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

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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 (SHW) 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 synchronously with southern hemispheric glacial warming events such as the Antarctic A-events, the postglacial warming following the LGM and the Younger Dryas chronozone. During these times, a combination of warmer climatic conditions with related 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 SHW 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 SHW 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 SHW 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.

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 (Knorr and Lohmann, 2003). Recent studies have underlined the relevance of the southern hemisphere oceanic and atmospheric circulation to global climate changes. 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 and Burckle (2009) suggest that the shift of the SHW caused CO_2 to increase at the onset of the

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Antarctic warming period at ca 17 ka cal. BP. 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. Its key location has attracted scientific attention to this climate archive; in the framework of the "South American Lake Sediment Archives and Modeling" (SALSA) project a 19 m core that 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 into time the ICDP deep drilling campaign "Potrok Aike Maar Lake Sediment Archive Drilling Project" (PASADO) was initiated. In this paper, Diffuse Reflectance Fourier Transform Infrared Spectrometry (DRIFTS) technology (Rosén et al., 2010, 2011; Hahn et al., 2011) was used in order to efficiently achieve high resolution analyses of the 106 m long PASADO record and 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 aim to 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.

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 no more than about 200 mm and the potential evaporation rate is in the range of 1000–1600 mm per year (Borrelli and Oliva, 2001; Ohlendorf, submitted for publication). 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.

3. Materials and methods

3.1. Previous and concurrent work

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). Drilling operations were performed by DOSECC (Drilling, Observation and Sampling of the Earth's Continental Crust, Inc.) using the GLAD800 platform with 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. Logging data and lithological descriptions

