productivity indicator needs to receive support from correlation with other paleoindicators of productivity change (Cohen, 2003). We assume that dissolution effects are less important if correlations between TOC and BSi profiles are strong (Blake et al., 1992; Colman et al., 1995; Shemesh et al., 1989), as it is the case in units B and C of the studied record (Fig. 4 d-e).

5.3. Correlations between indicators

5.3.1. Carbonate-free system (below 13.7 m cd-ec)

Throughout most of the glacial period the three productivity indicators (C/N, BSi and TOC) roughly covary (Fig. 3, 4). Relatively low correlation coefficients (around 0.5) may be due to the various sources of error when comparing various proxies that are all influenced by distinct lake-internal processes and are in part measured with different techniques. TOC and C/N are not independent variables; their correlations should therefore be regarded with care. Peaks in the three proxies are associated with layers of aquatic macro remains. We suggest that the controlling climatic conditions favor the development of aquatic macrophytes and diatom blooms. Aquatic moss growth is promoted in a warm, calm and nutrient-rich photic zone (Berger et al, 2007; Strand and Weisner, 1996; Janauer and Kum, 1996). There are several diatom species that thrive under similar conditions (Recasens et al., 2012; Williams, 1994). Thus, we assume that peaks of productivity indicators can be interpreted as warmer periods with probably moderate wind speeds.

5.3.2. Carbonate-bearing system (above 13.7 m cd-ec)

During the Holocene TIC serves as an indicator for calcium supersaturation during lake level lowstands of Laguna Potrok Aike (Haberzettl et al., 2005; 2007). TIC variations can be weakly correlated to those of TOC and C/N ratios (Fig. 5). However, these are assumed to not only reflect productivity, but also input of reworked aquatic mosses from freshly exposed terraces (Haberzettl et al., 2005; 2007; Fearnside, 2012). Mayr et al. (2009) suggest that higher sedimentation rates during lowstands dilute productivity signals. High resolution studies of stable isotopes ($\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$) and elemental parameters of Laguna Potrok Aike's bulk OM indicate low lake productivity in the Holocene compared to the Late Glacial (Zhu et al., submitted). Even though periods of lake level lowstands due to increases in SHW strength are characterized by warmer air temperatures, this may not have triggered increases in productivity since high wind speeds would have inhibited the formation of a stable epilimnion. Furthermore, nutrient input from the catchment area would have been limited during drier conditions. During the Holocene, where high amounts of TIC indicate more pronounced saline conditions, decreased amounts of BSi are found in the sediment (Fig. 3, 5). Chemical dissolution of silica in waters with high salinity (Barker, 1992) represents a limitation for the use of BSi as a productivity indicator during the Holocene. Such brackish conditions are also inferred from diatom data (Recasens et al., 2012). One of the most important factors controlling the rate of diatom dissolution is lake water pH (Lewin, 1961). Present day studies show that lake water pH can increase to 9 during summer low lake level conditions (Haberzettl et al., 2005). Lake water pH above 9 causes the dissolution rate to increase exponentially due to the dissociation of silicic acid (Marshall, 1980). Increasing temperatures would have further contributed to increased dissolution (Lewin, 1961). Based on visual inspection during diatom counting, a high degree of dissolution is observed only in the upper part of the record (Massaferro et al., submitted). A further indication for silica dissolution is the lacking correlation between TOC and BSi, even though C/N values indicate that most of the OM is of algal origin. The last two millennia present an exception; here TOC, TIC, C/N and BSi are well correlated (Fig. 4a-b, 5). It seems that the lake water environment did not promote dissolution during this time span. Possibly diagenetic processes have not yet changed the BSi structure significantly in the youngest sediments. Geomicrobial investigations of Laguna Potrok Aike sediments show that post-burial microbial alteration persists long after burial and is especially active in sediment with high OM content (Vuillemin et al., submitted).

5.4. Paleoenvironmental reconstructions

5.4.1. Glacial conditions (Unit C-1, C-2 and C-3: 51.2 to 33.1 cal. ka BP)

5.4.1.1. High lake level

TIC values in this part of the record are generally below the 0.1% detection limit of the CNS elemental analyzer (Fig. 3). Furthermore, smearslide and XRD analyses reveal only neglible amounts of carbonate in this unit (Nuttin et al., submitted; Hahn et al. submitted) support these findings. According to Haberzettl et al. (2007) the lack of calcite precipitation during glacial conditions can be attributed to dilution effects during high lake levels. This is supported by seismic and geomorphological data (Anselmetti et al., 2009; Gebhardt et al., 2011; Kliem et al., submitted, b) which indicate that glacial lake levels during the past 51 ka were never below the early Holocene lake level minimum. Ice wedges in the vicinity of the lake (Kliem et al., submitted, b) indicate permafrost formation during the last glaciation. These conditions could have inhibited infiltration and thus directed runoff directly into the lake. Furthermore, a more northerly position of the SHW (Maldonado et al., 2005; Lamy and Kaiser, 2009) could have caused a decrease in evaporation due to lower wind speeds. Moreover, without SHW blocking easterly winds, Atlantic precipitation could have reached Laguna Potrok Aike more frequently.

5.4.1.2. Interstadial conditions

Unit C-2 shows increases of productivity indicators, which suggest periods of ameliorated climatic conditions and/or increased nutrient input. Relatively high BSi values and a low C/N signature indicate that the main source of OM in Unit C-2 is algal matter (Fig. 3). This is typical for highly diluted oligotrophic lakes with low vascular plant OM input such as in arctic tundra settings (Meyers and Lallier-Vergès, 1999) which are probably similar to what Wille et al. (2007) describe as an open vegetation during the glacial. Further information about the source of OM in unit C-2 is contained in lithological descriptions and core photographs of sediment sections. In sections with increased TOC and C/N values these commonly show organic macro remains, aquatic mosses, finely dispersed in the sediment or in discrete cm-scale layers. Warmer surface waters, promoting the growth of aquatic mosses and some diatom species, could be related to slightly warmer conditions and moderate wind speeds as the area was still probably south of the SHW belt. Mixing could have been less pronounced due to the larger water column. A more vegetated catchment area due to warm and humid conditions would reduce erosion and thus water turbidity and at the same time lead to increased nutrient availability. During Oxygen Isotope Stage (OIS) 3 (65 to 25 cal. ka BP) dust input has been reported as reduced in Laguna Potrok Aike as well as in the Vostok ice core (Delmonte et al., 2004; Haberzettl et al., 2009). From marine and ice cores OIS 3 has been interpreted to be warmer (Fig. 3; EPICA community members, 2004; Kaiser et al., 2005) with reduced extension of Antarctic sea ice (Crosta et al., 2004). A reduced Patagonian ice shield and soil and vegetation formation in a more humid climate was also suggested by Lamy and Kaiser (2009). During this generally more productive phase, there are three distinct peaks in all three proxy indicators accompanied by the presence of organic macro remains in the sediment record. The first peak is from 49 to 50 cal. ka BP (Fig. 3), coinciding with a diatom bloom related either to a preceding mass wasting event or to climatic factors; the latter interpretation being supported by a shift in $\delta^{13}C$ values that indicate a change in environmental conditions (Recasens et al., 2012). Nuttin et al. (submitted) infer increased hydrolysis in the Potrok Aike catchment from clay rich sediments deposited around 51 ka cal. BP. Other archives recording synchronous climatic changes are not known. This may, however, also be related to the very large error margin associated with the age-depth model in this part of the record (Kliem et al., submitted, a). The following two peaks in productivity (especially BSi) from 47.8 to 45 cal. ka BP and from 39.2 to 36.5 cal. ka BP (Fig. 3) are probably associated with diatom blooms induced by warmer water temperatures and nutrient input due to more precipitation and/or runoff and warmer air temperatures. Both periods have also been highlighted in previous Laguna Potrok Aike studies; they may be associated with the occurrence of diatoms indicating high lake levels (Recasens et al., 2012). The latter peak comprises a decrease in the Laguna Potrok Aike magnetic susceptibility record and an increase in clay content; both interpreted as indicating warmer conditions (Haberzettl et al., 2009; Nuttin et al., submitted). The Dome C non-sea-salt calcium (nss-Ca) shows a similar trend (Lambert et al., 2008). Within the uncertainty of the age model, the timing of both peaks in paleoproductivity may correspond to the so-called Antarctic A-events 1 and 2 which are periods of warming recorded in isotope data from Antarctic ice cores (Fig. 3; EPICA community members 2004; 2006).

5.4.2. Last Glacial Maximum (Unit C-1: 33.1 to 17.2 cal. ka BP)

Lower values for productivity indicators in unit C-1 (Fig. 3) imply that conditions were less favorable for autotrophic production. Air temperatures must have been low and the catchment was probably nutrient–barren. Stronger wind speeds than in unit C-2 may also have been an additional factor inhibiting the formation of a warmer photic zone necessary for some aquatic organisms. The BSi and TOC records also imply that productivity was low while minerogenic input was high. This may have inhibited primary productivity by increasing turbidity (Talbot and Laerdal, 2000; Meyers and Lallier-Verges, 1999; Ampel et al., 2008). Furthermore, minerogenic dilution has been observed to affect the Laguna Potrok Aike BSi record (Mayr et al., 2009). In previous Laguna Potrok Aike studies for the time period of 32/33 to 17 cal. ka BP Haberzettl et al. (2009) report high magnetic susceptibility values correlating with nss-Ca records from the Dome C ice core (Lambert et al., 2008). Along with reduced catchment vegetation and (peri-)glacial processes favoring wind erosion, Haberzettl et al. (2009) suggest stronger SHW as a possible explanation for changes in magnetic susceptibility. However, most Patagonian continental (Bradbury et al., 2001; Moreno et al., 1999; Maldonado et al., 2005), marine (Lamy and Kaiser, 2009; Lamy et al., 1999; Stuut and Lamy, 2004) and modeling (Hulton et al., 2002) studies suggest that, relative to OIS 3, there was a northward shift of the SHW during OIS 2. For the latitudes of Laguna Potrok Aike this would imply a weakening of wind strengths. As this study suggests a strengthening of wind speeds, rather than a weakening, we suggest that these winds are probably not related to the SHW, but to a generally intensified atmospheric circulation during glacial times with catabatic winds from the growing Patagonian ice sheets (Hulton et al., 2002). It is likely that the position of the SHW is too far north during glacial times to be able to effect Laguna Potrok Aike. The entire time period of unit C-1 (33.1 to 17.2 cal. ka BP) comprises the Last Glacial Maximum (LGM). Ice advances have been synchronously reported for the time between 31.5 and 17 cal. ka BP throughout Patagonia (Lowell et al., 1995; Hein, 2010; Kaplan et al., 2004; Sugden et al., 2005; Kaplan et al., 2008a; Clark et al., 2009). Marine sediment cores also record glacial conditions for the time interval 28 to 18 cal. ka BP (Lamy et al., 1999). Although there are no prominent fluctuations in unit C-1, the lowermost part from 33.1 to 24 cal. ka BP can be distinguished by constant small scale shifts in productivity. Indicators drop to values lower than in unit C-2, but also rapidly rise again to values above the C-3 mean. Scarce layers of organic macro remains often accompany these peaks. This small scale variability could also be related to mass movements or tephra layers which occur frequently in this period (Fig. 3).

The variability could also reflect a transition period from warmer to colder conditions. After 24 cal. ka BP, the productivity indicators remain constantly very low in unit C-1 (Fig. 3). This time frame corresponds to the global LGM from 24 to 18 cal. ka BP as defined by Mix et al. (2001) using marine and ice core datasets. The local LGM in Patagonia has been recorded as consistent with this timing, exhibiting maximal glacial advances between 23 and 18 cal. ka BP (Zech et al., 2009; Singer et al., 2004; Lowell et al., 1995; Denton et al., 1999) and minima in sea surface temperatures off the Chilean coast (Lamy and Kaiser, 2009). In the uppermost part of unit C-1 a positive trend in productivity marks the termination of the LGM. The timing of this event in Laguna Potrok Aike between 19 and 17 cal. ka BP has been reported to be synchronous between the northern and the southern hemisphere (Schaefer et al., 2006). There are, however, large variations in the timing of the onset of deglaciation throughout southern hemispheric records that have yet to be explained (Lamy and Kaiser, 2009). On the one hand, some marine cores as well as the Byrd ice core suggest an onset of deglacial warming as early as about 19 cal. ka BP (Martinez et al., 2006; Stott et al., 2007; Blunier and Brook, 2001). On the other hand, the EDML and Dome C ice cores show a rise in CO_2 and temperature starting at about 17 cal. ka BP (Fig. 3; Monnin et al., 2001; EPICA community members, 2004; 2006). The latter is supported by this study as well as by Patagonian continental data from peat and lake cores (Denton et al., 1999; Möller et al., 2010; Pendall et al., 2001) and from reconstructions of the glacial retreat synchronous at about 17 cal. ka BP throughout Patagonia (Hein et al., 2010; Rabassa, 2008; Kaplan et al., 2004).

5.4.3. Late Glacial to early Holocene (Unit B: 17.2 to 8.3 cal. ka BP)

5.4.3.1 Deglaciation

In the lowermost part of unit B (17.2 to 14.4 cal. ka BP) the data shows that conditions became favorable for diatom and aquatic macrophytes within little over a millennia pointing to a rapid climatic amelioration and increased nutrient input. The highest TOC, BSi and C/N values are found in this part of the record. The C/N ratios of generally above 10 indicate that there is substantial input from non–algal sources (Fig. 3, 5). Core photographs and descriptions show remains of aquatic macrophytes (Kliem et al., submitted, a), input of other vascular plants is likely. Stable isotope and diatom analyses report similar findings (Massaferro et al., submitted; Zhu et al., submitted). Conditions must have been warm, moist and only moderately windy with vast littoral areas for aquatic mosses to grow on. Wille et al. (2007) describe this period in the Laguna Potrok Aike area as humid and calm, based on microfossil and geochemical data, and interpret this as the result of Laguna Potrok Aike lying south of the zone influenced by the SHW. Moisture patterns throughout Patagonia are in accordance with this interpretation (Wille et al., 2007 and references therein). The SHW are suggested to have moved southward after the LGM, i.e. after Heinrich 1 event at 16.8 cal. ka BP (Anderson et al., 2009) which is supported by isotope data from the east Pacific (Martinez et al., 2006) and the glacial history of Isla de los Estados (Möller et al., 2010). However, our findings suggest that they probably did not reach their modern position over Laguna Potrok Aike until the early Holocene. Without the influence of the SHW the area would have been affected by easterly precipitation. The Late Glacial is described as warm and humid in the multiproxy study by Recasens et al. (2012). This warming following the LGM is also recorded in Antarctic ice cores (Fig. 3; Monnin et al., 2001; EPICA community members, 2004; 2006) and Patagonian continental records (Denton et al., 1999; Möller et al., 2010; Pendall et al., 2001; Hein et al., 2010; Rabassa, 2008; Kaplan et al., 2004). The general climatic warming would have caused the permafrost in the catchment to thaw. Permafrost degradation could have mobilized dissolved OM and nutrients accumulated in permafrost soils (Frey and Smith, 2005; Sturm, 2005). The release of old carbon stocks, in combination with changes in hydrology and respiration of soils, has been associated with increased carbon input to lakes at times of permafrost thaw in previous high latitude studies (Kawahigashi et al., 2004; Striegl et al., 2005). The postglacial formation of soils and vegetation in the catchment is commonly associated with an increase in lacustrine production (Leavitt et al., 2003; Bunting et al., 2010.) With permafrost still sealing the ground, the first flush of nutrients would have been directly washed into the lake. The productivity increase during this time is synchronous with the decrease in magnetic susceptibility in Laguna Potrok Aike (Haberzettl et al., 2007) and the nss-Ca flux from the Dome C ice core record from Antarctica (Lambert et al., 2008), both indicating milder conditions. Other marine and ice core records describe this deglacial period of rapid warming as well (Monnin et al., 2001; Lamy and Kaiser, 2009). After 16 cal. ka BP productivity decreases to minimum values for about one millennium in Laguna Potrok Aike (Figs. 3 and 5). In other archives abrupt environmental changes are not observed. There is only a slight decline in the rate of warming recorded in marine cores after about 16 cal. ka BP (Lamy and Kaiser, 2009; Martinez et al., 2006). The reason for low productivity may be a tephra layer from the eruption of the Reclus volcano at around 16 cal. ka BP which is deposited in Laguna Potrok Aike and is directly succeeded by a massive 1.4 m thick layer of redeposited tephra material. Although tephra can also supply nutrients, it is possible that this effect was outweighed by the increased lake turbidity reducing light penetration and thus photosynthetic activity (Birks and Lotter, 1994). This could have been a lasting effect for as long as the easily transportable tephra material was present in the catchment area. Jouve et al. (submitted) observed a prolonged input of micro pumice to Laguna Potrok Aike until as late as 14.4 cal. ka BP. In fact they indicate that the productivity peak starting at about 15 cal ka. BP and peaking at 14.4 cal. ka BP is at least in part attributed to the better conservation of OM trapped in micro pumices (Jouve et al., submitted). However, they do not exclude an organic pulse at this time and indeed we find large amounts of macro remains in associated sediment sections indicating that OM trapped in pumice is not the only cause for these high TOC values. There are no indications of TOC or BSi peaks correlating to the frequent tephra layers throughout the record (Fig. 3). We, therefore, suggest that the increased TOC and BSi productivity signal is related to climatic amelioration recorded in several continental Patagonian records during this time (Ariztegui et al., 1997; Massaferro et al., 2005; Heusser et al., 1989) and in Antarctic temperature records (Fig. 3; Lambert et al., 2008; EPICA community members, 2004). In fact, at 14.7 cal. ka BP Antarctic deglaciation was so fast that it released a major meltwater injection, called meltwater pulse A1 (Stanford et al., 2006).

