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The last Glacial–Interglacial transition in Patagonia, Argentina: the stable isotope record of bulk sedimentary organic matter from Laguna Potrok Aike

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An investigation of stable isotope ($\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$) and elemental parameters (TOC, TN contents and TOC/TN ratios) of bulk organic matter (<200 μm) from sediment cores recovered from the Patagonian lake Laguna Potrok Aike (Argentina) in the framework of the ICDP deep drilling project PASADO provided insights into past changes in lake primary productivity and environmental conditions in South Patagonia throughout the last Glacial–Interglacial transition. Stratigraphically constrained cluster analyses of all proxy parameters suggest four main phases. From ca 26,100 to 17,300 cal. years BP, lacustrine phytoplankton was presumably the predominant organic matter source in an aquatic environment with low primary productivity rates. At around 17,300 cal. years BP, abrupt and distinct shifts of isotopic and elemental values indicate that the lacustrine system underwent a rapid reorganization. Lake primary productivity (phytoplankton and aquatic macrophytes) shows higher levels albeit with large variations during most of the deglaciation until 13,000 cal. years BP. The main causes for this development can be seen in improved growing conditions for primary producers because of deglacial warming in combination with expedient availability of nutrients and likely calm wind conditions. After 13,000 cal. years BP, decreased $\delta^{13}C_{TOC}$ values, TOC, TN contents and TOC/TN ratios indicate that the lake approached a new state with reduced primary productivity probably induced by unfavourable growing conditions for primary producers like strengthened winds and reduced nutrient availability. The steady increase in $\delta^{15}N_{TN}$ values presumably suggests limitation of nitrate supply for growth of primary producers resulting from a nutrient shortage after the preceding phase with high productivity. Nitrate limitation and consequent decreased lacustrine primary productivity continued into the early Holocene (10,970–8400 cal. years BP) as reflected by isotopic and elemental values.

1. Introduction

Stable isotope analysis of bulk organic matter has been widely used in ecological research (e.g. Fry, 2006; Michener and Lajtha, 2007). However, these variables not only provide present day environmental information, but the isotopic composition of e.g. sedimentary organic matter preserves also evidence of past environmental changes (Meyers, 1994). Stratigraphic changes in carbon and nitrogen isotope composition of organic matter contained in lake sediments thus help trace histories of environmental and climate change (e.g. Meyers and Lallier-Vergès, 1999; Meyers, 2003; Lücke and Brauer, 2004).

Although several lacustrine isotope records have provided evidence for climate changes during the last deglaciation in the northern hemisphere (e.g. Yu and Eicher, 1998;; von Grafenstein et al., 1999;; Lücke et al., 2003;; Parplies et al., 2008) and in the mid-latitudes of the southern hemisphere (e.g. Valero-Garcés et al., 2005; Bertrand et al., 2010), understanding of late Quaternary climate changes in the southern hemisphere higher latitudes is still incomplete because of the lack of long, continuous and high-resolution terrestrial records. Hence, due to its unique geographic

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location, records from southernmost Patagonia can offer new palaeoclimatic insights and an important linkage with marine records from southern oceans and ice core records from Antarctica. The sediment archive of Laguna Potrok Aike, further developed by the Potrok Aike maar lake sediment archive drilling project (PASADO) within the framework of the International Continental Scientific Drilling Program (ICDP), has initiated interdisciplinary multiproxy investigations to advance the understanding of past environmental and climatic changes in South Patagonia throughout the last Glacial–Interglacial cycle (e.g. Recasens et al, in press; Hahn et al., 2013). Here we report on the results of high-resolution carbon and nitrogen isotope analyses of bulk sedimentary organic matter from Laguna Potrok Aike for a time window from 26,075 to 8400 cal. years BP, including the last Glacial Maximum (LGM) and the glacial–Interglacial transition period, and discuss their paleoenvironmental significance. Our investigation builds on the earlier studies of surface and older sediments as well as core catcher samples (Mayr et al., 2009; Kastner et al., 2010; Lücke et al., 2010) and expands their scope with respect to temporal resolution and depositional history.