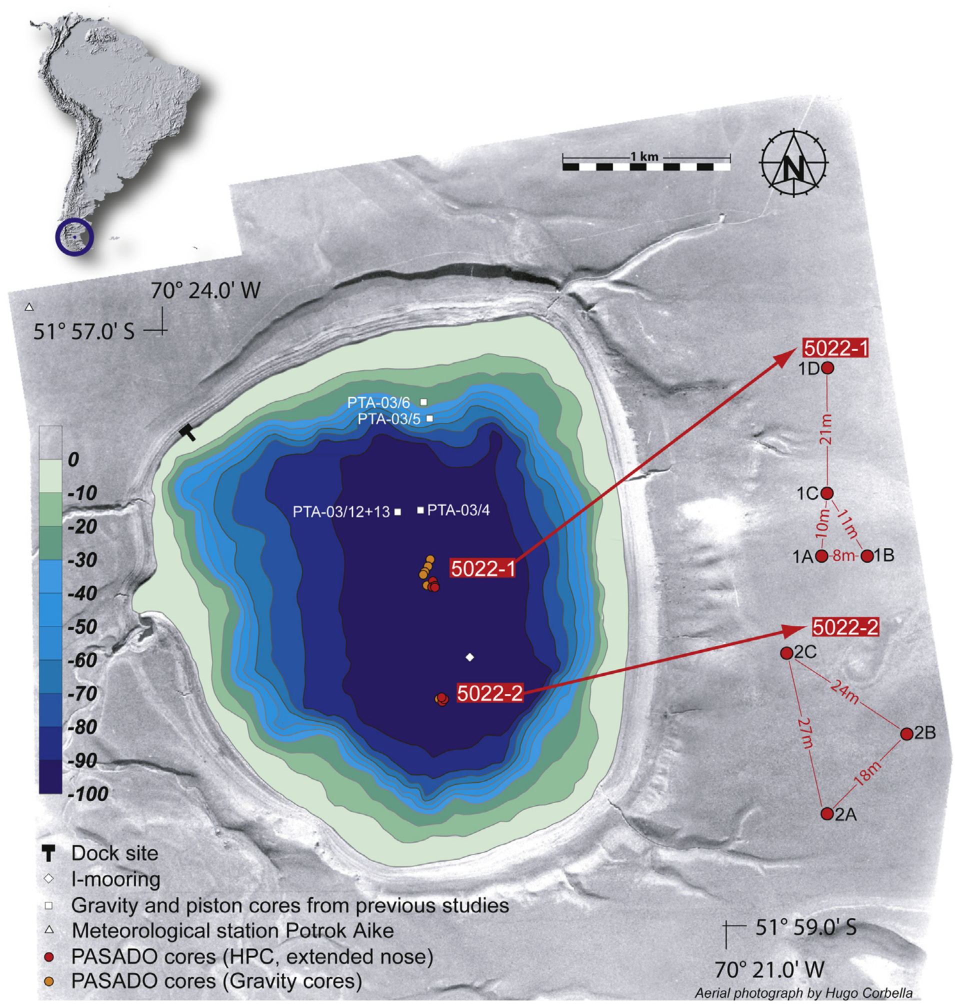

Fig. 1. Bathymetric map with coring sites of Laguna Potrok Aike and location in South America.

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 Lateglacial 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 Lateglacial, 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., 2013). The record was divided in three main lithographic units (A, B, C-1, C-2, C-3) by Kliem et al. (2013). In unit C sediments are dominated by poorly laminated silts and fine sands. 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. The lithology of unit A is described as pelagic laminated silts with a high content of calcite crystals.

3.2. Sedimentological analysis

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 afterward analyzed by the same device. 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. Carbonates were identified in 55 selected samples 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. Dry densities were measured by weighing a known volume of ca 10 g, freeze-drying and weighing again. We applied the DRIFTS technique on a set of high resolution sample, i.e. 2–4 cm (20–40 years), hence increasing the resolution by a factor of 4 (8–16 cm (80–160 years)) compared to the previous analyses conducted using conventional geochemical methods (Haberzettl et al., 2005, 2007). Due to the differences in their chemical composition and structure, organic and inorganic compounds in lake sediments have unique IR spectra. These allow 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 and Shenk, 2004). The DRIFTS technique has shown to be successful and promising for the assessment of TIC, TOC and BSi content in various lacustrine studies (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