5.4.3.2. Antarctic cold reversal (ACR)

Meltwater pulse A1 marks the beginning and probably initiated the ACR, a period of abrupt cooling in Antarctica from 14.5 to 12.7 cal. ka BP (Fig. 3; EPICA community member, 2004). A decrease in all productivity indicators can be observed after 14.7 cal. ka BP (Fig. 3, 5). It is disputed that the ACR has an influence as far north of Antarctica as Laguna Potrok Aike. However, a cold reversal synchronous with the ACR recorded in Antarctic ice cores (Pedro et al., 2011) and marine sediment cores (Lamy and Kaiser, 2009) is also reported in several other Patagonian continental archives (Moreno et al., 2009; Hajdas, 2003; Ariztegui et al., 1997; Douglass et al., 2006).

5.4.3.3. Younger Dryas

Following the ACR TIC values rise above detection limit at 13.5 cal. ka BP. Three TIC peaks are recorded until about 11.5 cal. ka BP. Each is accompanied by a rise in TOC and C/N values (Fig. 3, 5). Periods of synchronous peaks of TIC, C/N and TOC have been interpreted as low lake levels causing supersaturation linked with calcite precipitation during dry and warm periods. The rise of C/N and TOC contents may reflect higher productivity during these warmer phases and/or the erosion of aquatic macrophyte-rich freshly exposed terraces due to a lake level lowering (Haberzettl et al., 2007). The BSi profile, however, is a more unambiguous productivity indicator. Peaks in BSi and TOC correlate with the presence of the green algae *Phacotus lenticularis* that only occurs when surface water temperatures are above 15°C (Haberzettl et al., 2007; Jouve et al., submitted). Blooms of aquatic macrophytes and diatoms can also be attributed to these warmer surface waters. Strong westerly winds would have inhibited the formation of a stable and warm epilimnion. During this time span the presence of pollen from the aquatic macrophytes *Myriophyllum* and the lack of *Nothofagus* pollen indicate relatively calm conditions (Wille et al., 2007). According to Kliem et al. (submitted, a) the onset of TIC precipitation at 13.4 cal. ka BP has a potential chronological error of ± 0.6 ka. This event was dated to 13.1 cal. ka BP by Haberzettl et al. (2007) which falls into this margin. Considering the age uncertainty in this part of the core, the event may mark the beginning of the Younger Dryas chronozone. It is however still being debated if the Younger Dryas has a noticeable impact in this southern hemispheric region (Markgraf, 1993b; Andres, 2003; Kaplan et al. 2008b). Haberzettl et al. (2007) studied TIC, C/N and TOC records of the Younger Dryas and interpret this time period as being warmer and drier at Laguna Potrok Aike. The pollen based-precipitation model also reveals a dry phase in the area during the Younger Dryas (Schäbitz et al., submitted). Several additional continental records show that the Younger Dryas in Patagonia is not a cold event as on the northern hemisphere (Ashworth and Hoganson, 1993; Hajdas, 2003; Massaferro et al., 2005; Moreno, 2004; Moreno et al., 2009). A southward movement of the SHW during this time, probably did not reach the latitudes of Laguna Potrok Aike (Zech et al., 2009). TIC precipitation ceases at about 11.4 cal. ka BP (Fig. 3, 5); the end of the Younger Dryas chronozone which was probably associated with a return to cooler and moister conditions around Laguna Potrok Aike.

5.4.3.4. Early Holocene

In the uppermost part of unit B the TIC concentration shows higher values indicating a low lake level (Fig. 3, 5). This has been attributed to warmer Holocene conditions accompanied by strong, dry winds at the onset of postglacial SHW influence on southern Patagonia (Haberzettl et al., 2007; Mayr et al., 2007a; Wille et al., 2007; Massaferro et al., submitted). This event was previously dated to 8.6 cal. ka BP (Haberzettl et al., 2007) but the revised age-depth model suggests an age of 9.3 +/-0.7 cal. ka BP (Kliem et al., submitted, a). This is in accordance with a low lake level from 9 to 7 cal. ka BP in Laguna Potrok Aike as recorded by

Anselmetti et al. (2009). Laguna Azul, a lake ca. 56 km ESE of Laguna Potrok Aike, also records a dry period lasting from 9.8 to 8.4 cal. ka BP (M. Fey, 2012, pers. comm.). Aridity at these lakes is probably intensified by an increased foehn effect caused by stronger SHW wind intensities (Mayr et al., 2007b; Fey et al., 2009). Southward shifts in storm tracks to approximately 50°S at 9 cal. ka BP are also reported by Markgraf (1993a). Villa-Martinez and Moreno (2007) suggest that approximately between 11 and 7.5 cal. ka BP the SHW shifted to south of 51°S. Marine cores show an intensification of the SHW at 53°S around 10 cal. ka BP (Lamy et al., 2010 and references therein). Archives that are not in direct proximity to Laguna Potrok Aike but closer to the Andes generally have inverse precipitation patterns (Fey et al., 2009; Wille and Schäbitz, 2009). The increase in SHW with more arid conditions in south-eastern Patagonian lowlands is recorded as higher precipitation in Andean archives. Most Andean sites report wetter conditions at 9 cal. ka BP, for example Mercer and Ager (1983) and Markgraf (1993a). Increased precipitation in western Patagonia is inferred from pollen data after 10 cal. ka BP and found to be synchronous with other paleoarchives (Tonello et al., 2009 and references therein). The Laguna Potrok Aike lowstand after ca. 9.4 +/-0.7 cal. ka BP may also be attributed to stable climatic conditions (Holocene Climatic Optimum), which has been identified between ca. 9 and 6 cal. ka BP in many records south of Laguna Potrok Aike (McCulloch et al., 2000; Waldmann et al., 2010; Unkel et al., 2008; 1993; Huber et al., 2004; Heusser, 1989). These continental records show the establishment of a warm period starting at 11.9 cal. ka BP as also recorded in marine sediments (Kaiser et al., 2005) and Antarctic ice cores (EPICA community members, 2004; 2006; Masson et al., 2000; Fig. 3).

5.4.4. Mid- to late Holocene (Unit A: 8.3 cal. ka BP to present)

Variations in C/N, TOC and TIC profiles of this unit resemble those recorded by Haberzettl et al. (2007; Fig. 5). Deviations are mainly due to a revision of the age-depth model and are all within the error margin of dating (Kliem et al., submitted, a). Since the records of TOC, BSi and C/N are biased by reworking, decomposition and dissolution. Interpretations are based on TIC as an indicator for supersaturation at Laguna Potrok Aike lake level lowstands. In accordance with Haberzettl et al. (2007) we find that during the past 8 ka the lake level was variable with humid intervals including during the “Medieval Climate Anomaly” (around 800 cal. years BP) and in particular during the “Little Ice Age” (around 300-500 cal. Years BP).

5.5. Summary of paleoenvironmental implications

The permafrost present in the catchment area of Laguna Potrok Aike during the last glacial probably inhibited infiltration of surface waters. Even though the area was most likely not under the influence of the SHW, strong catabatic winds could have prevailed. During the Antarctic A-events less cold and less windy conditions promoted productivity in the lake and in the catchment. The highest productivity was observed during the Late Glacial as conditions were warmer, but permafrost was still present to direct nutrient-laden surface runoff into the lake. This effect is assumed to have ceased at around 14 ka cal. BP when productivity begins to decline. As large amounts of surface water were lost to infiltration, the lake´s water balance became negative. Climatic variations in Antarctica affected Laguna Potrok Aike causing cooling during the Antarctic Cold Reversal and warming during the Younger Dryas. The SHW probably did not influence the area before 9.4 ka. During the Holocene the strong and dry SHW inhibited an increase in productivity in and around the lake.

6. Conclusions

We conclude that in order to reconstruct paleoproductivity many direct and indirect factors controlling the abundance of different types of aquatic organisms in the lake system need to be taken into account. In order to deal with this complexity, we recommend the use of multiple paleoproductivity indicators. Concerning the study of lacustrine records covering long time periods, we demonstrate that the dynamics of a lake system may be subject to large changes. This case study at Laguna Potrok Aike shows alterations of catchment hydrology and variations in atmospheric circulation patterns. In consequence, the measured variations of one proxy may be influenced by different forcing factors over time. This can lead to variations in interpretation of the signature recorded in the sediment. The present study gives a first insight into the high resolution record of carbonate and OM content from Laguna Potrok Aike covering the last 51 ka. Future lake biogeochemistry studies will refine these interpretations. We suggest that warming events in the southern hemisphere during the last glacial (such as during the Antarctic A-events, the postglacial warming and the Younger Dryas chronozone) are reflected as high productivity events in Laguna Potrok Aike. There is no evidence of shifts in the SHW affecting paleoproductivity in Laguna Potrok Aike during the glacial. Until Holocene times, Southern Patagonia was probably not under the influence of the SHW as these were in a much more northerly position. Paleoproductivity can only give speculative indications of wind speeds and should be seen as a supplement to ongoing studies of the Laguna Potrok Aike dust record which is a more direct proxy for wind intensity.

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Chapter 4:

Elemental composition of the Laguna Potrok Aike sediment sequence reveals paleoclimatic changes over the past 51 ka in southern Patagonia, Argentina

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[3] PASADO Science Team cited at: http://www.icdp-online.org/front_content.php?idcat=1494

Abstract

During the lake deep drilling campaign PASADO in 2008 more than 500 m of lacustrine sediment was recovered from the maar lake Laguna Potrok Aike, Argentina. The major element composition was assessed at high resolution with an ITRAX X-ray fluorescence core scanner. The sharp boundary between a carbonate-bearing and a carbonate-free depositional system occurs at 13.5 cal. ka BP and marks the transition from glacial to the Late Glacial sediments. Holocene and Late Glacial sediments can be distinguished by elements that are indicative of organic matter (Br, Cl) or calcite (Ca). Glacial sediments are characterized by elements that represent minerogenic terrigenous clastic input (Fe, Ti, K, Si). Trace elements (Mn, Rb, V, Ni) accumulate with the bulk of lithogenic elements indicating frequent oxic conditions and rare diagentic remobilization. Based on a principal component analysis we interpret the scores of the first principle component as a summarizing indicator for climate-related variations of depositional conditions. During the Holocene they mirror the total inorganic carbon profile which was used as a proxy for lake level reconstructions of the past 16 ka in previous studies. High scores in the first principle component probably reflect periods of increased chemical over mechanical weathering and developing soils and vegetation cover limiting sediment availability for erosional processes. These intervals often also show increases in total organic carbon values and total organic carbon/total nitrogen ratios, which are associated to periods of Antarctic warming in the last glacial. Geochemical variations of the clastic glacial sediments are explored by excluding carbonate-bearing sediments from the principal component analysis. Although Ca is a purely clastic signal in carbonate-free sediments, it does not correlate with the bulk of indicators for terrigenous input. Instead it dominates a second principal component together with Sr. This component mainly distinguishes coarse grained layers from the remaining sediment. The main provenance of this coarse grained material is suggested to be a basalt outcrop at the western shore. Low lake levels, high waves and flash flood events may have increased the availability of basaltic sand, during extremely cold, arid and windy conditions. High wind speeds and lacking vegetation may have facilitated the increased transport of coarse grained material into the center of Laguna Potrok Aike. Decreases in the second principal component can be observed during Oxygen Isotope Stage 2 during which increased dust input has been found in cores from Laguna Potrok Aike, the Southern Ocean and Antarctica.

Keywords:

PASADO, ICDP, lake sediments, paleoclimate, ITRAX, XRF scanning, geochemistry, principal component analysis

1. Introduction

The importance of the southern hemispheric mid-latitudes for the global climate system has become more and more evident in recent studies. Toggweiler and Lea (2010) propose that the ventilation of the deep Southern Ocean and thus the flux of CO_2 from the ocean into the atmosphere is controlled by the strength and position of the Southern Hemispheric Westerlies (SHW). Anderson et al. (2009) suggest that a shift in the SHW caused CO_2 to increase 17 ka ago. The cause of variations in southern hemispheric glacial dust fluxes and their implications for global climate also remain unclear (Weber et al. 2012; Fischer et al. 2007). Patagonia has been identified as a major dust source and the SHW as a main dust transport agent (Basile et al. 1997; Iriondo 2002). The climate archive Laguna Potrok Aike, in southern Patagonia, is well positioned to make a contribution to these ongoing discussions. Furthermore, the continuous ~100 m long PASADO (Potrok Aike Maar Lake Sediment Archive Drilling Project) record, reaching back 51 ka, is an important step towards closing the spatial gap of high resolution climate studies which persists in the southern hemisphere (Voelker, 2002). To improve the temporal resolution of climatic reconstructions in southern Patagonia and thus contribute to the understanding of mechanisms of centennial to millennial-scale climate change Laguna Potrok Aike sediments are analyzed at high resolution via X-ray fluorescence (XRF) scanning. XRF scanning is a useful tool for the high resolution qualitative geochemical analyses of sediment cores (Courdace et al., 2006; Zolitschka et al., 2001). It has been successfully applied to several long lacustrine records (Daryin et al., 2005; Brown et al., 2007; Shanahan et al., 2008a; Otu, 2010; Lyons et al., 2009). In previous studies, Laguna Potrok Aike elemental profiles have been successfully used for paleoenvironmental reconstructions (Haberzettl et al., 2007; 2009; Jouve et al., submitted). The geochemical data contains information on variations of the clastic, carbonaceous and organic input to the lacustrine system. These can be attributed to changes of climatic and environmental conditions at Laguna Potrok Aike related to regional atmospheric and oceanic circulations. By means of comparative studies with other archives we obtain insights into inter-hemispherical climate coupling and regional differences in the manifestation of past climate change.

2. Study Site

Laguna Potrok Aike (52°S, 70°W; 116 m a.s.l.) is a 100 m deep maar lake with a diameter of 3.5 km (Zolitschka et al., 2006) located 80 km north of the Strait of Magellan (Fig. 1). The surface of the catchment area consists predominately of fluvioglacial sediments and basal moraine tills with sporadic exposures of alkali-olivine basalts (Coronato et al., 2004; submitted; Zolitschka et al., 2006). At present, this area is under the influence of the SHW belt. The Andes cause an uplift of the air, which results in precipitation on the west coast and semi arid conditions with dry catabatic winds east of the Andes (Gaiero, 2007). The low annual precipitation (often below 200 mm per year) and the potential evaporation of 0.5-10 mm per day (Ohlendorf et al., submitted; Borrelli and Oliva, 2001; Endlicher, 1993) lead to a dry steppe vegetation where dust deflation is an important geomorphological agent (Clapperton, 1993).

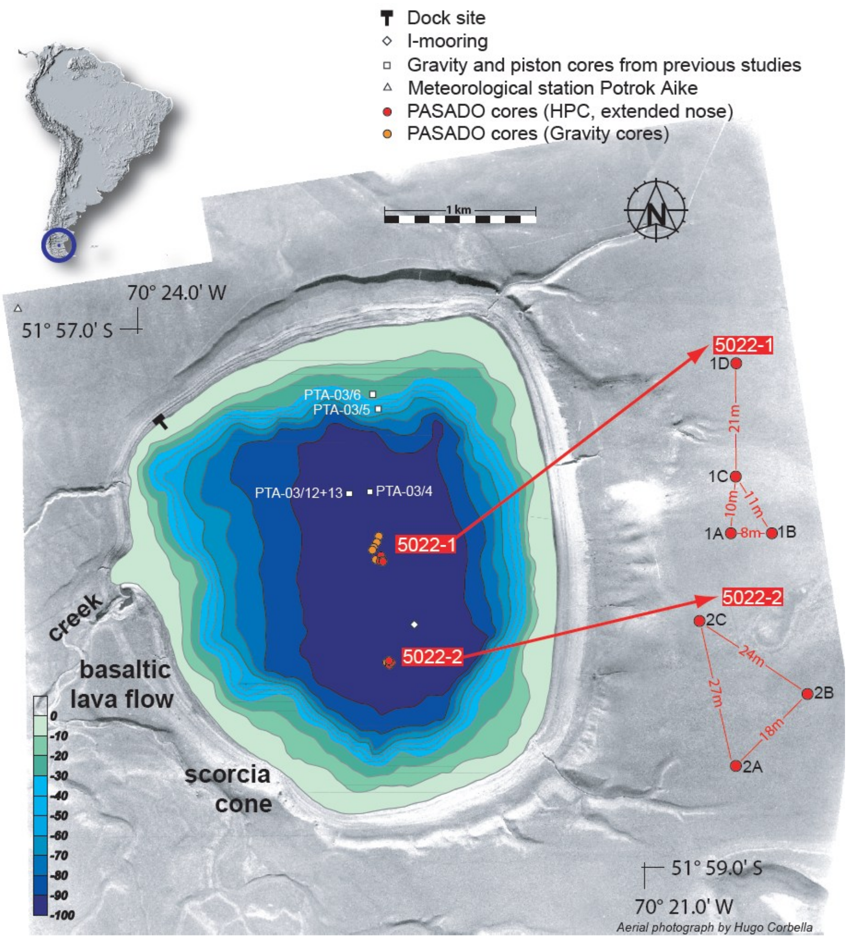


Fig. 1 Location of Laguna Potrok Aike in southern Patagonia, Argentina. Relevant locations are indicated on the map.