2. Site description

Laguna Potrok Aike is located at 113 m above sea level in the Pali Aike Volcanic Field in southern Patagonia, Argentina (51° 58′ S, 70° 23′ W, Fig. 1A) and originated from a phreatomagmatic explosion (Zolitschka et al., 2006). A detailed description about geomorphological characters and landscape evolution of the Laguna Potrok Aike area can be found in Coronato et al. (2013). During the last Glacial the catchment of the lake was not covered by the Patagonian glaciers (Zolitschka et al., 2006). Under modern conditions, Laguna Potrok Aike is a polymictic, phosphorous-rich and subsaline lake with a surface area of 7.58 km^2 and a maximum depth of 100 m (further lake characteristics in Zolitschka et al., 2006). The lake has presently only several episodic inflows through gullies and canyons and a catchment area of about 200 km^2. Subaerial and submerged paleoshorelines around and in the lake indicate pronounced lake-level fluctuations resulting from past hydrological changes (Zolitschka et al., 2006; Anselmetti et al., 2008; Gebhardt et al., 2011; Kliem et al., 2013a). The littoral zone of Laguna Potrok Aike is covered by aquatic macrophytes (e.g. *Potamogeton pectinatus* and *Myriophyllum* cf. *quitense*) from a water depth of ca 1.5–15 m (Wille et al., 2007). Phosphate, as an important nutrient, appears to be unlimited in Laguna Potrok Aike (total phosphorus measurements: 1297–3609 μg/L), since the total phosphorus concentration is rather high presumably related to the regional geology (Zolitschka et al., 2006). The observed nitrate concentrations in lake water were considerably variable (nitrate measurements: <0.05–3.07 mg/L) and indicate a potential nitrate limitation for primary production (Zolitschka et al., 2006). The climate at Laguna Potrok Aike is influenced by the rain shadow of the Andes and nowadays characterized by semiarid steppe with a high annual evaporation/precipitation ratio of up to 24 (Wille et al., 2007; Ohlendorf et al. 2013). The modern vegetation in the area around Laguna Potrok Aike is a dry Magellanic steppe with grasses, shrubs, bushes and cushions as a result of overgrazing because of sheep farming during the last 100 years (Aagesen, 2000; Wille et al., 2007).

Laguna Potrok Aike is located at the center of the present-day Southern Hemisphere Westerlies that are characterized by their strong intensity associated with a strong meridional pressure gradient between the semi-permanent high pressure cells located over the subtropical South Pacific and South Atlantic oceans and the subpolar low pressure belt at approximately 60° S (Cerveny, 1998; Paruelo et al., 1998). As topographic barrier for the Westerlies, the Andes play a crucial role in determining the Patagonian precipitation pattern in the lee of the cordillera. Precipitation in the eastern part of South Patagonia is additionally affected by air masses coming from the Atlantic Ocean resulting in a more evenly distributed seasonal precipitation (Paruelo et al., 1998). Meteorological data of Laguna Potrok Aike have also shown the influence of rain-bringing easterly winds on the precipitation in the area (Mayr et al., 2007). A mean annual precipitation of 251 ± 62 mm and a mean annual temperature of 7.4 ± 0.7 °C are recorded at the weather station in Río Gallegos at the Atlantic coast, ca 90 km east of Laguna Potrok Aike where both mean annual precipitation and temperature are 30–40% lower compared to the coastline (Zolitschka et al., 2006). Mean annual values of wind speed vary between 4 and 6 m/s in the central part of Patagonia (Paruelo et al., 1998) and around 7.4 m/s at Río Gallegos (Baruth et al., 1998). The seasonal distribution of the wind speed, particularly in southern South Patagonia, shows a maximum during austral summers and a minimum during austral winters (Baruth et al., 1998; Garreaud et al., 2009).