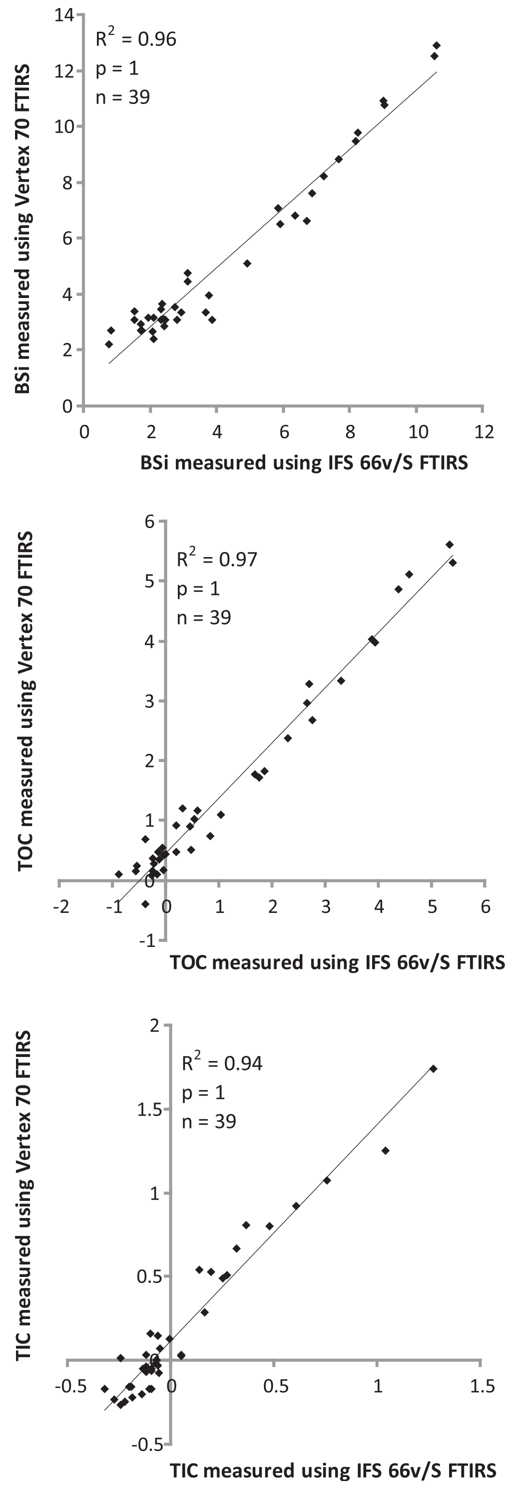

Fig. 2. Correlation between measurements of BSi, TOC and TIC obtained with the two devices used for DRIFTS analyses (IFS 66v/S FTIR spectrometer and Vertex 70 FTIR spectrometer).

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), Rosén et al. (2011) and Hahn et al. (2011). Six outliers were detected and excluded using principal component analysis. The occurrence of outliers can arise from the conventional

TIC, TOC 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 relationships between the spectra and the conventionally measured sediment properties (Geladi and Kowalski, 1986). These 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. 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: 45.8–15.2 m cd-ec

In unit C-3 (43.9–45.8 m cd-ec) BSi is below 3% and TOC values are so low (<0.3%) that C/N is unreliable. Unit C-2 (29.1–43.9 m cd-ec) is characterized by an increase in C/N (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). Throughout unit C, correlation between TOC and BSi content is weak ($R^2 = 0.41$, Fig. 4e).

4.2. Unit B: 9.1–15.2 m cd-ec

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). Afterward, C/N, TOC and BSi steadily decrease to lower values, i.e. ca 9, ca 1% and ca 2% respectively. 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 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 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: 0–9.1 m cd-ec

In unit A, 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

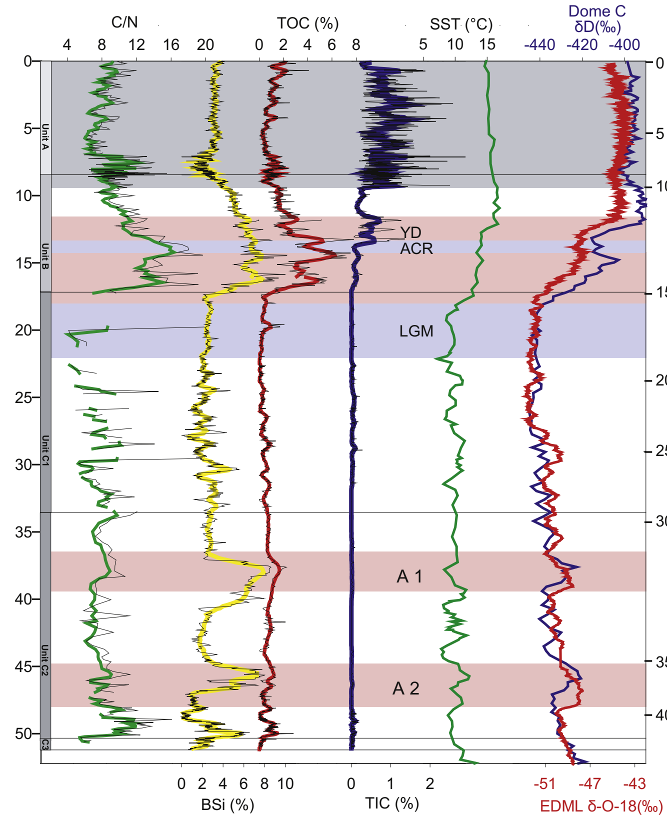

Fig. 3. Laguna Potrok Aike event-corrected composite records of C/N, BSi, TOC, and TIC (thin black lines). Plotted also are 5 pt running means (TIC: blue; TOC: red; BSi: yellow) and 3 pt running mean (C/N: green). C/N values of samples with TOC <0.3% were not calculated. These parameters are compared 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. (2013). 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. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

continues 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

TIC is well established as a lake level indicator for Laguna Potrok Aike (Haberzettl et al., 2005, 2007; Oehlerich et al., 2013). The underlying assumption is that low lake levels with a reduced water volume promote supersaturation and thus carbonates precipitate (Haberzettl et al., 2005, 2007). However, the relationship between the global mechanism (climatic change), the regional phenomenon (lake level oscillations) and carbonate precipitation as registered by TIC may not be as straightforward as assumed, especially since Laguna Potrok Aike is a groundwater-fed lake (Mayr et al., 2007a).