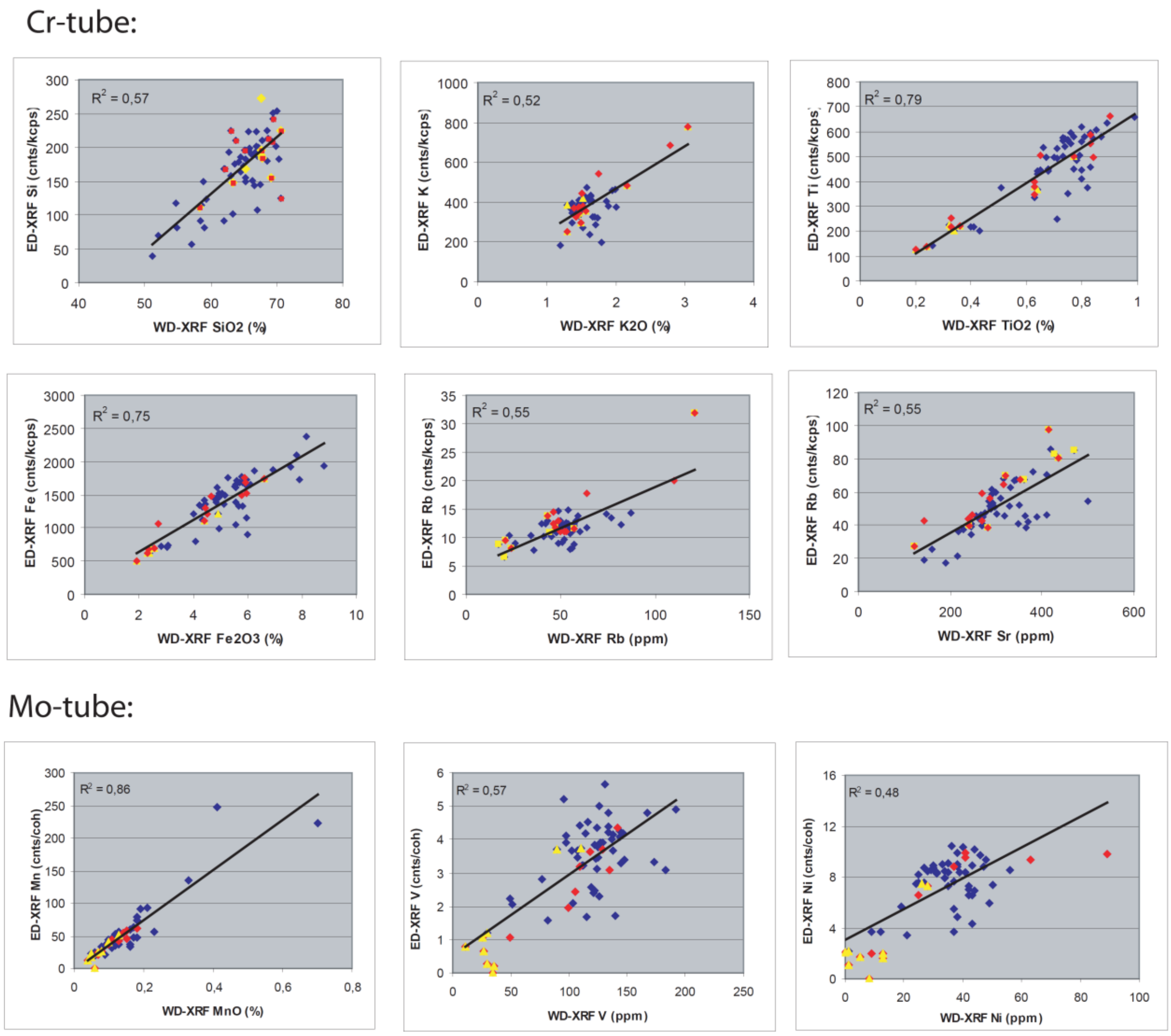
3. Methods

3.1. Cores and measurements

Drilling was conducted by DOSECC using the GLAD800 (Global Lake Drilling 800 m) system. During this operation the Hydraulic Piston Coring (HPC) system was mainly used for core recovery. The analyzed data set is based on the composite profile from site 2 with a total length of 106.08 m. The composite profile was constructed from 99 core sections from triplicate holes recovered from site 2 and correlated visually (Fig. 1; Ohlendorf et al., 2011). Cores were recovered during the PASADO field campaign in 2008. After splitting cores in the lab, energy dispersive (ED)-XRF core scanning was performed with an ITRAX core scanner (COX analytical systems, Croudace et al., 2006) in 5 mm steps with a Mo-and Cr-tube. The Mo-tube produces good excitation for a range of elements with medium atomic numbers. Excitation of elements with lower atomic number may be achieved with the Cr-tube. XRF-tube current settings varied between 18 and 34 mA for the Mo-tube and between 26 and 50 mA for the Cr-tube. Settings were selected by the operator depending on the prevailing lithology of the section. A large variation in Laguna Potrok Aike lithologies requires different element detection sensitivities. Tube voltage and exposure time per step were kept constant at 30 kV and 10 s, respectively. Interaction of the electron beam with the sample produces X-ray emissions. The detector is able to separate characteristic X-rays emitted by different elements into an energy spectrum. A dispersive energy spectrum peak is acquired for each element as well as the coherent and incoherent X-ray scattering. Peak area integrals are directly related to element concentrations within the sediment (Rothwell and Rack, 2006). The software Q-spec is used to calculate the abundance of specific elements. Peaks are evaluated by a fitting procedure during which mathematical models of characteristic X-ray peaks are compared to the actual spectrum with the square error being minimized. The measurement was discarded if the detector-sediment distance was too large or if the threshold of 27 kilo counts per second (kcps) was not reached. Wavelength dispersive (WD)-XRF measurements were performed on selected composite profile samples using an automatic wavelength dispersive spectrometer (MagiX Pro, Panalytical) with a Rh-tube. Pellets for WD-XRF measurements were pressed from 600 mg of sediment ground to smaller than 63 µm and 3600 mg of lithiumtetraborat. Grain size distribution of selected samples was measured using a Beckmann Coulter LS 200. Mineral assemblages of 53 selected, dried and carefully grounded bulk samples were determined by powder X-ray diffraction (XRD) analyses (Philips X'Pert Pro MD equipped with an X'Celerator Detector Array). Nickel filtered Cu-$K\alpha(1,2)$ radiation (λ = 1.541818 Å) was used for the powder diffraction and the data was collected in the 2 theta-range 2-85° in 0.02° steps with counting times for individual scans of 50 s. For quantitative Rietveld analysis all phases with >1 weight percent (wt %) have been considered and evaluated with the software Maud. (Lutterotti et al., 2007). The sediment composition, regarding grain size and color spectra, was described during core opening.

3.2. Data processing

Split core surfaces, even when very carefully cut, do not offer ideal measuring conditions (Jansen et al., 1998). Variations in surface roughness, water content, grain size, organic matter (OM) content, mineral crystallinity, compaction and porosity influence the accuracy of XRF scanning results (Croudace et al., 2006; Löwenmark et al., 2011; Rothwell and Rack, 2006; St-Onge et al., 2007; Tjallingi et al., 2007; Weltje and Tjallingi, 2008). Analytical artifacts can also be caused by element interactions, variations in the detection of elements according to atomic number, poor discrimination of closely placed element peaks, tube ageing and different measurement settings (Jenkins, 1999; De Vries and Vrebos, 2002; Kido et al., 2006). In the specific case of Laguna Potrok Aike, tube currents were changed due to large variations of the sediment matrix. In conclusion, XRF scanning measurements can be considered semi-quantitative (Rothwell and Rack, 2006). We therefore refrain from calculating element concentrations from total counts (cnts). In order to correct for the above named effects, an often applied normalization method is division of cnts by scattering (Borkhodoev, 1998; Kylander et al., 2011; Croudace et al., 2006). Fluctuations in sediment mineralogy, matrix, grain size and water content affect the mean atomic number of the sediment volume excited by the X-ray beam of the XRF core scanner (Kylander et al., 2011; Rothwell and Rack, 2006; Tjallingi et al., 2007). Changes in mean atomic number are recorded in coherent and incoherent scattering (Beckhoff et al., 2006; Thomson et al., 2006). Effects of sample composition can therefore be corrected using the intensity of the coherent and incoherent scatter peaks (Potts et al., 1997; Araujo et al., 1990; Rao et al., 1995). Scanning results measured with a Mo-tube are normalized by dividing the cnts by the coherent scattering expressed as cnts/coh. In Cr-tube spectra, the coherence scattering peak is unfortunately overlapped by Ca- and Fe-peaks and can therefore not be assessed. Instead division by kcps as a standardization method (expressed as cnts/kcps) improves the quality of the data by counteracting the closed sum effect. Another way of avoiding grain size effects is expressing elements as ratios to a detrital phase element (e.g. Ca/Ti) (Croudace et al., 2006; Richter et al., 2006). However, following Weltje and Tjallingi (2008), we refrain from using ratios due to their asymmetry. A possibility of correcting for the absorption of X-ray fluorescence by water is estimating the water content of marine sediments using measured Cl content (Tjallingi et al., 2007). In the lacustrine Laguna Potrok Aike record this is not feasible due to down core variations in pore water Cl contents (Vuillemin et al., submitted). In order to estimate element concentrations, assess the quality of XRF scanning data and select the best standardization technique for each element, 60 discrete (WD)-XRF measurements were compared to wet continuous measurements (Fig. 2). The scanner uses an ED-XRF system. However, WD-XRF measurements on pressed pellets, which minimize the effects of sample inhomogeneities, packing and particle size effects, is a more accurate tool for measuring the geochemistry of lake sediments (Boyle, 2000). Deviations between WD- and ED- XRF measurements may not only be linked to measurement quality but also to differences in device settings and/or differences in measuring the sediment surface as opposed to bulk sediment. Relatively good correlations (R^2 between 0.48 and 0.86) were found for the elements Fe, Ti, Mn, V, Ni, Rb, K, Si, Ca and Sr. Coarse grained and tephras samples mostly plot close to regression lines documenting that effects of grain size or lithological variations on the scanning data are limited (Fig. 2). The measured element concentrations are all above the detection limit reported for the Itrax core scanner by Croudace et al. (2006). Furthermore, only a very weak correlation between the measured sediment water content and element cnts was found for the element K (R^2=0.23). Grain size and WD-XRF measurements in a turbidite show that geochemical variations with grain size are not caused by matrix effects, but rely on changes in sediment composition (Fig. 3). The penetration depth of X-rays is dependent on the atomic number of the element. In general, heavier elements (V to Rb) show better results when measured with a Mo-tube while it is generally necessary to use a Cr-tube for lighter elements (Si to K). Some intermediate elements (Rb, Ca and Ti) show comparable results when using both tubes. There is no information on the reliability of the Cl and Br data as these were not assessed with WD-XRF. However, Cl and Br profiles appear to contain an interpretable geochemical signal defined by low noise, high variability and a sufficiently high number of cnts. PCA (principal component analysis) is a useful tool for analyzing large datasets like element profiles from XRF-scanning (Lotter et al., 1995; Ammann, 2000; Birks and Birks, 2006; Bradshaw et al., 2005). The data set is reduced to a few primary components explaining the majority of the variation. It thus permits a summarized overview of scanning results and at the same time helps to remove redundancy and to reduce noise and/or element-specific biases (Shanahan et al., 2008a; Birks, 1998). It has been used in geochemical characterization of



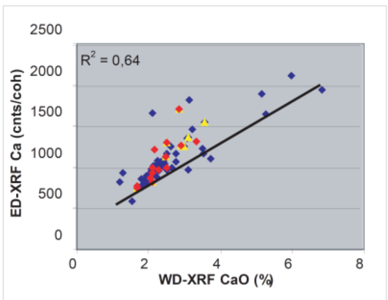


Fig. 2 Scatter plots of best fits between wavelength dispersive XRF (WD-XRF) measurements versus energy dispersive XRF (ED-XRF) scanning data. Coarse grained samples and tephra samples are marked in red and yellow respectively. Correlation coefficients are indicated.

sediments in previous studies (e.g. Monien et al., 2010). For PCA statistical analysis, logarithmic transformations of primary data to achieve a normal distribution was necessary for the elements Br, Si, and Sr. The data of every element was centered to zero by subtraction of averages and scaled with its variance in order to give each element equal importance. A PCA was applied to centered and scaled data of all elements with an interpretable geochemical signal (Fe, Ti, Mn, V, Ni, Rb, Si, K, Ca, Sr, Cl, Br).

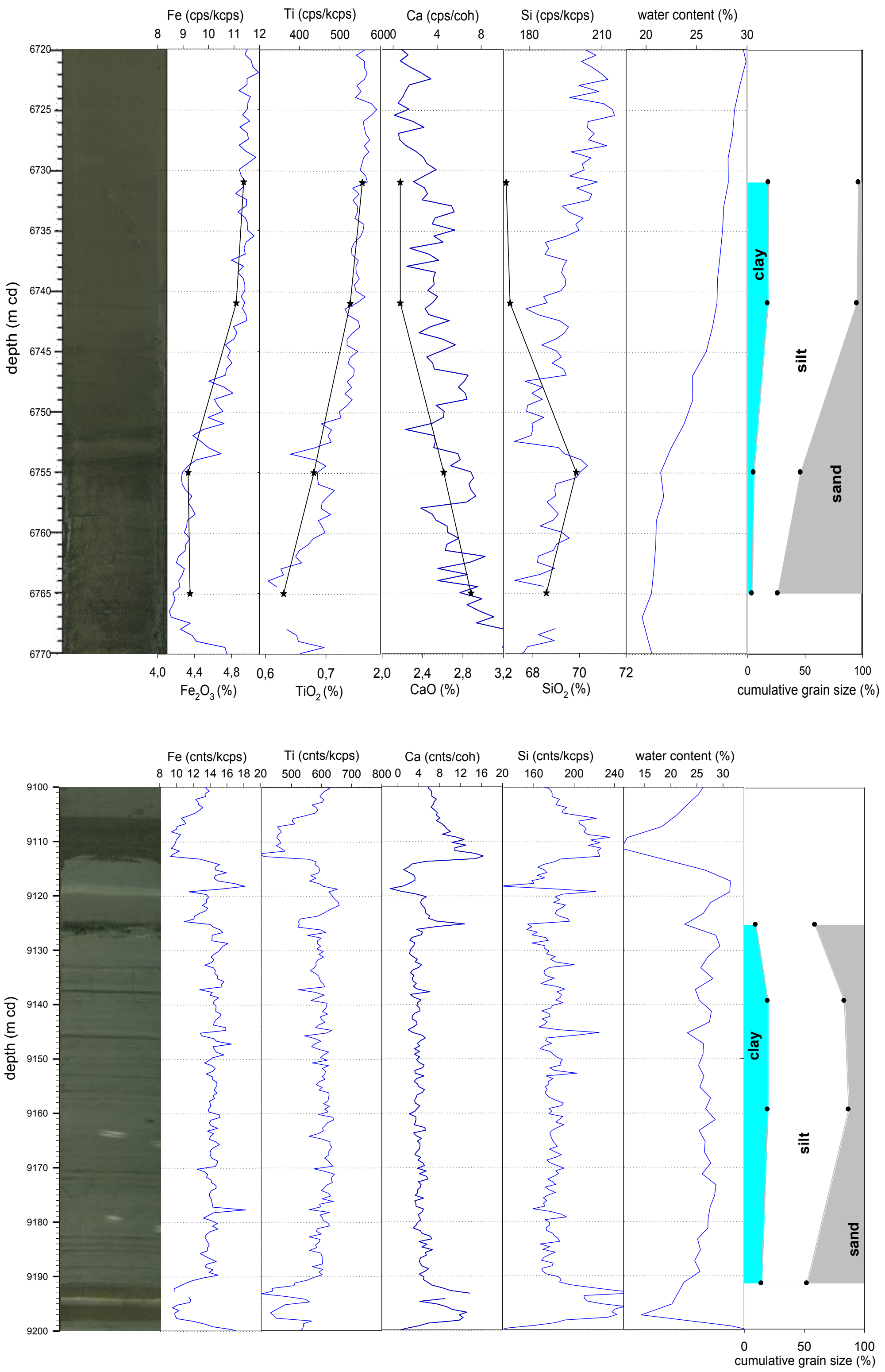


Fig. 3 Core images and XRF data show the correlation between coarse grain size, increases in Ca and Si and decreases in Fe and Ti at the base of a turbidite (above) and in discrete layers(below). Furthermore, WD- XRF measurements in the turbidite confirm that geochemicalvariations are not an artifact of grain size and water content effects on ED- XRF scanning measurements.