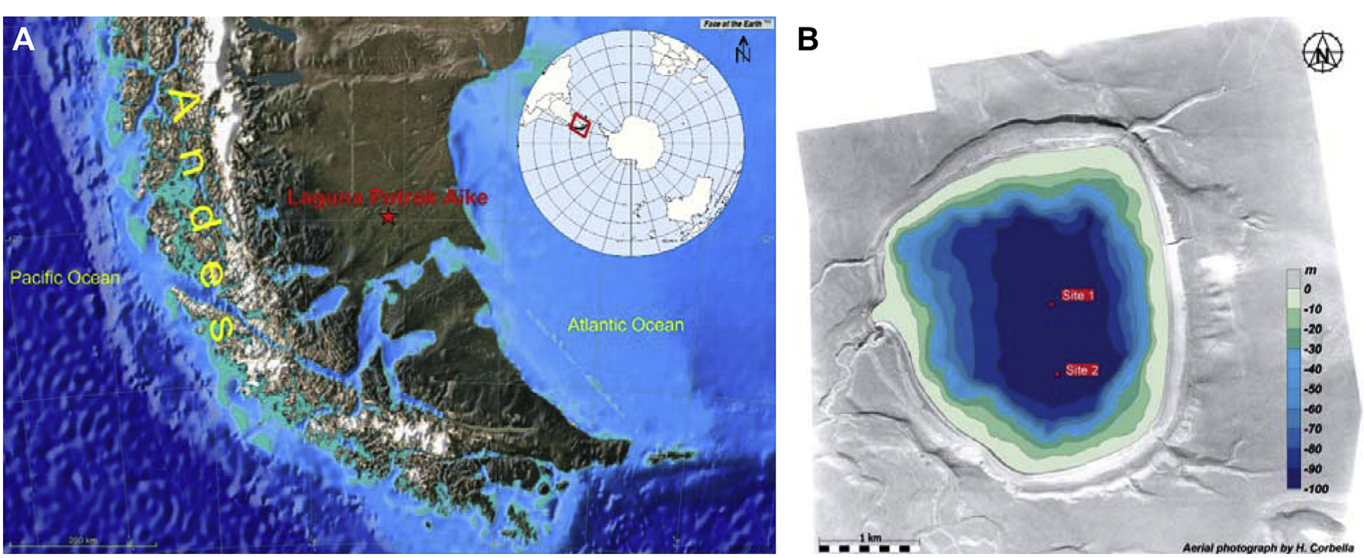

Fig. 1. A) Location of Laguna Potrok Aike (red star) in South Patagonia in the relief map modified from http://jules.unavco.org/voyager/EarthScope. Red frame marked in the inserted map (source: Sean Baker/Wikipedia) shows the location of South Patagonia on the Southern Hemisphere. B) Drilling sites in 2008 in the aerial photography of Laguna Potrok Aike with bathymetry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Material and methods

A total of 533 m of sediment cores was recovered from two drilling sites in Laguna Potrok Aike in 2008 in the framework of the ICDP deep drilling project PASADO (Zolitschka et al., 2009; Ohlendorf et al., 2011, Fig. 1B). In this study, we used the samples collected from the 106 m long Site 2 composite profile 5022-2CP (Ohlendorf et al., 2011) that covers the last 51,000 years according to the age–depth model (version 3) of Kliem et al. (2013b). The profile consists of undisturbed pelagic sediments, tephra layers and mass movement sediments that result from lake internal sediment redistribution. The mass movement deposits are characterized by ball and pillow structures, normally graded beds, structureless sand and fine gravel layers, matrix supported layers and one folded sediment structure (Kliem et al., 2013b). Mass movement deposits and tephra layers were removed from the composite profile resulting in an event-corrected composite depth profile (m cd-ec) of 45.80 m to establish the age model. The age–depth model is based on radiocarbon dates of undisturbed pelagic sediments and was developed using the mixed-effect regression approach of Heegaard et al. (2005). For our analysis we chose the composite depth (cd) from 30.03 to 10.03 m (21.56–9.57 m cd-ec) covering the period between ca 26,100–8400 cal. years BP including the LGM and the last Glacial–Interglacial transition. The age–model for this sediment section relies on nine radiocarbon dates. A lithostratigraphic description for the composite profile has been given by Kliem et al. (2013b). Accordingly, our investigated sediment depths cover the parts of lithostratigraphic units B (8.82–18.72 m cd) and C-1 (18.72–40.23 m cd). Unit B consists mainly of pelagic laminated silts varying between dark grey (in the upper part) and brownish and light grey (in the lower part) intercalated with thin fine sand and coarse silt layers. Unit C-1 is also dominated by pelagic laminated silts which are greenish, bluish grey and have poor lamination compared with unit B. More mass movement deposits are found in unit C-1. Around 600 samples with 2 cm spatial resolution from sections with undisturbed pelagic sediments defined by Kliem et al. (2013b) were measured contiguously with an average temporal resolution of 28 years. In addition, about 100 samples from sections with re-deposited sediments were measured at 8 cm intervals (every 4th) for carbon and at 16 cm intervals (every 8th) for nitrogen isotope analyses, respectively.