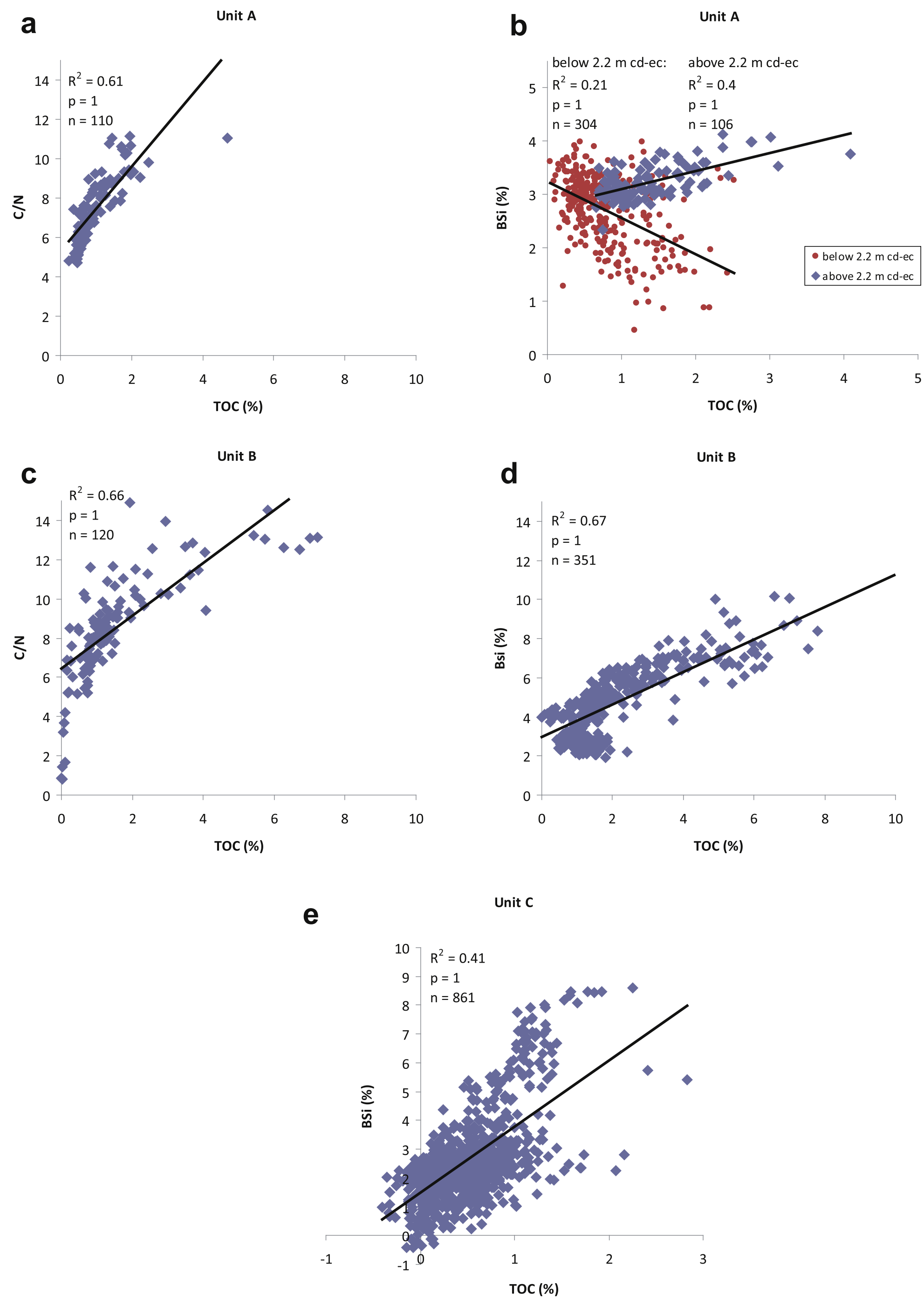

Fig. 4. Correlations of main productivity indicators for sediment units A, B and C. With the exception of the upper part of unit A correlation is acceptable. C/N values of samples with TOC <0.3% were not calculated. Due to the very low TOC contents in unit C, the C/N record is very incomplete and could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