3. Results

3.1. Lithology and chronology

The PASADO composite profile was dated and divided into lithologic units (A, B, C-1, C-2, C-3) by Kliem et al. (submitted). Pelagic sediment was distinguished from remobilized material, and tephra layers. In unit A, lithology consists mainly of laminated pelagic silts with a high content of calcite. Unit B is rich in organic material (aquatic mosses) and described as being dominated by laminated pelagic silts with some occurrences of calcite and fine sand layers. Poorly laminated silts and fine sands dominate unit C. Layers related to mass movement deposits are thicker and more frequent further down core.

3.2. Element concentrations

The main element present in Laguna Potrok Aike sediment is SiO_2 (51-71 wt %); other major (more than 1 wt %) elements are Fe_2O_3 (2-9 wt %), CaO (1-7 wt %), and K_2O (1-3 wt %). MnO and TiO_2 are less common (0.04-0.7 wt % and 0.2-1 wt %, respectively) and can be considered as minor elements. The dry weight mass of the trace elements (Sr, Rb, Ni, V) is below 0.1 wt % (Fig. 2).

3.3. Elemental profiles

The Laguna Potrok Aike element composition varies with depth according to lithological changes (Fig. 4). Relative to unit C, contents of the elements Fe, Ti, V, Mn, Rb and Ni are decreased in lithological units A and B, especially in the lowermost third of unit B. Sr, Cl and Br show trends that are exactly inverse to this; high amounts in unit A and B, especially in the lowermost part. Ca cnts/coh are ~100000 fold higher in unit A and in the upper part of the unit B than in the remaining parts of the core. K and Si show a roughly inverse trend with especially low contents in the upper part of unit A and peaks at the bottom of unit B as well as increased abundance in unit C. Tephra layers are often associated with negative peaks in the elements Fe, Ti, Mn, V, Rb and Ni and positive or no peaks in the remaining element profiles. In remobilized sediments the elements Fe, Ti, Mn, V, Rb and Ni are often depleted while the Ca, Sr, K and Si generally show peaks.

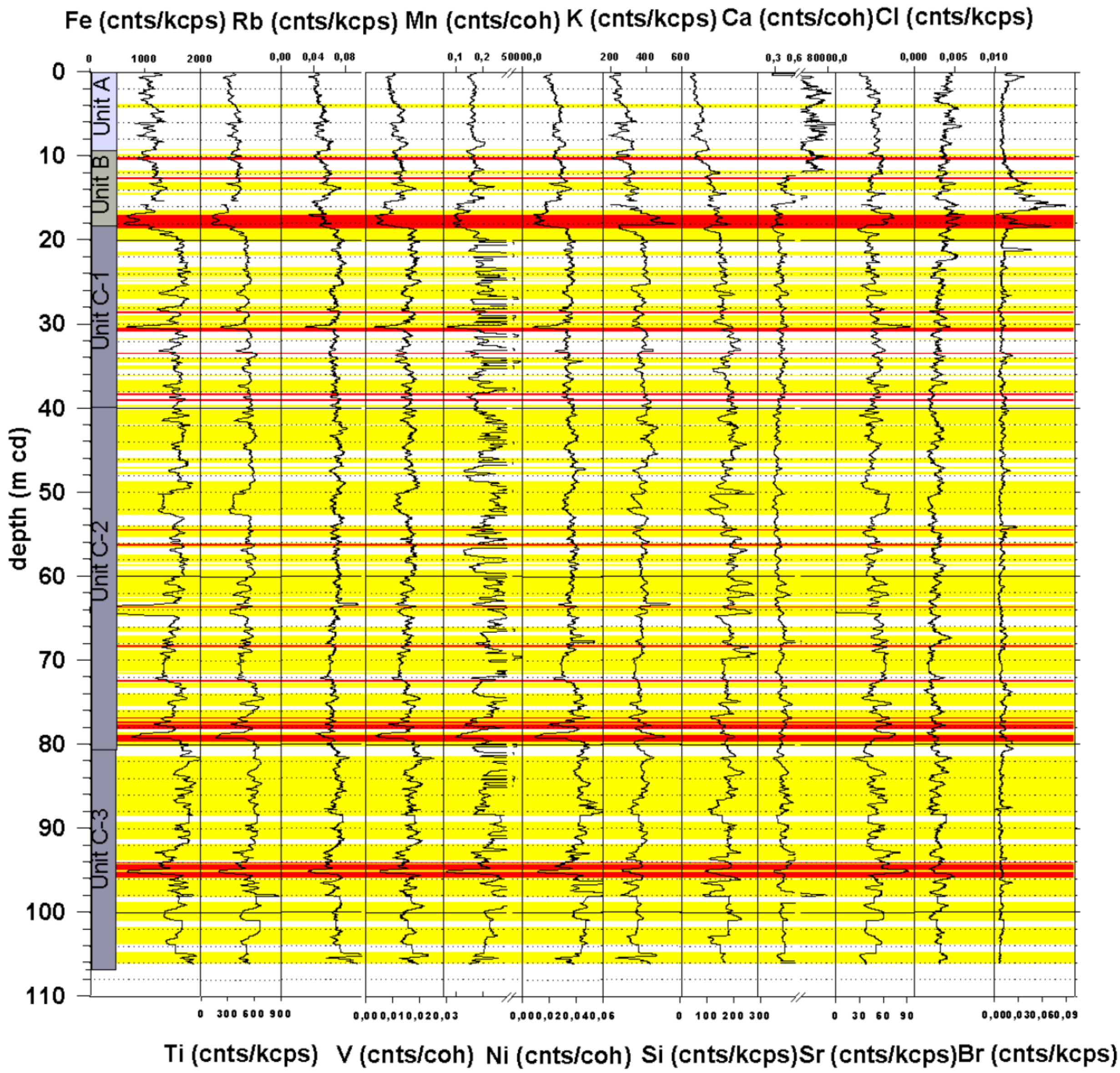


Fig. 4 XRF-data of the PASADO site 2 composite profile plotted against composite depth (m cd) as 11 point running means. Horizontal yellow bars indicate redeposited sediment and red bars refer to tephra layers. Lithological units A, B and C are indicated according to Kliem et al. (2012).

3.4. Principal component analysis

In the PCA of XRF data (Fig. 5a), the various lithologies of the Laguna Potrok Aike sediments have similar scores in the first and second components. Therefore, they form clusters, which indicate that different lithologies have different geochemical signatures. Certain lithologies can be clearly identified; tephra samples, Holocene and Late Glacial sediments can be distinguished geochemically. Redeposited sediments, however, have a geochemistry that is hardly distinguishable from glacial sediments. Two significant principal components can be extracted from the data set representing about 49% of the total variability.

The first component explains about 34% of the variation in the dataset and the second component another 15%. In order to facilitate a component based sediment classification we use the PCA to divide the dataset into four main groups (Fig. 5b). The first two groups have positive loadings in the PC2 and are characterized by the elements Ca, Sr, Br, Cl. Group 1 has positive PC2 loadings and contains elements common in Holocene and Late Glacial sediments (Br and Cl). Group 2 (Ca and Sr) has negative PC2 loadings and mainly describes the tephra layers (subgroup 2a). However, it is also often associated with Holocene and Late Glacial sediments (subgroup 2b). Group 3 (Si, K, Ti, Fe, Mn, Rb, Ni, V) has negative loadings in PC1 and is representative of redeposited and glacial sediments. Within this group 3 subgroups can be distinguished; subgroup 3a (Mn, Rb, Ni, V) with neutral loadings in PC2, subgroup 3b (K and Si) with negative loadings in PC2 and subgroup 3c (Ti and Fe) with positive loadings in PC2. The PCA of carbonate-free sediments shows a similar distribution, merely the loading of Ca changes from being positive to negative forming a group 4 with Sr.

4. Component-based sediment classification

4.1. Organic sediments (Group 1)

Late Glacial and Holocene sediments can be distinguished from glacial sediment by higher element counts of Br and Cl (Figs. 5a and 6). This can be attributed to the fact that these sediments are relatively rich in OM (with total organic carbon TOC contents of up to 7%) and that Br and Cl can be adsorbed to OM (Thomson et al., 2006). Moreover, Br has been used to estimate the presence of OM in marine (Ziegler et al., 2008; Ten Haven et al., 1988; Mercone et al., 2001) and lacustrine sediment studies (Croudace et al., 2006; Thomson et al., 2006; Ten Haven et al., 1987). For Laguna Potrok Aike a correlation (R^2=0.41) between TOC and Br is notable (Fig. 6). Modern Cl concentrations in the subsaline waters of Laguna Potrok Aike are relatively high (approx. 500 mg/l, Zolitschka et al., 2006). The Cl content in the sediment suspension of PASADO core catchers varies with sediment porosity and probably reflects the contribution of Cl-bearing pore water to the sediment suspension (Recasens et al., 2012). Organic rich layers tend to show a higher water content (Shanahan et al., 2008b). Cl, aside from being adsorbed to OM, has been used as a proxy for porosity linked to organic rich sediments (Thomson et al., 2006; Tjallingi et al., 2007). However, sands and tephra layers also tend to be highly porous and water-saturated. Therefore, these layers represent confounding factors when interpreting the Cl profile.

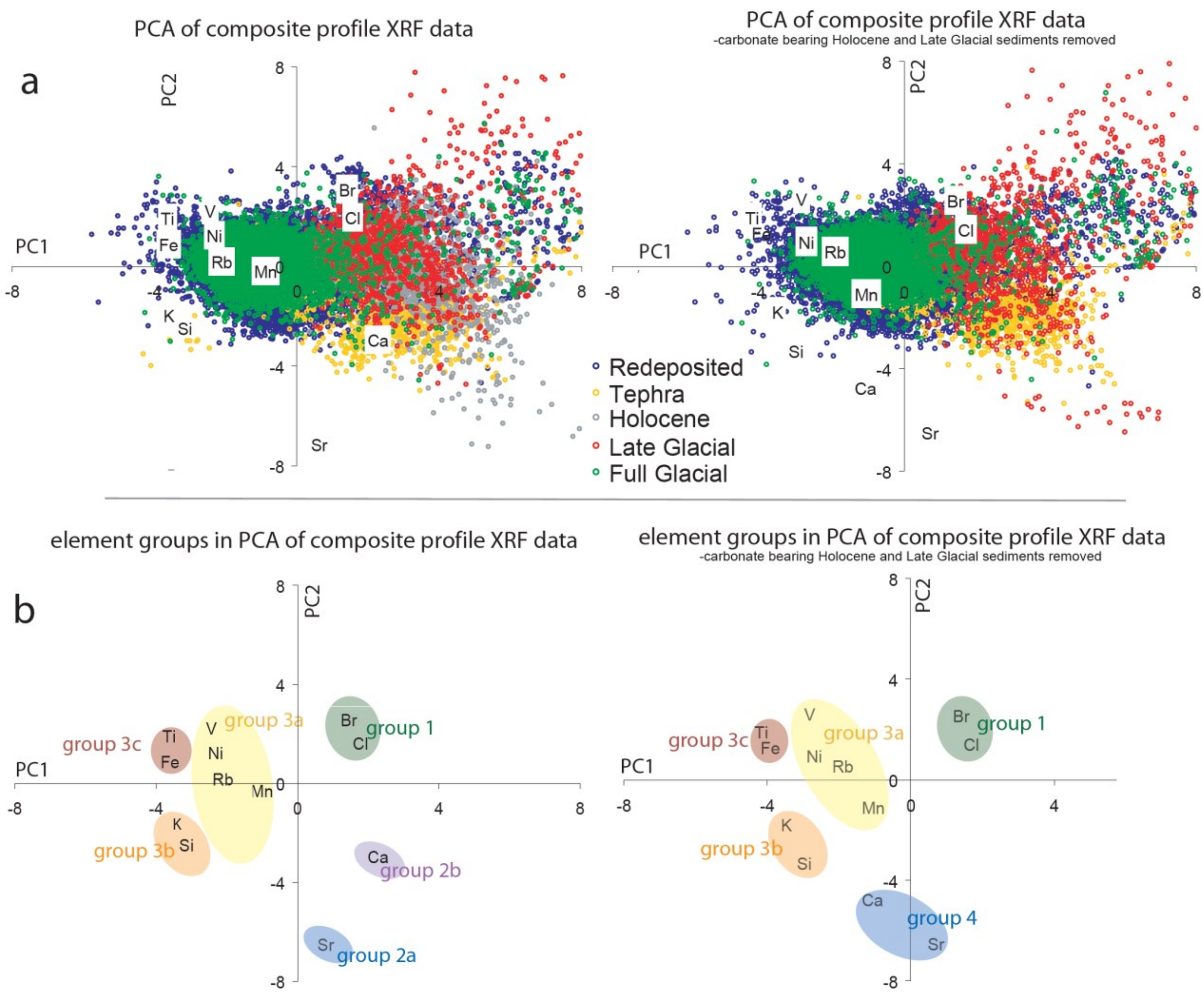


Fig. 5 Scores and loadings of the PCA of Laguna Potrok Aike site 2 composite profile XRF data. (a) Scores (marked by a colored circles for each measurement point) show the location of redeposited, tephra, Holocene, Late Glacial and full glacial sediments in the PCA. Loadings (indicated with the element symbols) show which elements are responsible for the distribution of the data points in the PCA. (b) The distribution of the elements within the PCA is used to divide the dataset into 4 main groups and several subgroups.

4.2. Tephra layers (Group 2a)

Apart from high levels of Cl in the layers that have a high water content, tephra layers in Laguna Potrok Aike are often characterized by Ca, Sr and/or K peaks and also distinguished by their negative peaks in Ti, Fe, V, Ni and Mn. Several studies have described and identified tephra layers using XRF scanning techniques (Francus et al., 2009; Langdon et al., 2011; Moreno et al., 2007). In general, the major elements are used (Kylander et al., 2011) for example Fe (Peck et al., 2007), K and Ti (Unkel et al., 2010) or volcanic glass associated with titanium-iron oxides (Marsh et al., 2007). Unkel et al. (2010) conclude that tephra layers show peaks in various different elements, but a clear correlation between a specific element in the

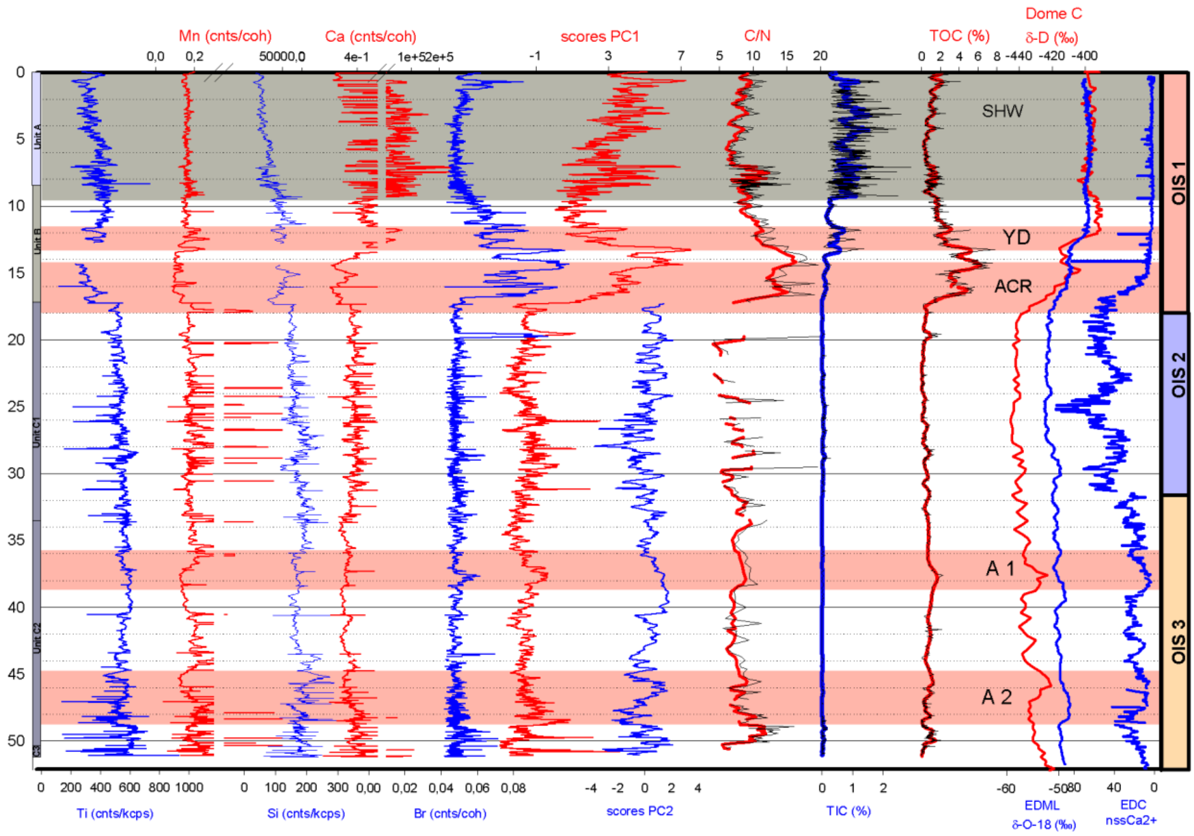


Fig. 6: XRF-data of selected elements, PC1 and PC2 scores of the pelagic PASADO site 2 composite profile plotted as 11point running means against age (age model v.3, Kliem et al. 2012). The deuterium record from the Dome C ice-core (blue; EPICA Community Members, 2004), the oxygen isotope record from the Dronning Maud Land (DML) ice-core (red; EPICA Community Members, 2006), the EDC nss Ca+ record (Fischer et al, 2007) and Laguna Potrok Aike geochemical data (Hahn et al. 2012) are plotted for comparative purposes. Lithological units A, B and C are indicated according to Kliem et al. (2012). Colored horizontal bars mark warm (red) and cold (blue) climatic events such as the Antartic A-events 1 and 2 (A1; A2), Oxygene isotope stage 2 (OIS2), the Antartic Cold Reversal (ACR) and the Younger Dryas (YD).Gray coloring represents an increases in southern hemispheric westerlies (SHW) influence.