Freeze-dried samples were cautiously homogenized and sieved at 200 μm to remove coarse organic debris. An aliquot (<200 μm) for carbon isotope analysis was pre-treated with HCl (5%) in a water bath (50 °C) for 2 h to remove carbonates and rinsed with distilled water three times to remove reagents. The samples were weighed before and after treatment to estimate HCl-insoluble content in weight percentage. Nitrogen isotope analysis was performed on the untreated freeze-dried samples of the same sediment fraction (<200 μm). For isotope analyses, samples were weighed into tin capsules to provide approx. 100 μg of carbon and 80 μg of nitrogen, respectively, for analyses. Isotope ratios were measured using a continuous flow system that comprises an elemental analyzer (Flash 2000, Thermo Scientific for carbon and Euro EA 3000, Eurovector for nitrogen) directly attached to an isotope ratio mass spectrometer (IRMS; Delta V Advantage, Thermo Scientific for carbon and IsoPrime, Micromass for nitrogen). The samples were combusted in a He atmosphere with an excess of oxygen in the elemental analyzer and the analytical gases were transported into the IRMS in a continuous He flow through a series of traps and a GC column for purification and isolation of the target analyte. Isotope ratios are expressed as δ-values in per mil (‰), where $\delta = (R_{sample}/R_{standard} - 1)*1000$, with R_{sample} and $R_{standard}$ as isotope ratios ($^{13}C/^{12}C$ and $^{15}N/^{14}N$) of samples and international standards. For carbon and nitrogen, results are reported against the Vienna PeeDee Belemnite (VPDB) and atmospheric nitrogen (AIR), respectively. Laboratory standard materials were inserted between samples to monitor the working conditions of the instrument. Analytical precision (one standard deviation) was ±0.10‰ for carbon and ±0.15‰ for nitrogen isotope ratios.

Carbon and nitrogen contents were calculated according to the amounts of CO_2 and N_2 after sample combustion in the elemental analyzer. The obtained carbon content values and HCl-insoluble contents were used to estimate the total organic carbon (TOC) contents expressed in weight percentage (wt. %). Total nitrogen (TN) content (wt. %) was obtained directly from the nitrogen contents measured. The TOC/TN mass ratio is multiplied by 1.167 (the ratio of atomic weights of nitrogen and carbon) to yield the TOC/TN molar ratio (Meyers and Teranes, 2001), which is used in this study.

Stratigraphically constrained cluster analyses of all proxy parameters were performed by the CONISS program (Grimm, 1987) to identify the stratigraphical boundaries for the period investigated.

To further elaborate on the composition of the grain-size fractions and their isotope compositions, 11 HCl-untreated samples were selected from the total profile to be further sieved into four size fractions (<10 μm, 10–63 μm, 63–125 μm and 125–200 μm) by wet sieving. These fractions were analysed separately with the above described methods to obtain the $\delta^{13}C_{TOC}$, $\delta^{15}N_{TN}$ values for each fraction.

4. Results

4.1. Geochemistry

For all measured samples, TOC contents range from 0.02 to 9.87% (mean 1.00%, $n = 737$) and TN contents from 0.01 to 0.66% (mean 0.12%, $n = 700$) (Fig. 2). TOC/TN ratios range between 1.73 and 29.44 (mean 7.33, $n = 696$). Carbon and nitrogen isotope compositions vary from −28.1 to-22.3‰ (mean −25.6‰, $n = 741$) and 1.3–7.6‰ (mean 3.4‰, $n = 685$), respectively. Below 18.73 m (cd) most samples show comparably low and stable values of TOC and TN contents and TOC/TN ratios. $\delta^{13}C_{TOC}$ values here are almost all lower than −25.5‰ and $\delta^{15}N_{TN}$ values vary between 2.0 and 4.0‰. In terms of measured variables, there is no clear difference between undisturbed pelagic and re-deposited mass movement sediments in this depth range. The majority of samples with high TOC, TN contents, TOC/TN ratios, $\delta^{13}C_{TOC}$ values and low $\delta^{15}N_{TN}$ values in the total profile can be found between 18.60 and 13.00 m (cd). Except nitrogen isotope compositions, all variables exhibit high variability with e.g. 9% range for TOC contents and 5‰ range for carbon isotope compositions. By comparison with pelagic sediments, re-deposited sediments present here a different character with generally low TOC, TN contents, highly variable TOC/TN ratios and carbon isotope compositions. Above 13.00 m, most samples display low TOC, TN contents and TOC/TN ratios as well as decreased $\delta^{13}C_{TOC}$ values and increased $\delta^{15}N_{TN}$ values.