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 modeling (Haberzettl et al., 2005; Anselmetti et al., 2009; Ohlendorf, submitted for publication) supporting the idea that TIC is a qualitative paleo-lake level indicator of Laguna Potrok Aike. For the Holocene and Lateglacial 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.

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 (Mayr et al., 2009; Kastner et al., 2010) 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

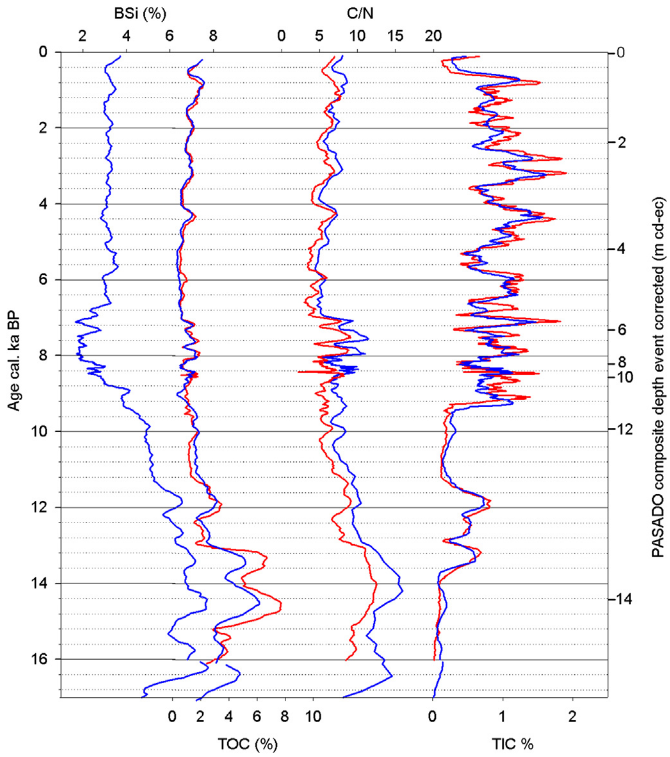

Fig. 5. Lateglacial and Holocene PASADO (blue) record of BSi, TOC, C/N and TIC compared to the SALSA (red: Haberzettl et al., 2007) TIC, TOC and C/N record plotted against event corrected composite depth and age according to the PASADO v.3 age model (Kliem et al., 2013). The non-equidistant scaling of the depth axis marks variations in sedimentation rate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 relative to aquatic components of OM which reflect climate related changes in vegetation communities in and around a lake (Meyers and Lallier-Vergès, 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 organic matter 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 24–49 and are considered to be the origin of high C/N values (Mayr et al., 2009). Layers of aquatic mosses and dispersed macro remains are dominating constituents among the organic matter 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. (2013). The low (4–10) C/N values 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., 2013). 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 organic matter content (Müller, 1977; Lehmann et al., 2002). 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 organic matter.

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., 2011). 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 (Colman et al., 1995), as it is the case in units B and C of the studied record (Fig. 4d,e).

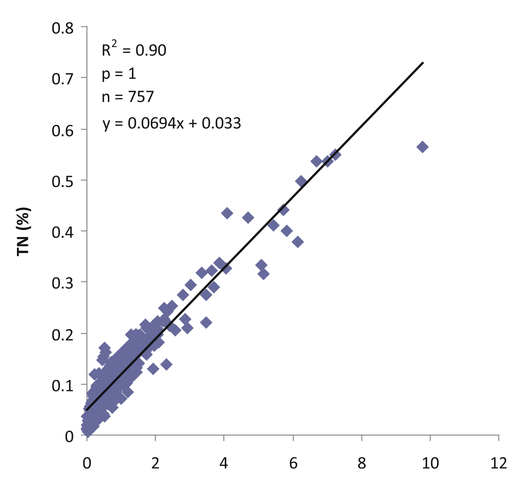

Fig. 6. Correlation between conventionally measured TOC and TN contents indicates that the nitrogen in the sediment is mainly organic.