XRF data and tephra geochemistry has not yet been found. The geochemical signature of tephra layers is not only dependent on the composition of the tephra itself and its sorting via eolian distribution, but also on the geochemistry of the tephra layer with respect to the surrounding sediment (Kylander et al., 2011). In the specific case of Laguna Potrok Aike the negative peaks in Ti, Mn and Fe can be explained by the fact that almost all Laguna Potrok Aike tephras are rhyolitic (Wastegard et al., submitted). Jouve et al. (submitted) demonstrate that Fe and Ti concentrations are much higher in the rocks of the watershed than in micropumices found in Laguna Potrok Aike. Instead, rhyolithic tephras may show for example K peaks (Brown et al., 2007). Furthermore, the Reclus and Mt. Burney tephras which comprise more than 50% of all Laguna Potrok Aike tephras have been described as abundant in Ca (up to 1.5 and 2.3 wt % respectively; McCulloch et al., 2005; Wastegard et al., submitted). Ca and Sr are probably associated with the plagioclase of rhyolithic tephras. Sr enrichment in tephra layers is common (Unkel et al., 2010). In sediments most Sr is contained in organic and carbonate sediment components and only in small amount in silicates, lithic fragments and detric feldspars (Salminen et al., 2005). Since Laguna Potrok Aike sediments are low in carbonates and organics (Hahn et al., submitted), Sr peaks of tephra layers are probably particularly prominent.

4.3. Carbonate sediments (Group 2b)

Carbonate sediments are easily identifiable by their extremely high Ca values which mirror the inorganic carbon (TIC) content (Bryden and Kinder, 1991; Haberzettl et al., 2009). In Laguna Potrok Aike carbonate generally only occur in Holocene and Late Glacial sediments resulting mainly from chemical precipitation - primarily inorganically precipitated calcite and/or ikaite derived calcite (Oehlerich et al., submitted). Carbonaceous microfossils of the green alga *Phacotus lenticularis* occur rarely and only in the Late Glacial (Haberzettl et al., 2007; Hahn et al., submitted). The mineral rhodochrosite (up to 2.3 wt %), has been detected in several glacial samples with TIC values near the detection limit (Fig. 7). The distribution of Sr is affected by the substitution of Sr^{2+} for Ca^{2+} in carbonate minerals (Salminen et al., 2005). However, in Laguna Potrok Aike carbonate sediments, especially in phacotus-rich sections, the correlation of Sr to Ca peaks is not always very strong (R^2=0.06). Ca may be more available in lake water and preferably integrated into calcite crystals and especially phacotus shells. Bluszcz et al. (2009) report Sr/Ca ratios of phacotus shells (~0.005) that are lower than those reported for primarily inorganically precipitated calcite (up to 0.01) and also pseudomorphs after ikaite (~0.01) (Burchardt et al., 2001). Furthermore, the integration of Sr into phacotus shells or calcite crystals may be affected by the calcite precipitation rate (Lorens, 1981) or the sediment clay content (Mirkhani et al., 2012).

4.4. Clastic sediments (Group 3)

Negative scores in PC1 are associated with the elements Fe, Si, K, Ti and, to a lesser extent with Ni, V, Mn and Rb. The glacial sediments are characterized by this element group (Fig. 5a). These lithogenic elements represent terrigenous sediment fluxes and are indicators for detritic input (Cohen, 2003; Croudace et al., 2006; Rothwell and Rack, 2006; St-Onge et al., 2007). Ti, Fe, K and Co have proven to be reliable lithogenic indicators in previous Laguna

Potrok Aike studies (Kastner et al., 2010; Haberzettl et al., 2005; 2007). Down core XRD analysis shows low variability in mineral assemblages of Laguna Potrok Aike sediments (Nuttin et al., submitted). Likewise, strontium and neodymiun isotopic studies do not detect a great variability in the Laguna Potrok Aike sediments which are assumed to mainly derive from the Patagonian gravel formation - the moraine material that covers large parts of southern Patagonia (A. Stopp, 2008 pers. comm.). However, these studies focused on Holocene and Late Glacial sediments and/or were performed at relatively low temporal resolution. Therefore, they were not able to capture the variability in clastic input that is highlighted by the high resolution geochemical data of this study (Fig. 5a). A division of the clastic sediments in 3 groups is possible; Fe and Ti, Si and K and trace elements. Phase shifts in the clastic elements Ti, K, Rb and Si are common (Kylander et al., 2011). They have been associated with the fact that the chemistry of sediments is controlled by the grain size of the

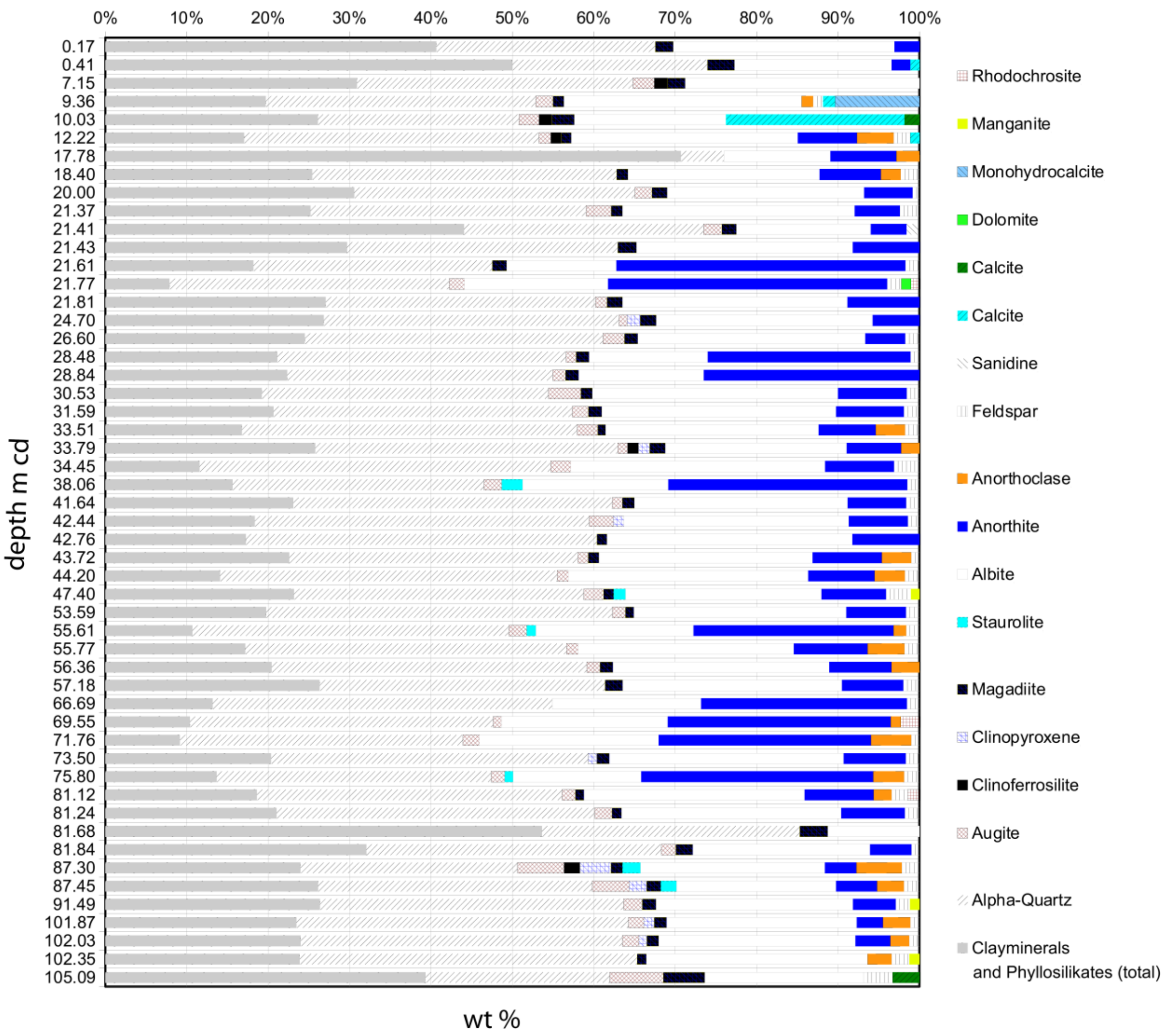


Fig. 7 Histogram of relative mineralogical abundances using XRD from 53 selected samples versus meters composite depth (m cd) along the composite record. All clay minerals and phyllosilikates are summarized in the chart.

dominant host mineral and therefore by particle size sorting (Koinig et al., 2003; Jin et al., 2006). For studying these variations in the composition of the clastic material itself, XRF scanning is an ideal tool. This geochemical dataset contains information about the nature of weathering and transport. Rates and intensities at which weathering provides sediments are controlled by bedrock type and availability as well as by climate forcing affecting weathering mechanisms, soil and vegetation cover. Transport mechanisms include marginal colluvial action, eolian and/or fluvial input (Cohen, 2003).

4.4.1. Fe Ti (Group 3a)

In the PCA Fe and Ti group very close together (Fig. 5a) and their profiles correlate (R^2=0.59) (Fig. 4). In Laguna Potrok Aike the elements Fe and Ti occur simultaneously in the minerals staurolite and the relatively common augite (Fig. 7). Ti is often used as an indicator of detrital mineral input in the sedimentary record (Croudace et al., 2006; Haberzettl et al., 2005). Iron usually enters lakes as Fe-oxides which can prevail in stable oxic conditions unless they meet anoxic water or organic material which reduces them to soluble ferrous iron (Cohen, 2003). The correlation with Ti indicates that this is not the case for Laguna Potrok Aike. Furthermore, this correlation may indicate the presence of titano-magnetite as suggested by Kastner et al. (2010). The grain size of magnetite in Laguna Potrok Aike is found to be relatively fine (Lise-Provnost et al., submitted). Ti and Fe have been used as indicators for silt and clay (Voigt et al., 2008; Rothwell et al., 2006; Cuven et al., 2010; Koinig et al., 2003; Deer et al., 1992). A further similarity between Fe and Ti is that they are both unreactive, insoluble (under oxic conditions) and abundant in heavy minerals, resistant to chemical and physical weathering (Croudace et al., 2006; Shanahan et al., 2009; Mischke et al., 2010; Cohen, 2003; Demory et al., 2005; Haberzettl et al., 2007). Therefore, material that is chemically altered becomes enriched in Ti and Fe (Cohen, 2003, Brown et al., 2007). Ti and Fe can be enriched if the material is transported over large distances before being deposited in a lake (Rothwell, 2006; Mischke et al., 2006). Paleoclimatic interpretations of XRF data from Lake Malawi are based on these assumptions (Brown et al., 2007). In the Laguna Potrok Aike catchment high amounts of fine grained weathered material rich in Fe and Ti may be found in the Plio-to-Pleistocene fluvioglacial sediments and in basal tills that cover the catchment area today (Coronato et al., 2004; Zolitschka et al., 2006). This till has a clayey sandy matrix and is easily transportable by eolian or fluvial agents (Coronato et al., submitted).

4.4.2. Trace elements (group 3b)

Variations in trace elements are related to the rate of supply and to the processes that control the degree of preservation (Cohen, 2003; Boyle et al., 1998). In Laguna Potrok Aike the correlation (R^2 arround 0.4) between trace elements (Mn, Rb, V, Ni) and major lithogenic elements is relatively strong (Fig. 4); both groups show negative loadings in PC1 (Fig. 5a). This can be attributed to the fact that Mn, Rb, V and Ni are common detrital elements found in silts and clays (Shanahan et al., 2009; Guyard et al., 2007; Rothwell et al., 2006; Croudace et al., 2006; Schulte and Speijer, 2009; Kylander et al., 2011). They can be derived from chemical weathering of catchment rocks or reach the lake attached to mineral particles (Unkel et al., 2008). Therefore, they may be interpreted in the same way as alkaline and earth-alkaline elements (Engstrom and Wright, 1984; Unkel et al., 2008) represented in this study by K. The association of clastic elements with trace metals suggests that oxic conditions prevailed in Laguna Potrok Aike and that trace elements were rarely remobilized (Fig. 5a; Cohen, 2003). Especially strong wind events cause a frequent mixing (Laguna Potrok Aike is a cold polymictic and holomictic lake) and increased oxygenation of the hypolimnion (Recasens et al., 2012; Giguet-Covex et al., 2012). Other studies of the Laguna Potrok Aike record have noted that the formation of strong redox gradients at the sediment water interface may have been inhibited by low primary productivity (Nuttin et al., submitted). Mn/Fe is often used as an indicator for these paleo-redox conditions (Koinig et al., 2003). However, in Laguna Potrok Aike the presence of vivianite, basaltic rock, high phosphat contents and pumice perturb this signal. Following the note of caution given by Jouve et al. (submitted) we refrain from using the Fe/Mn ratio as a redox indicator for the analysis of Laguna Potrok Aike sediments. The slightly decreased PC1 values of the trace elements, relative to major lithogenic elements, indicate that trace metal concentrations in sediments do not always imply supply events. A confounding factor may be that Mn, Ni and V adsorb on OM and have been associated with organic layers (Guyard et al., 2007; Thomson et al., 2006). Furthermore, the trace metal distribution is frequently affected by redox mobilization and thus dependant on water column mixing, water depth, trophic conditions and diagenetic processes (Cohen, 2003; Shanahan et al., 2009; Schaller et al., 1997). Trace metals may also be concentrated in redeposited layers (e.g. Thomson et al., 2006; Marsh et al, 2007; Granina et al, 2004). Under steady state conditions mobile trace metals are concentrated at the redox front close to the sediment water interface. If the sedimentation rate is low, this front migrates with the sediment water interface. However, if the sedimentation rate suddenly increases, for example during a mass movement deposit event, a layer of increased trace metal concentration may remain trapped in the sediment

4.4.3. K and Si (Group 3c)

A correlation (R^2=0.53) between the profiles of Si and K is observed and these elements plot closely together on the PCA (Figs. 4 and 5a). Although the K scanning shows a relatively good correlation (R^2=0.52) with WD-XRF measurements (Fig. 2), we find a weak correlation of K with water content (R^2=0.23). Light elements are especially prone to distortions and it should be considered that high K counts may be caused by K X-rays being absorbed by Cl in especially porous sediments (Rothwell et al., 2006). Nevertheless, in previous XRF studies, K counts have been used as a proxy for mineralogical by-products of soil weathering and erosion and/or as an indicator for clay (Cuven et al., 2010; Kylander et al., 2011; Unkel, 2008). More specifically, K has been associated with illite and chlorite minerals (Minyuk et al., 2007; Deer et al., 1992). In Laguna Potrok Aike, these minerals occur preferably during cold arid climates when there is a dominance of mechanical weathering over chemical weathering (Nuttin et al., submitted; Singer, 1984). Contrary to Ti and Fe (under oxic conditions), K is not stable and unreactive, but easily weathered (Shanahan et al., 2009; Mischke et al., 2010). Therefore material that is chemically altered is low in K (Kortekaas, 2007; Brown et al., 2007; Rolland, 2008). The elements K and Si occur simultaneously in the minerals sanidine and anorthoclase especially during the glacial period (Fig. 7). Si, the main component of Laguna Potrok Aike sediment, is similarly unreactive and insoluble like Fe and Ti (Cohen, 2003). Yet it is not commonly associated with these elements. While Ti and Fe are common in clays and silts, Si occurs mainly in coarser grain sizes (Cuven et al., 2010; Cohen, 2003; Kylander et al., 2011). Quartz grains may originate from fluvioglacial sediments and basal tills described as having high contents of medium to fine sands (Coronato et al., 2004; Zolitschka et al., 2006). Due to low biogenic silica (BSi) contents and lacking correlation between BSi and Si profiles at Laguna Potrok Aike, it can be excluded that the Si profile is influenced by biogenic rather than detrital sources of silica (Fig. 6; Hahn et al.,submitted).