The samples below 20 m (cd) from lithostratigraphic unit C-1 have a generally high proportion of the finest sediment fraction (<10 μm) and a low proportion of the coarsest fraction (125–200 μm) in the bulk sediment (<200 μm) compared to the samples from the upper part of the profile of lithostratigraphic unit B (Fig. 3A). The coarsest fraction found in the samples between 14 and 19 m (cd) is usually composed of visible organic material, such as remains of aquatic vascular plants and mosses. Three samples at 18.49, 21.17 and 23.21 m (cd) show highly various TOC/TN ratios in the sieve fractions with higher ratios in the coarser fractions and lower ratios in the fine fractions. Other samples exhibit a general small range of TOC/TN ratios with highest ratios in the coarsest

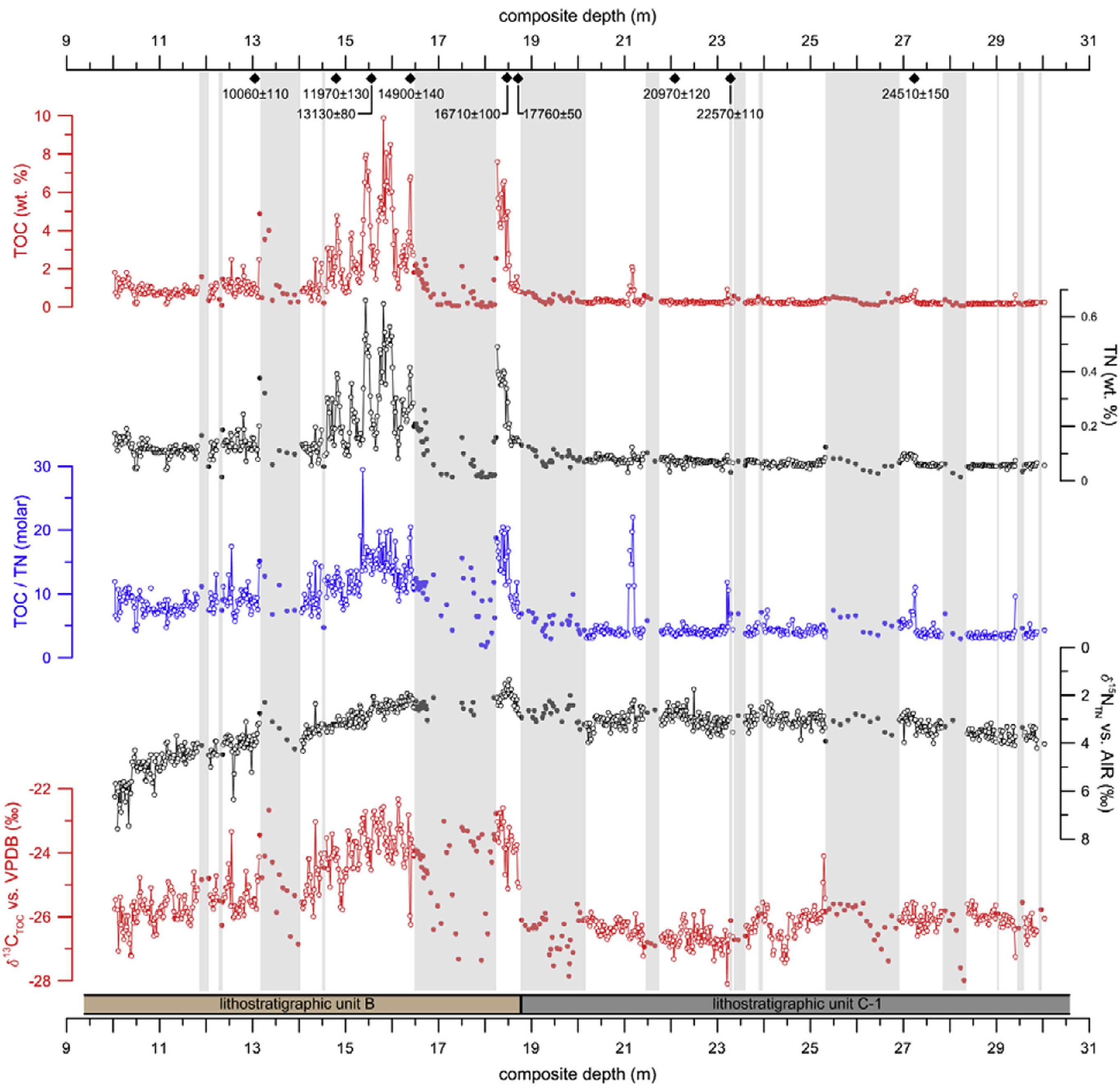

Fig. 2. Downcore changes in carbon and nitrogen isotope compositions, TOC and TN contents (wt. %) and TOC/TN ratios during the investigated period (ca 10–30 m cd) for core 5022-2CP from Laguna Potrok Aike. Measured samples from sections with undisturbed pelagic sediments as well as from disturbed and re-deposited sediments are plotted. Composite depths of sections with re-deposited sediments like mass movement and tephra deposits (Kliem et al., 2013b) are marked by grey bars. Lithostratigraphic units B and C-1 are described in Kliem et al. (2013b). Note inverse scale of $\delta^{15}N_{TN}$ values. Black diamonds with numbers on the upper depth scale show the depths of AMS radiocarbon ages (cal. years BP) with error (1σ) given by Kliem et al. (in this 2013b, Table 2).

fraction (Fig. 3B). The differences in $\delta^{13}C_{TOC}$ values between the coarsest and the finest fraction range from 0.08 to 3.36‰ (mean 1.47‰, $n = 11$) whereby the samples between 15 and 19 m (cd) show the largest differences. The coarsest fraction is always most depleted in ^{13}C (Fig. 3B). Nitrogen isotope compositions of sieve fractions show a trend in the samples below 20 m (cd) of least ^{15}N enriched values associated with the finest fraction. Both carbon and nitrogen isotope compositions of bulk sediments smaller than 200 μm show a pattern similar to that of the sieve fraction between 10 and 63 μm.

4.2. Cluster analysis

The CONISS cluster analysis included all proxy parameters from undisturbed pelagic samples. Three main clusters with highest dispersion and two main boundaries at around 17,300 and 13,000 cal. years BP were determined (Fig. 4A). Analyses without the outliers have confirmed that the absence or presence of outliers has no substantial influence on the division of the main clusters.

Considering the data structure of single variables it is evident that the distribution function of total organic carbon and total nitrogen follows more a logarithmic than a linear law (Fig. 5, lower