5.3. Correlations between indicators

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

The number of factors influencing the three productivity indicators (C/N, BSi and TOC) in lake sediments is large. TOC and C/N are not independent variables; their correlations should therefore be regarded with care. The three profiles covary throughout most of the glacial period (Figs. 3 and 4). Visually a correlation can generally be detected even though R^2 is often low (around 0.5) 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. Furthermore, we observe that peaks in the three proxies are associated with layers of aquatic macro remains. We therefore 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). There are several diatom species that thrive under similar conditions (Recasens et al., 2011). 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 organic matter indicate low lake productivity in the Holocene compared to the Lateglacial (Zhu et al., 2013). 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 (Figs. 3 and 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., 2011). 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 only observed in the upper part of the record (Massaferro et al., 2013). 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 one and a half millennia present an exception; here TOC, TIC, C/N and BSi are well correlated (Figs. 4a,b and 5) and diatom dissolution is no longer observed (Massaferro et al., 2013). 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 organic matter content (Vuillemin et al., 2013).

5.4. Paleoenvironmental reconstructions

5.4.1. Glacial conditions (units C-3 and C-2 from 51.2 to 33.1 cal. ka BP)

5.4.1.1. Glacial 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 analyses did not revealed the presence of carbonate in this unit. XRD analyses by Nuttin et al. (submitted for publication) 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 for publication) 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 for publication) 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) described as an open vegetation during the interglacial. 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. Haberzettl et al. (2009) also inferred a weaker dust input at Laguna Potrok Aike with the analysis of a core from the littoral zone. Regional climate signal seems to agree with this interpretation: indeed Oxygen Isotope Stage (OIS) 3 (65–25 cal. ka BP) experienced reduced dust input in the Vostok ice core (Delmonte et al., 2004). OIS 3 has been interpreted to be warmer from marine and ice cores (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. The first peak is from 50 to 49 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., 2011). Nuttin et al. (submitted for publication) 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., 2013). 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., 2011). 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). 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: 33.1–17.2 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 (Meyers and Lallier-Vergès, 1999; Talbot and Laerdal, 2000; 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 ca 32.5–17 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; Maldonado et al., 2005), marine (Lamy et al., 1999; Stuut and Lamy, 2004; Lamy and Kaiser, 2009) 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 (33.1–17.2 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 (Kaplan et al., 2004; Sugden et al., 2005; Kaplan et al., 2008a; Clark et al., 2009; Hein et al., 2010). Marine sediment cores also record glacial conditions for the time interval 28–18 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 high frequency variability could also be related to mass movements or tephra layers which occur frequently within this period. 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 (Singer et al., 2004; Zech et al., 2009) 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 (Blunier and Brook, 2001; Martinez et al., 2006; Stott et al., 2007). 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 (Pendall et al., 2001; Möller et al., 2010) and from reconstructions of the glacial retreat synchronous at about 17 cal. ka BP throughout Patagonia (Kaplan et al., 2004; Rabassa, 2008; Hein et al., 2010).