4.4.4. Non-carbonaceous Ca (Group 4)

In non-carbonaceous sediments the Ca profile shows common trends with the clastic elements Fe, Ti and especially K and Si. Ca occurs together with Ti, Fe and/or Si in minerals such as anorthite, augite and clinoferrosisite Laguna Potrok Aike (Fig. 7). However, the correlation with Ti and Fe does not persist in redeposited sediment units where Ca and Sr are enriched and well correlated (Fig. 4). In the PCA, when carbonate-bearing sediments are removed, Ca loadings in the PC1 change from positive to negative, i.e. Ca is no longer associated with elements indicative of the organic fraction. However, instead of plotting with the bulk of indicators for terrigenous input, i.e. the other elements along PC1, Ca dominates a second principal component (PC2; Fig. 5a). Visual core inspection shows that peaks in Ca correspond to sediments that are coarse-grained and dark colored (Fig. 3). They occur at the base of turbidites as well as in discrete, coarse-grained, mm-cm scale layers (Fig. 3). XRD analysis of a dark coarse grained layer shows significantly increased amounts of anorthite (>20 wt %) compared to other Laguna Potrok Aike samples (0-10 wt %; Fig.7). Sr and Ca release from volcanic rocks (basalt und tephra), due to the weathering of feldspar (plagioclase), has been observed in previous studies of lacustrine sediments (Benson et al., 1998; Salminen et al., 2005). At Laguna Potrok Aike, the basaltic rock in the catchment is assumed to be a main source of Ca (Haberzettl et al., 2005). Sr and Ca in the detric fraction often behave like K (Cohen, 2003), i.e. they are easily mobilized during weathering and therefore common in freshly eroded sediments (Kortekaas et al., 2007). In the direct proximity of Laguna Potrok Aike, on the southwest shore, the basaltic lava flow "Bandurrias" and remnants of an eroded scorcia cone "Policia" are cut by the primary inflow and eroded directly by wave action (Fig. 1; Coronato et al., submitted). Kastner et al. (2010) find higher Ca values in the surface sediments near the southern shore due to the direct influence of the basalt outcrop. Therefore, we suggest, that this can be regarded as the main source for the Ca-rich coarse material found in Laguna Potrok Aike.

5. Paleoenvironmental Interpretations

Once event deposits are removed from the composite record from Laguna Potrok Aike, the pelagic deposits mainly consist of clays and silts. These lithologies should be exempt from grain size and water content effects which could influence XRF counts and therefore suitable for paleoenvironmental studies (Tjallingi et al., 2007). Furthermore, tephra layers are excluded from the pelagic composite profile, their diverse and distinct geochemistry is thus no longer a confounding factor (Fig. 4 and 5a). However, because only event deposits thicker than 2 cm were removed, artifacts of redeposited sediments and tephra layers remain in the record.

5.1. Indicator of productivity and clastic input

Obtaining an overview over the numerous elemental profiles whilst keeping in mind element interactions and closed sum effects is challenging. Therefore, we propose the scores of PC1 as a summarizing indicator of clastic vs. organic sediment reflecting climate-related variations in depositional conditions. In carbonate-bearing sediment PC1 is mainly driven by the Ca content of the sediment and correlates well with the TIC curve which is used as a proxy for lake level reconstructions of the past 16 ka (Haberzettl et al., 2007; Hahn et al., submitted). PC 1 shows the mid Holocene Climate Optimum (around 9-7 ka), a dry phase between 4.5-4 ka (Haberzettl et al., 2009), the Medieval Climate Anomaly (around 1-0.5 ka) and also the 20th century warming in the uppermost part of the record. Additionally, we note a dry phase with slight increases of Ca and PC1 peaking around 3 ka that is also described in Haberzettl et al. (2009). In the carbonate-free sediments PC1 is driven by the difference between clastic and organic sediment. Increases in PC1 during warm phases may be due to soil and vegetation development in the catchment reducing eolian and fluvial erosion and thus dilute the clastic fraction by increased organic sediment input as suggested by Lise-Provonoste et al. (submitted) for the Late Glacial period. A negative correlation between C/N ratios and Ti in Laguna Potrok Aike has previously been observed by Mayr et al. (2009). Likewise, high scores in PC1 roughly correspond to increases in TOC values and C/N ratios that are associated with pulses of organic productivity (Fig. 6; Hahn et al., submitted). Increases in PC1 (49 to 45 ka, 38.5 to 37.5 ka, 17.2 to 14.4 ka, and 13.5 to 11.4 ka) show some correlation with southern hemispheric glacial warming events (Antarctic A-events 1 and 2, postglacial warming and Younger Dryas chronozone, respectively) suggested by ice core records (Fig. 6; EPICA Community Members 2004, 2006). However, this correlation is only moderate because, during glacial conditions in Laguna Potrok Aike, climatic ameliorations primarily evoke diatom blooms. These are best recorded in the BSi rather than in the TOC profile (Hahn et al., submitted). With Br we only have an indicator for TOC and not for BSi; the large detrital Si fraction in the sediments inhibits the detection of BSi by XRF. This limits the amount of climatic information that can be obtained from the PC1 of the XRF dataset. XRF records are a much better tool for analyzing the clastic fraction of the sediment. However, a clear interpretation may still be difficult to obtain because the amounts of terrigenous material and the mineral compositions are dependent on multiple factors (Wefer et al., 1999). On the one hand, increased clastic input can be related to rapid erosion and reduced soil stability after or during cold and dry glacial episodes. On the other hand, during warmer and wetter conditions typical clastic indicators are dependent on the rate of chemical weathering which is accelerated by vegetation (Cohen, 2003). Increased clay input related to hydrolysis during warming periods has been observed in Laguna Potrok Aike (Nuttin et al. submitted). Clastic elements have been found to indicate terrestrial runoff linked to elevated rates of precipitation in marine (Haug et al., 2001) and lacustrine sediments (Shanahan et al., 2009; Kastner et al., 2010; Haberzettl et al., 2005). Such multiple climatic influences on one proxy may lead to discrepancies in the record and to an ambiguous climate signal.

5.2. Indicator of grain size and provenance

For a more detailed study of the clastic fraction of the sediment we remove the carbonate-bearing sediments from the dataset that dominate the PCA. Furthermore, this part of the record is of special interest, as the Holocene sediments have been thoroughly studied during the former South Argentinean Lake Sediment Archives and Modeling (SALSA) project (Haberzettl et al., 2007). PC2 is dominated by Ca derived from basaltic rocks at the southwestern shore of Laguna Potrok Aike which is eroded by the Bandurrias Creek flowing directly into the lake (Fig. 1). Since the Cabo Vírgenes Glaciation (0.78 - 1.05 Ma) this creek has probably only been active during seasonal precipitation and spring snow-melt events (Coronato et al., submitted). At times of lake level lowstands, a lower base level may have promoted fluvial erosion of the basalt outcrop during infrequent but extreme runoff events (Coronato et al., submitted). Furthermore, the basalt outcrop is directly attacked by wave erosion forming basaltic sands especially during times of high wind speeds. Consequently, on the western shore gravel beach-levels and accumulation of coarse-grained, delta-type material can be found (Gebhardt et al., 2011; Coronato et al., submitted). The frequency of mass movement events going off these delta-type sediments and transporting basaltic sands into the lake center is increased during glacial conditions (Gebhardt et al., 2011; Kliem et al., submitted). Ca rich dark sands are found at the base of mass movement deposits but also in discrete layers. Therefore, we suggest strong winds as a trigger for further transport mechanisms to the lake centre. Coronato et al. (submitted) suggest wind as the most continuous geomorphic agent in the Laguna Potrok Aike area, typical for lakes in arid and barren regions (Cohen, 2003). At low lake level stands large basaltic sand deposits would have been uncovered and available for transport. Ca values are increased in dark sand layers and are accompanied by enrichments in Si which also has negative loadings in PC2 (Figs. 3 and 5a). The SiO_2 content of the dark sand layers and in the lake sediment in general is higher (around 60%) than the SiO_2 content of the basalt outcrop (around 50%; D'Orazio et al., 2001).

Apart from basaltic sands, quartz sands derived from till are also abundant in the area. They are assumed to be present in the coarse-grained layers of Laguna Potrok Aike due to grain size specific transport (Fig. 3). Further elements with a negative PC2 are Mn and K. These are related to redeposition events; K is enriched in clay caps and a Mn layer is common in turbidites. Elements indicative of fine-grained tills (Ti, Fe) and organic material (Br, Cl) have a positive PC2. Fe and Ti values in the sediment are not increased during intervals that are characterized by high magnetic susceptibility in Oxygen Isotope Stage (OIS) 2 (Haberzettl et al., 2009; Lisé-Pronovost et al., submitted). This may be related to dilution effects of the large clastic influx causing an absolute increase in ferromagnetic minerals to appear as a relative decrease. It is also possible that the presence of magnetite in basalt is responsible for the increases in magnetic susceptibility (Mullins, 1977; Money and Bleifuss, 1953). In conclusion, negative scores in PC2 are interpreted as an increase of mechanical over chemical weathering and more frequent high wind speeds during the coldest glacial periods. The frequency of redeposition is probably also reflected in PC2. The signal of PC2 is again somewhat confounded by the multi-provenance, multi-transport-mode characteristic of the clastic material. Nevertheless, decreases in PC2 (between 18 ka and 32 ka) correspond to increased dust deposition during OIS 2, which has been observed in Laguna Potrok Aike (Haberzettl et al., 2009) and correlated to southern hemispheric dust records (Fig. 6; Weber et al., 2012; Fischer, 2007). Correlation between our lake sediments and the Antarctic dust record demonstrates the already often cited contribution of dust from South American Patagonia to Antarctica (Grousset et al., 1992; Basile et al., 1997). Increases in PC2 (between 45 and 49 ka and between 36 and 40 ka) occur simultaneously with increases in the productivity record and Antartic warming events A-1 and A-2 (Fig. 6; Hahn et al., submitted; EPICA Community Members, 2004, 2006).

6. Conclusion

For the thorough exploration of the XRF scanning dataset, PCA is an important tool and provides means of deciphering the relationships between the different elements in a sample. Analysis of the elemental composition reveals a profile that is dominated by clastic sediments; organic and carbonate input is sparse and diagenetic remobilization is limited. This suggests an unproductive, well mixed lake in cold, semiarid and windy conditions throughout the past 51 ka. Geochemical variations in the sediment can be attributed mainly to external input from allochthonous sources (watershed and atmosphere) and to a smaller extent the lakes internal productivity and biogeochemical processes. All of these factors are influenced by regional environmental and climatic changes in the area. The alternating occurrence of clastic and organic/carbonate sediments can be interpreted as shifts between stadial and interstadial conditions, respectively. XRF scanning is especially adept at capturing variations in lithogenic elements, making it particularly useful for the analysis of clastic lakes such as Laguna Potrok Aike and allowing us to detect variations in the minerogenic input to the sediment. The different geochemical signatures of fine-grained alluvial sediment originating from the till covering the catchment and coarse-grained sands derived mainly from the adjacent basaltic rock outcrop reflect the intensity of dust deflation in southern Patagonia. However, a clear climatic interpretation is challenging to obtain from the record because the geochemical profiles are not a direct and continuous record of environmental changes. The response of various components of the lake system may be mediated by non-climatic factors. Processes such as changes in background sedimentation, diagentic effects, reworking and bioturbation may blur the climate-related geochemical signal (Engstrom and Swain, 1986; Cohen, 2003). Elemental composition is dependent on multiple factors that are often not distinguishable. It can therefore be difficult to infer the magnitude or sometimes even the direction of the climate change from geochemical records (Fritz, 1989). While a warmer and wetter climate may reduce clastic input by stabilizing soils, it may also increase weathering and transport processes. Furthermore, relationships derived from contemporary data are not invariably valid; links between a proxy and climatic forcing may change over time. In the case of Laguna Potrok Aike the content of Ca is influenced by different mechanisms throughout the lake´s history. Although deciphering the climatic signal from the XRF dataset is not always straightforward, general trends of Holocene lake level variations detected in previous studies can be confirmed. For the glacial period the elemental composition of Laguna Potrok Aike suggests climatic variations similar to those recorded in Antarctic ice cores. The elemental composition suggests a windy, arid, cold OIS 2 and warmer conditions during the Antarctic A-events, after the LGM and during the Younger Dryas.

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Chapter 5

Conclusions and Outlook

1. Conclusion

From a methodological perspective, our results demonstrate that the DRIFTS method is the most reliable tool for IR analysis for lake sediments. Its application to a long lacustrine ICDP deep drilling core was successful and, in combination with geochemical data from XRF scanning, provided a first high resolution multiproxy data set of the complete 51 ka PASADO record. The paleoenvironmental changes reconstructed from variations in organic, carbonaceous and clastic deposition complement the paleoclimatic studies by Haberzettl et al. (2005, 2007; 2009), adding particularly the glacial period. High productivity events of aquatic moss growth and diatom blooms in Laguna Potrok Aike reflect periods of warming in the southern hemisphere during the last glacial, such as the Antarctic A-events, the postglacial warming and the Younger Dryas chronozone. In turn, clastic coarse-grained sediment intervals correspond to windy, arid and cold periods with increased dust fluxes such as during Oxygen Isotope Stage 2. We suggest that at the latitudes of Laguna Potrok Aike the paleoenvironmental conditions are directly linked to variations in Antarctic climate as registered in ice cores (EPICA community members, 2004; 2006). Studies based on marine cores from the Southern Ocean (Lamy et al., 2007, Anderson et al., 2009) confirm this for the mid-latitudes. We find no evidence for shifts in the SHW affecting the site during glacial times as they were probably located in a more northerly position until ca. 9.4 cal. ka BP.

2. Outlook

Biogeochemical analysis using DRIFTS technology should become common practice in paleolimnological studies. IR application at more sites will enhance our understanding of IR spectra and increase the reliability of calibration models. In order to obtain a complete picture of past environmental conditions, interpretations presented in this thesis will be complemented by a large array of sediment characteristics measured on PASADO sediments by various international project members. The exact nature of the carbonaceous fraction will be analyzed in more detail and a multitude of bio-proxies will provide additional details on lacustrine paleoproductivity. These analyses will facilitate quantitative multi-proxy reconstructions of temperature, precipitation and hydrological variations. The mineralogy, geochemistry and physical properties of the clastic fraction will also be analyzed in further detail with a special focus on characterizing eolian material. This may reveal variations in atmospheric dust influx over the past 51 ka. Furthermore, several intervals of high climatic variability will be analyzed in detail with even higher mm-scale resolution. Overall, these results will contribute to the understanding of variations in the southern hemispheric climate system and make an important contribution to discussions concerning the role of the southern hemispheric mid-latitudes in the global climate system and dust fluxes during the glacial period.

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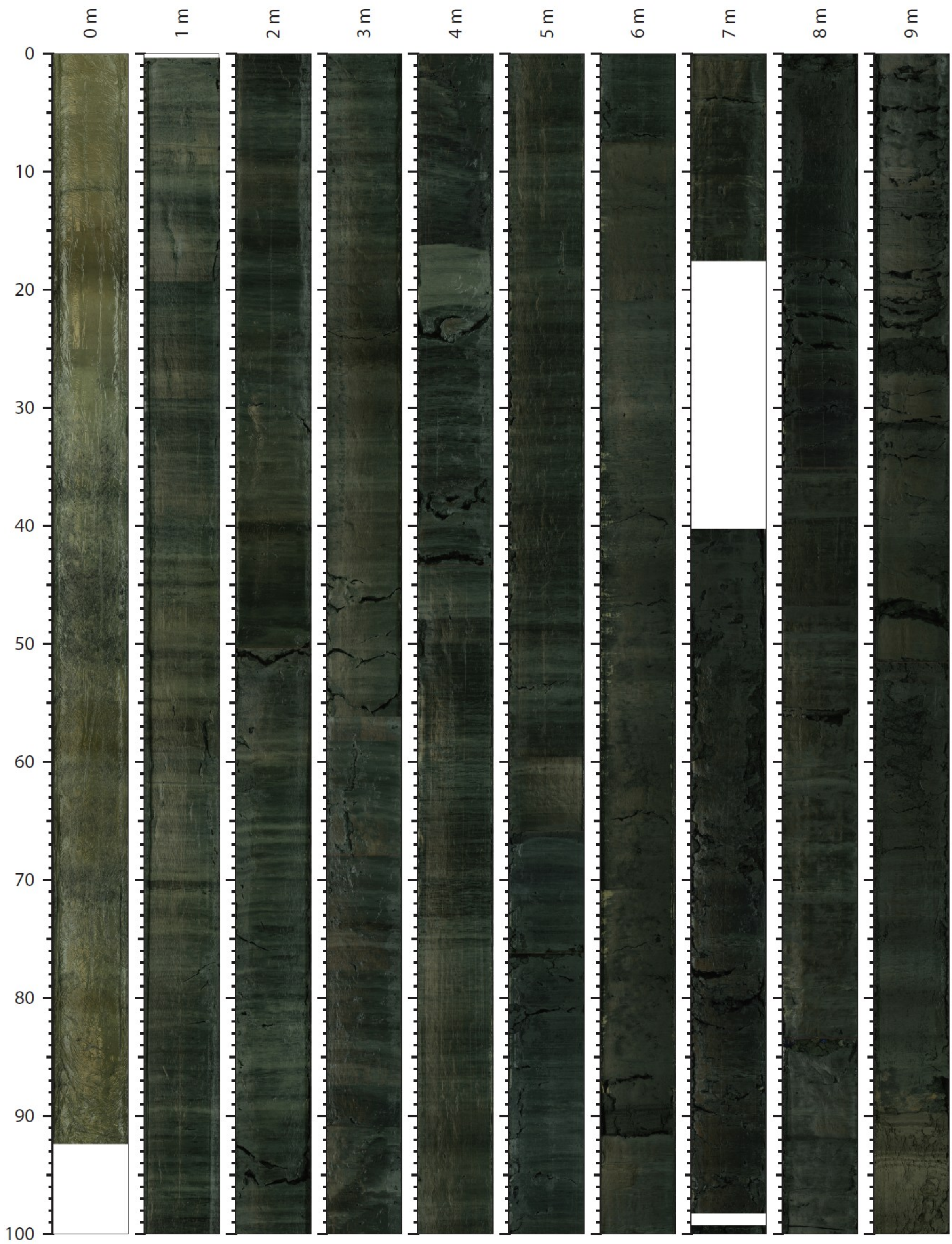
Appendix