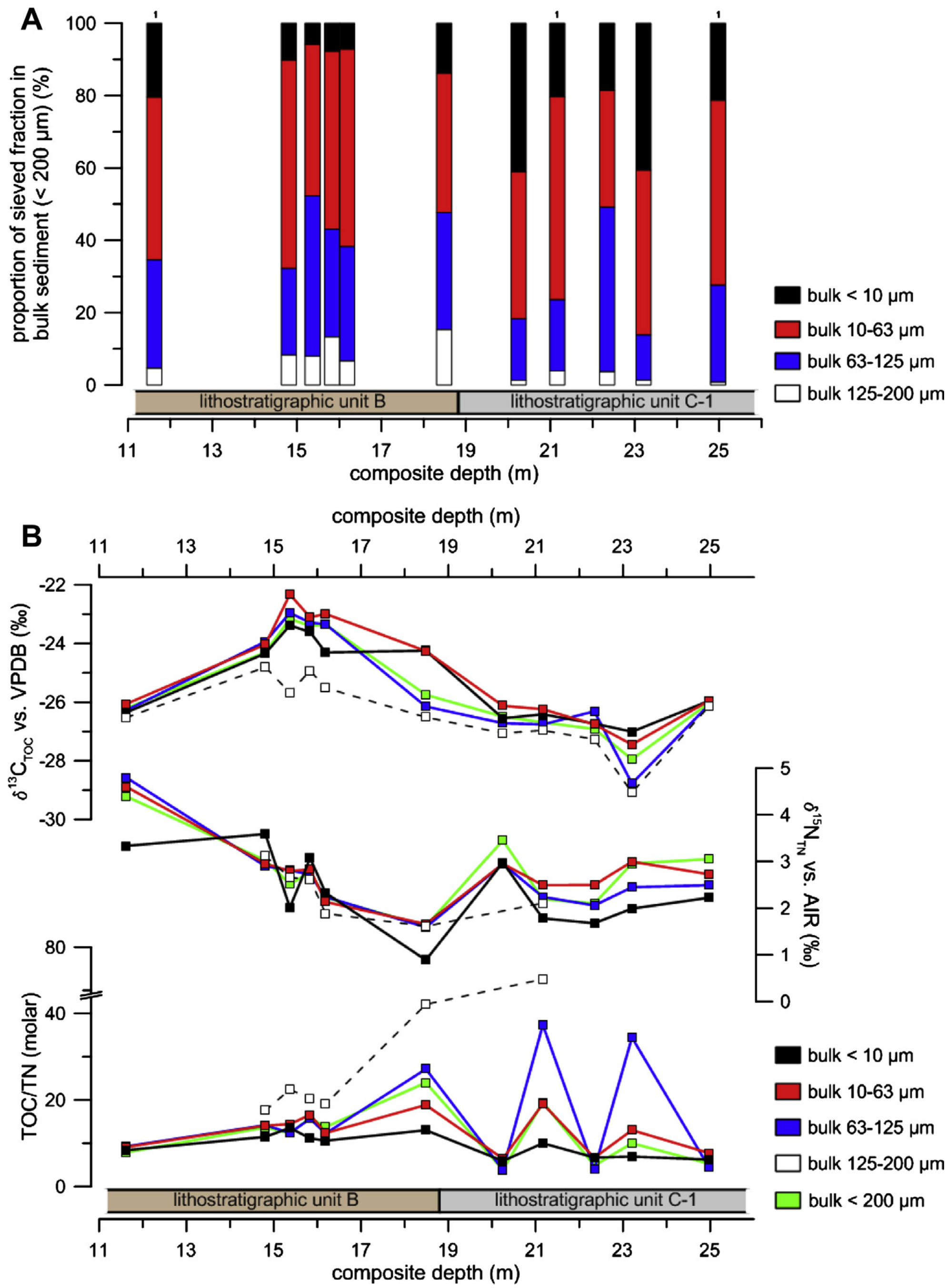

Fig. 3. Proportion of four grain-size sieving fractions (<10 µm, 10–63 µm, 63–125 µm and 125–200 µm) and its isotopic and elementary values of samples of core 5022-2CP from Laguna Potrok Aike. A) proportion of four sieving fractions in percentage. [1]small proportion loss of the fraction smaller than 10 µm due to tube breakage during centrifuge. B) Carbon and nitrogen isotope compositions and TOC/TN ratios of bulk sediments (<200 µm) and four sieving fractions. Samples from the composite depth between 11 and 19 m correspond to the early Holocene and late Glacial time interval (lithostratigraphic unit B), whereas sediments at 19–25 m composite depth (lithostratigraphic unit C-1) were deposited prior to 17,300 cal years BP (see Kliem et al., 2013b for age–depth model).

right). Accounting for this difference by using logarithmic TOC and TN data for the cluster analysis indeed changes the outcome. The basic structure of three main clusters remains and the older boundary at around 17,300 cal. years BP (18.73 m cd) is confirmed but the younger boundary is shifted from 13,000 to 10,970 cal. years BP (Fig. 4B). While the boundary at around 17,300 cal. years BP matches with the transition from lithostratigraphic unit B to unit C-1 (s. Kliem et al., 2013b), no lithostratigraphic change is described for either of the younger boundaries. Justification for the demarcation of clusters can be found in the data for both linear and log-scaled element contents. Whereas a change in variance of TOC and TN seems to determine the classification in the latter case (Fig. 4B), the development of absolute values seems to be more important in the former case (Fig. 4A). As there are no lithostratigraphic criteria to decide the case and the data justify both scenarios, we suggest respecting both divisions. Because after 10,970 cal. years BP the elemental contents of organic carbon and nitrogen in the sediments of Laguna Potrok Aike remain on one and the same reduced level with minimal variance, we are inclined to assign higher palaeoenvironmental importance to this than to the