5.4.3. *Lateglacial to early Holocene (unit B: 17.2–8.3 cal. ka BP)*

5.4.3.1. *Deglaciation.* In the lowermost part of unit B (17.2–14.4 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. C/N above 10 indicates that there is substantial input from non–algal sources (Figs. 3 and 5). Core photographs and descriptions show remains of aquatic macrophytes (Kliem et al., 2013), while input of other vascular plants is likely. Stable isotope and diatom analyses report similar findings (Massaferro et al., 2013; Zhu et al., 2013). 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 and Burckle, 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 Lateglacial is described as warm and humid in the multiproxy study by Recasens et al. (2011). 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 (Pendall et al., 2001; Kaplan et al., 2004; Rabassa, 2008; Hein et al., 2010; Möller et al., 2010). The general climatic warming would have caused the permafrost in the catchment to thaw. Permafrost degradation could have mobilized dissolved organic matter 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 (Martinez et al., 2006; Lamy and Kaiser, 2009). 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. (2013) 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., 2013). 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 (Heusser, 1989; Massaferro et al., 2005) 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 Members, 2004). A decrease in all productivity indicators can be observed after 14.7 cal. ka BP (Figs. 3 and 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 (Hajdas et al., 2003; Ariztegui et al., 1997; Douglass et al., 2006; Moreno et al., 2009).

5.4.3.3. Younger Dryas. Following the ACR, at 13.5 cal. ka BP, TIC values rise. Three TIC peaks are recorded until about 11.5 cal. ka BP. Each is accompanied by a rise in TOC and C/N values (Figs. 3 and 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 lowering lake level (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., 2013). Blooms of aquatic macrophytes and diatoms can also be attributed to these warmer surface waters. 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). Moreover, strong westerly winds would have inhibited the formation of a stable and warm epilimnion. According to Kliem et al. (2013) the onset of carbonate 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 et al., 2003; Kaplan et al., 2008b). Haberzettl et al. (2007) already 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 for publication). Several additional continental records show that the Younger Dryas in Patagonia is not a cold event as on the northern hemisphere (Hajdas et al., 2003; Moreno, 2004; Massaferro et al., 2005; Moreno et al., 2009). However, a southward movement of the SHW during this period probably did not reach the latitudes of Laguna Potrok Aike (Zech et al., 2009). Carbonate precipitation ceases at about 11.4 cal. ka BP (Figs. 3 and 5) and corresponds to the end of the Younger Dryas chronozone. Cooler and moister conditions probably returned around Laguna Potrok Aike.

5.4.3.4. Early Holocene. In the uppermost part of unit B, TIC shows higher values indicating a low lake level (Figs. 3 and 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., 2013). 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 9.4 ± 0.7 cal. ka BP (Kliem et al., 2013). 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-Martínez 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 low stand 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 (Heusser, 1989; McCulloch et al., 2000; Huber et al., 2004; Unkel et al., 2008; Waldmann et al., 2010). 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 (Masson et al., 2000; Fig. 3; Masson-Delmotte et al., 2004; EPICA Community Members, 2004, 2006).

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). Since, the records of TOC, BSi and C/N are biased by reworking, decomposition and dissolution, interpretations by Haberzettl et al. (2005, 2007) are based on TIC as indicator for supersaturation at Laguna Potrok Aike lake level lowstands. This is supported by our study. The lake level was variable with humid intervals during the past 8 ka, including during the “Medieval Climate Anomaly” (around 800 cal. BP) and in particular during the “Little Ice Age” (around 300–500 cal. BP); the most important humid phase of the Mid- to late Holocene. Deviations from the interpretation of Haberzettl et al. (2007) are mainly due to a revision of the age-depth model and are all within the error margin of dating (Kliem et al., 2013).

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. Glacial conditions were however punctuated by less cold and less windy conditions that promoted productivity in the lake and in the catchment. These intervals may have corresponded to Antarctic A-events within the errors of our age model. The highest productivity was observed during the Lateglacial (17.2–14 ka cal. BP) 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 probably became negative around this time. 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 and caused lake level lowering.

6. Conclusions

This study clearly illustrates that 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 reconstruct paleoproductivity. The use of multiple paleoproductivity indicators allows to deal with this complexity. This study also demonstrates that the dynamics of a lake system may be subject to large changes when lacustrine records cover long time period. Laguna Potrok Aike experienced 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 organic matter content from Laguna Potrok Aike covering the last 51 ka. 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 higher productivity events in Laguna Potrok Aike. There is no evidence of shifts in the SHW affecting paleoproductivity in Laguna Potrok Aike during OIS 3 and 2. Southern Patagonia was probably not under the influence of the SHW before the Holocene 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. Future lake biogeochemistry studies will also refine these interpretations.

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