Site 2 composite profile (0-10 m cd)



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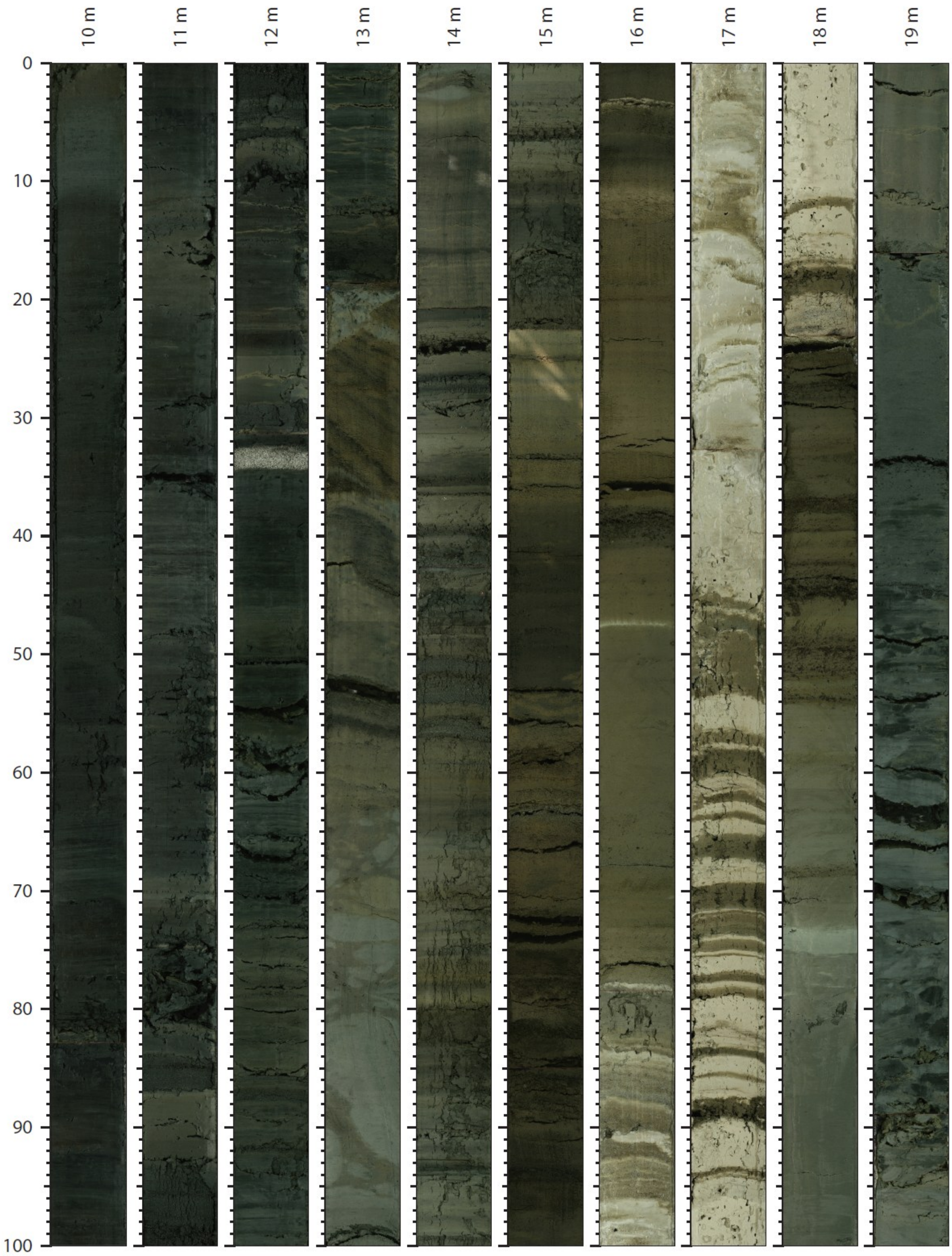

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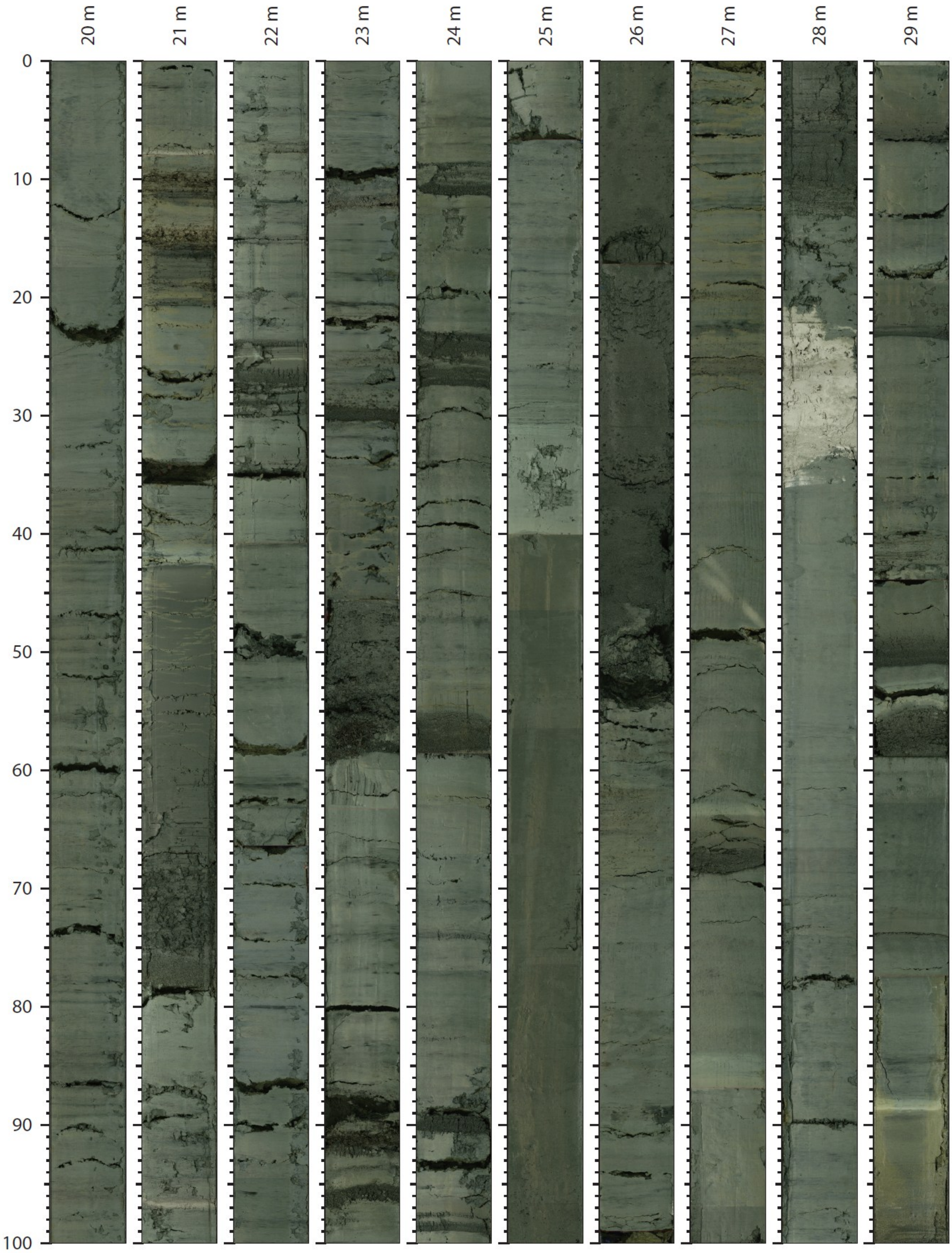

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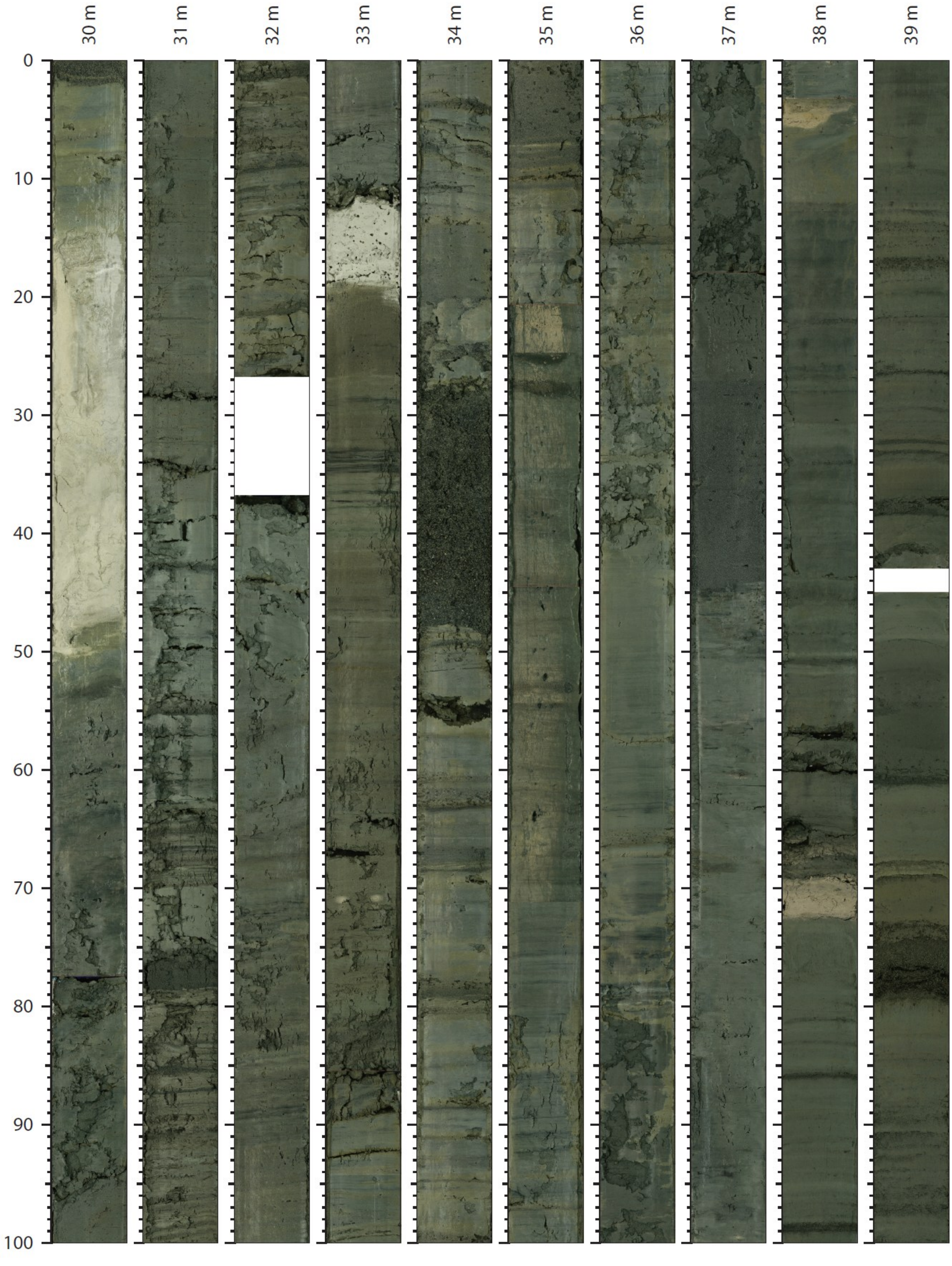

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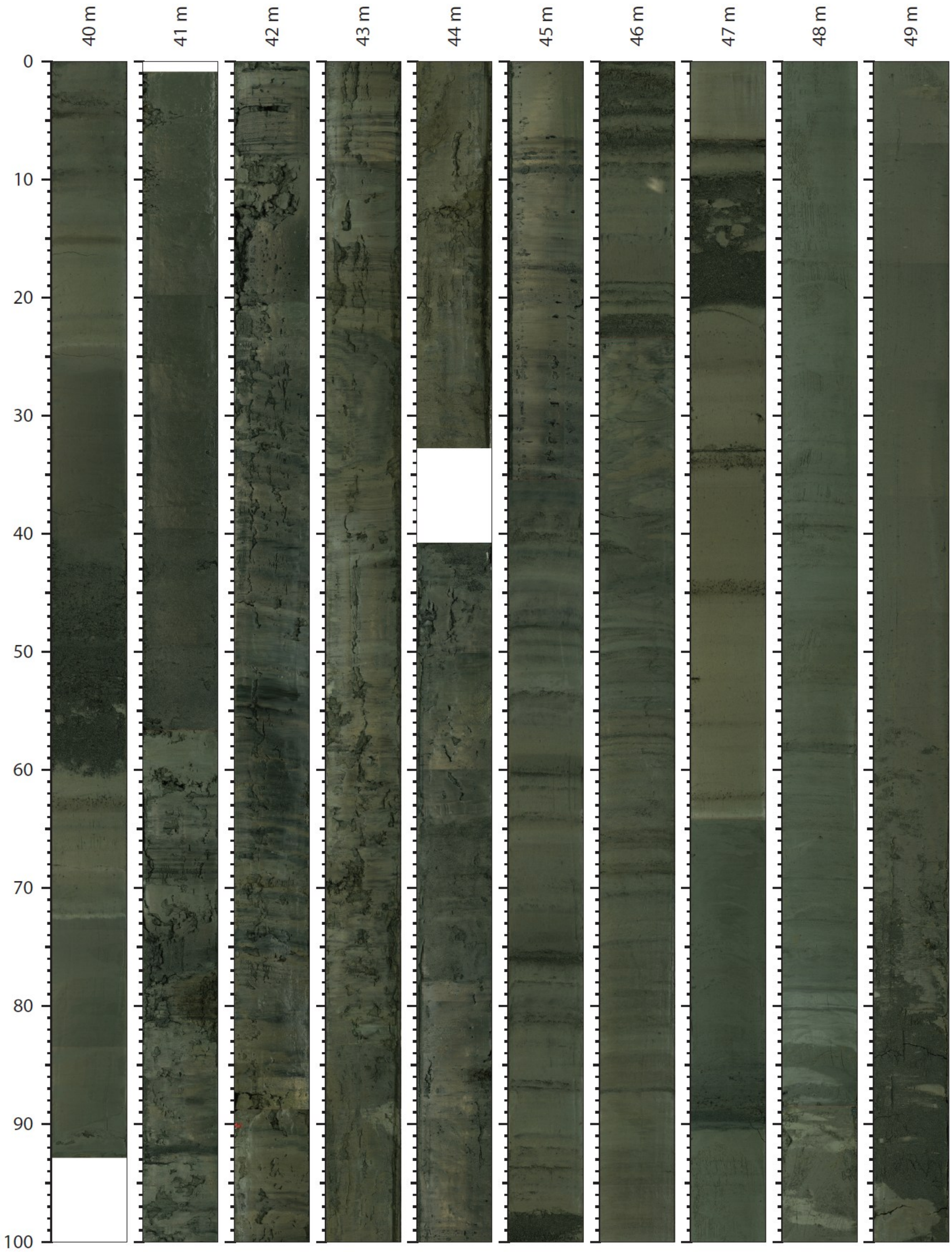

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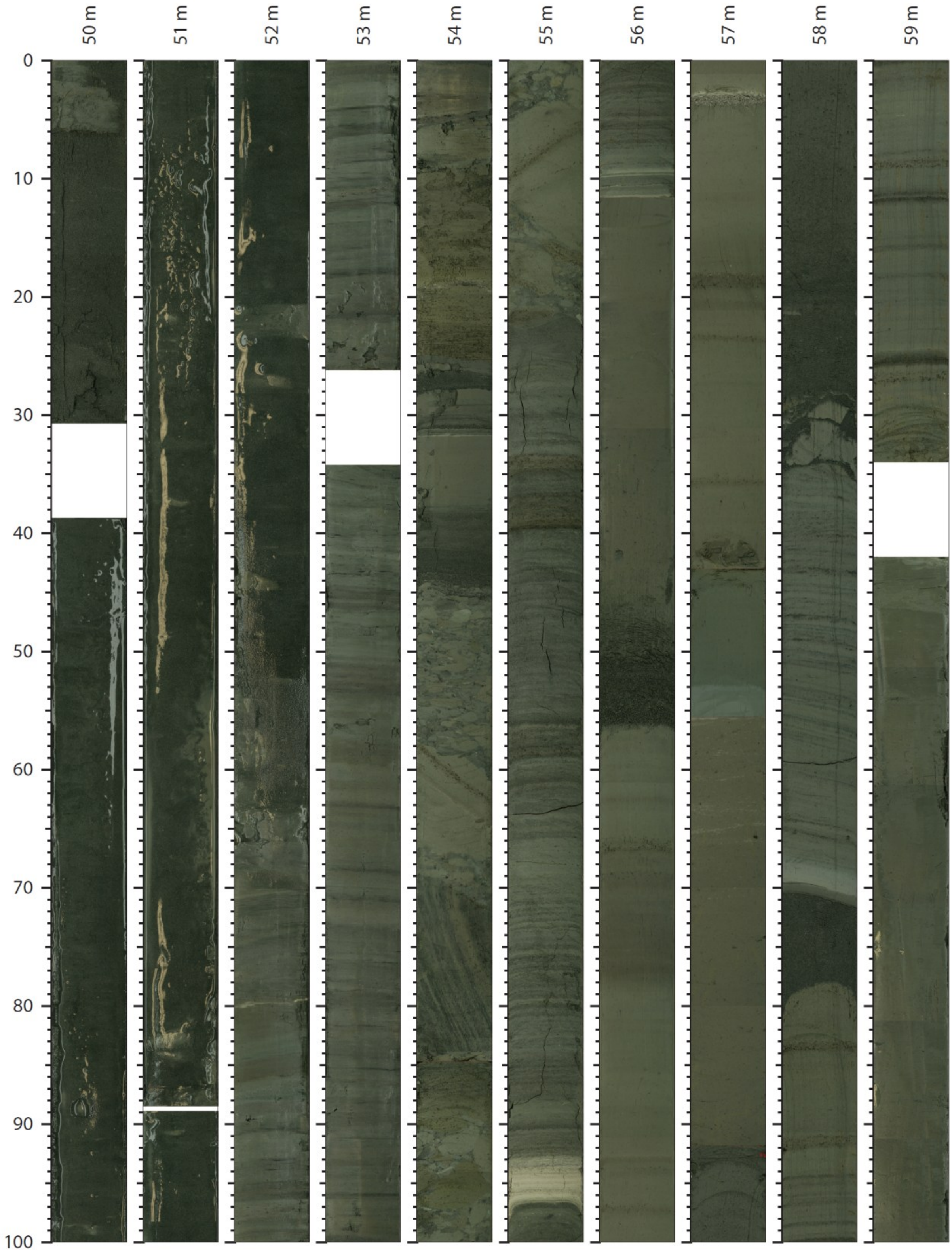

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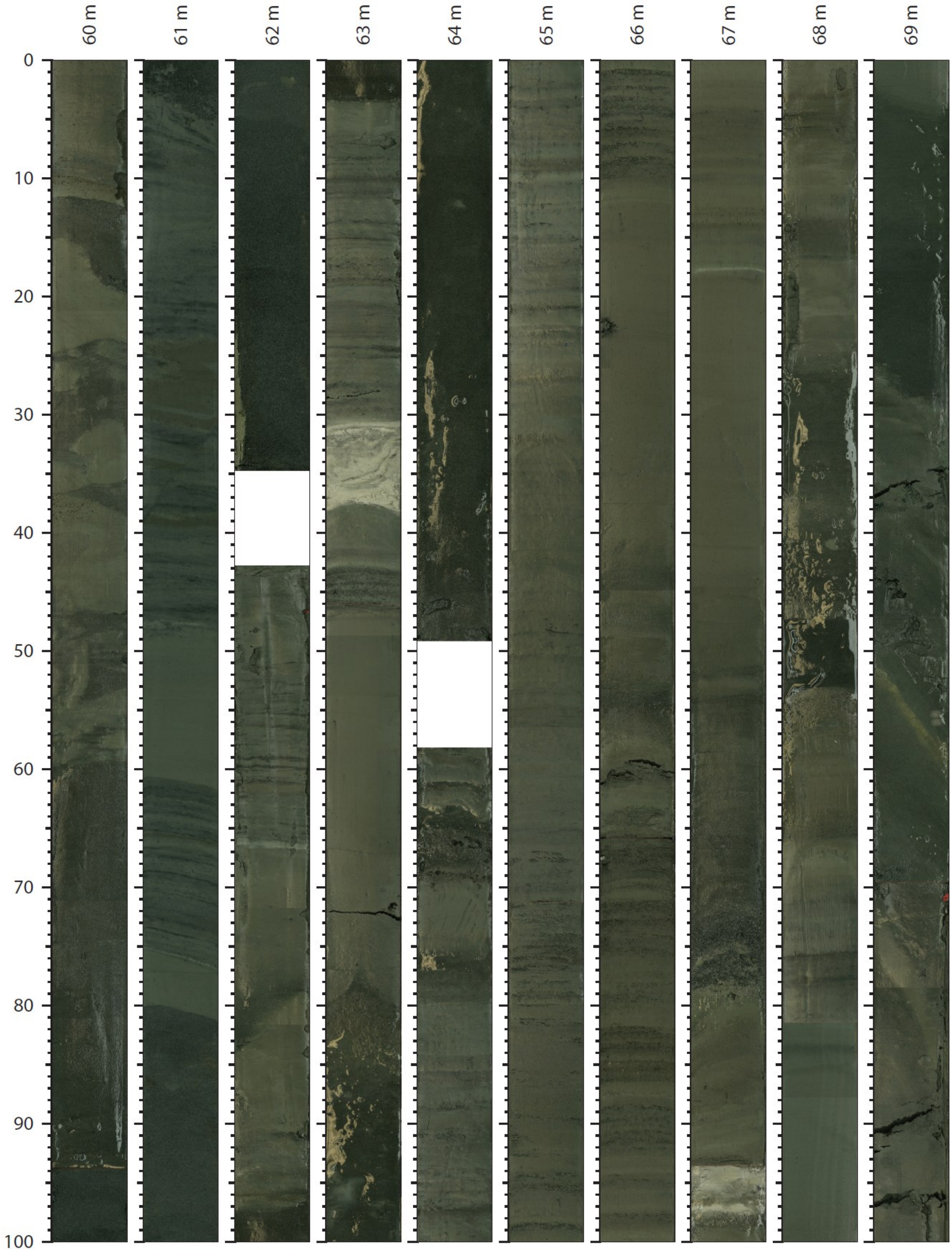

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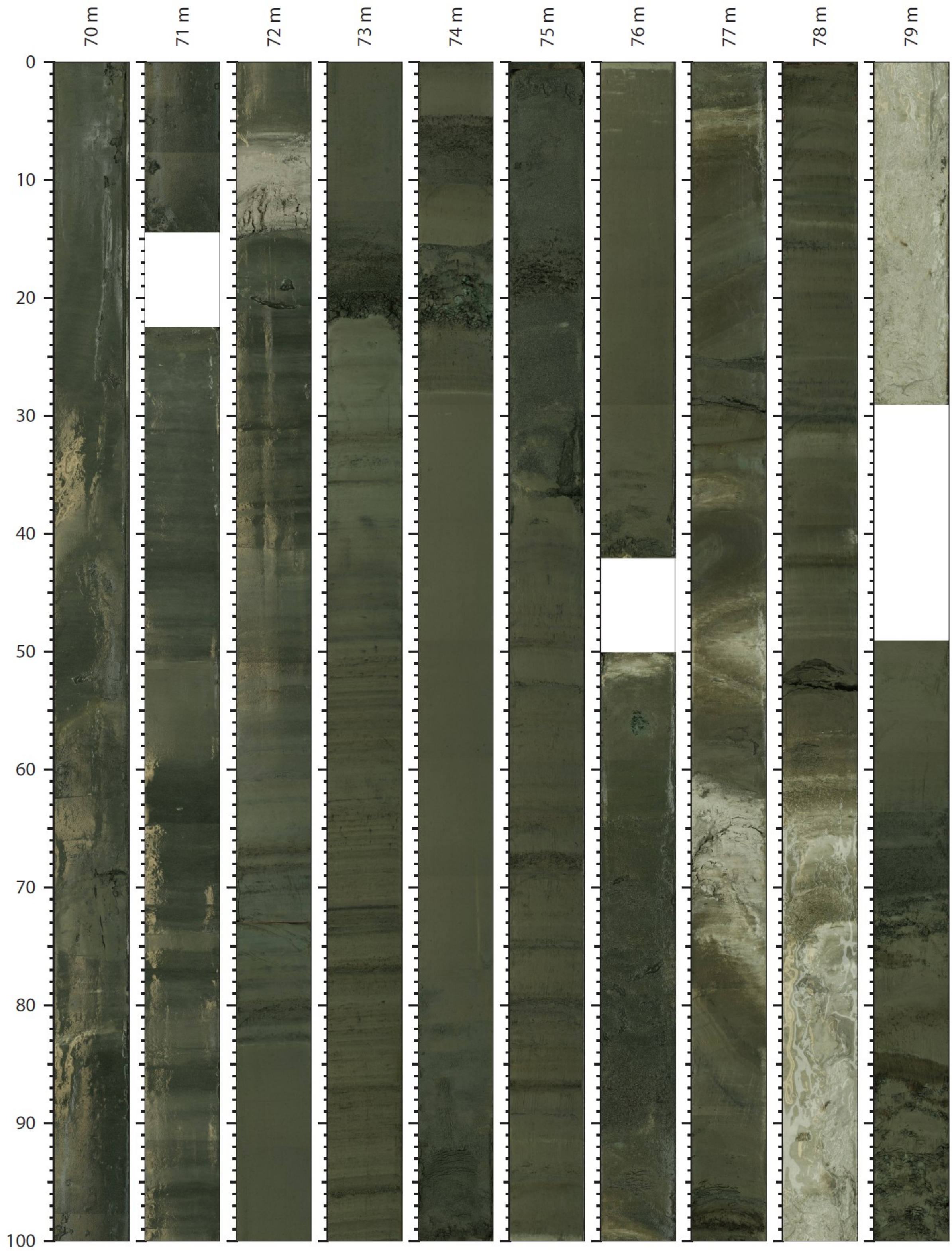

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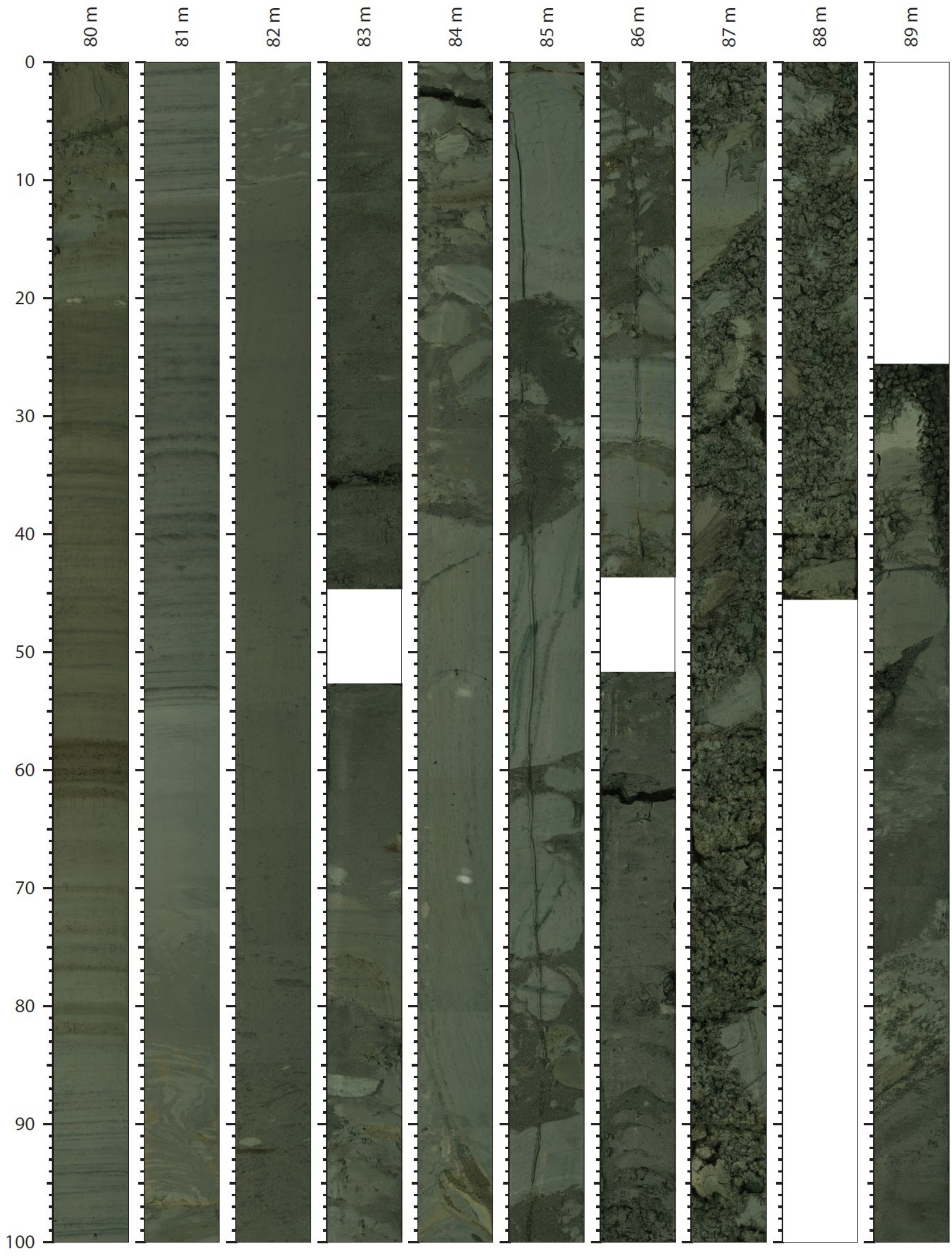

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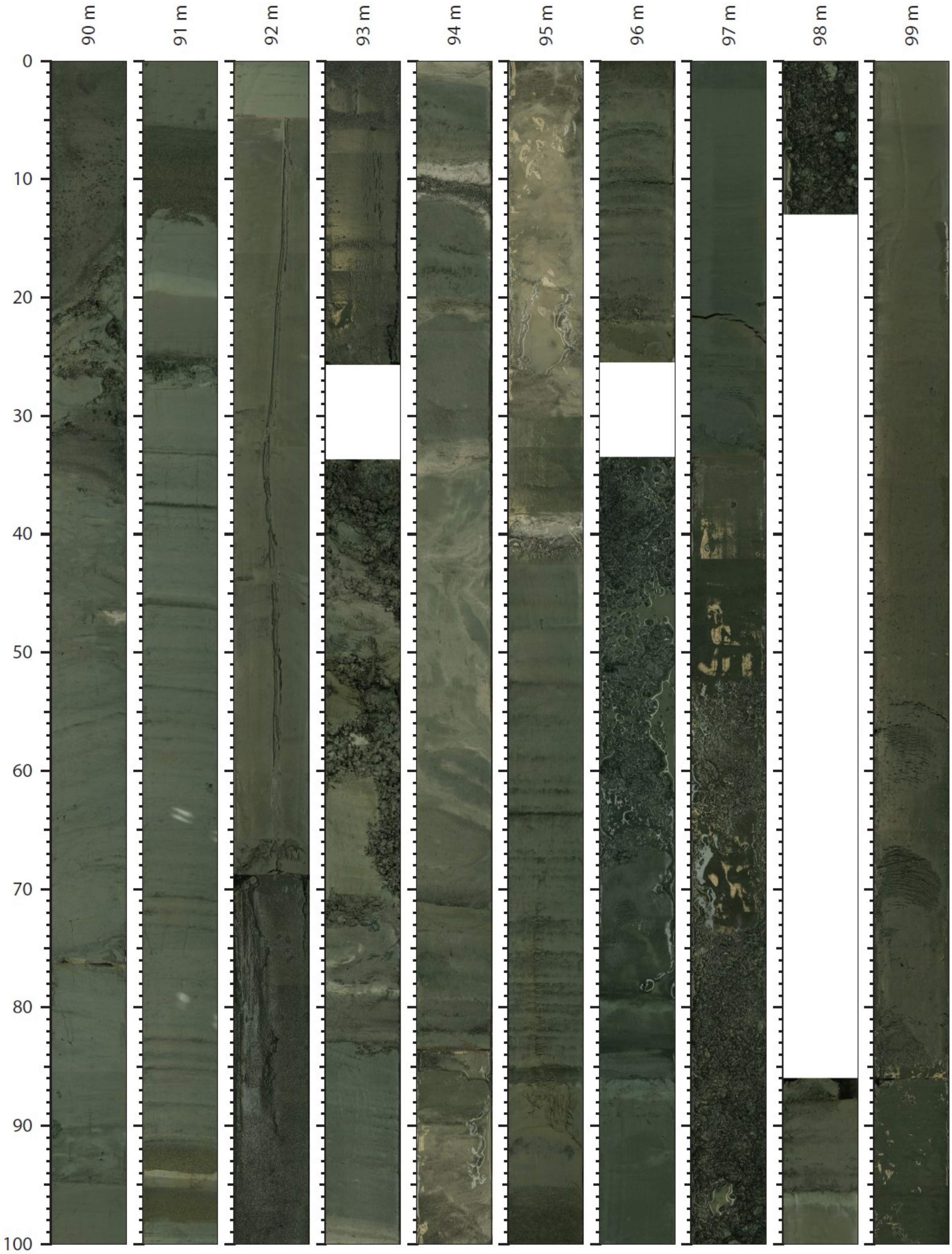

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