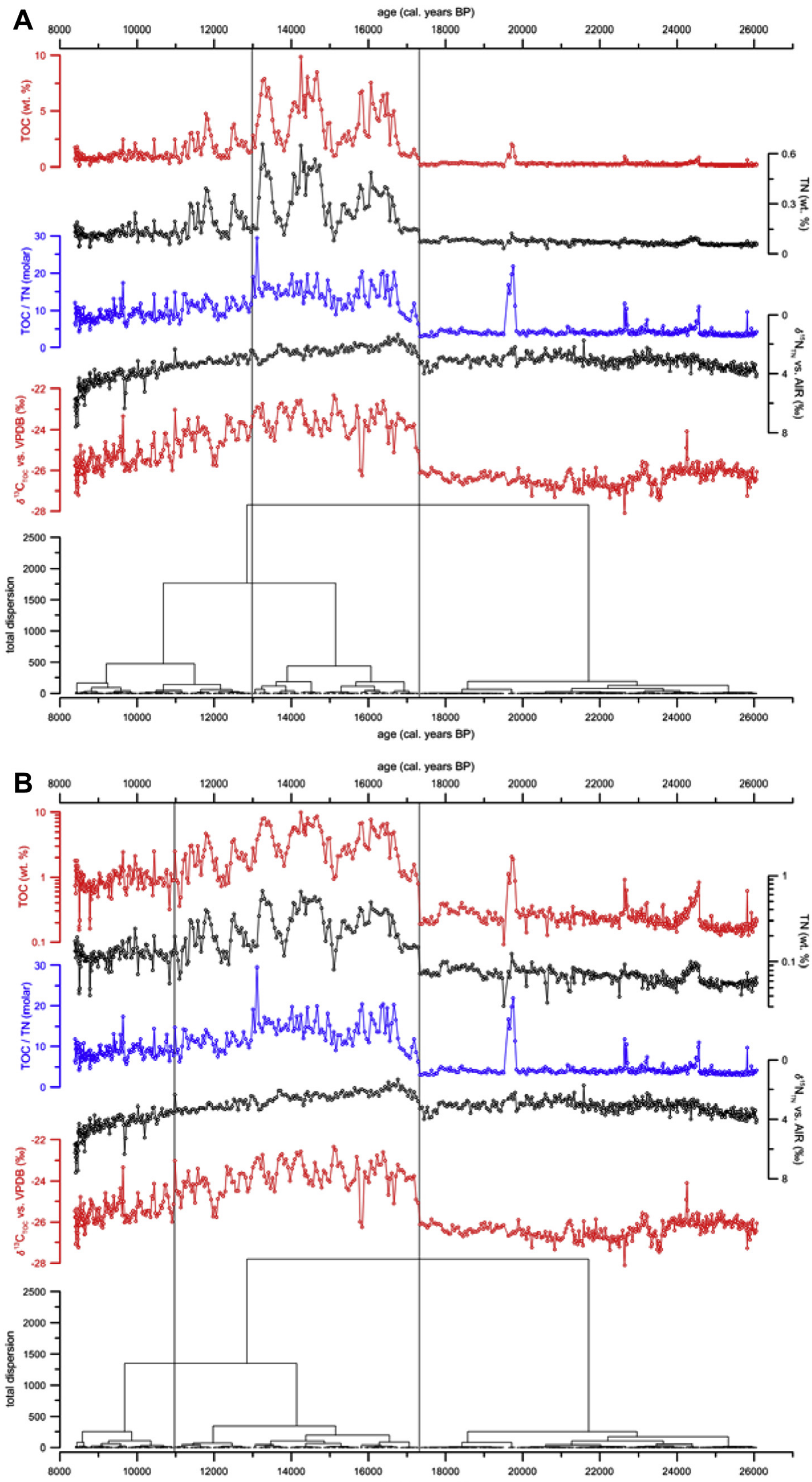

Fig. 4. Three main phases with boundaries (grey lines) in measured proxy parameters during the last Glacial–Interglacial transition for core 5022-2CP from Laguna Potrok Aike suggested by cluster analysis (CONISS program by Grimm, 1987). Samples from sections of re-deposited sediments are excluded for the analysis. A) TOC and TN used on the linear scale. B) TOC and TN values logarithmized for the cluster analysis and used on the log scale. For details refer to the text. Note inverse scale of $\delta^{15}N_{TN}$ values.

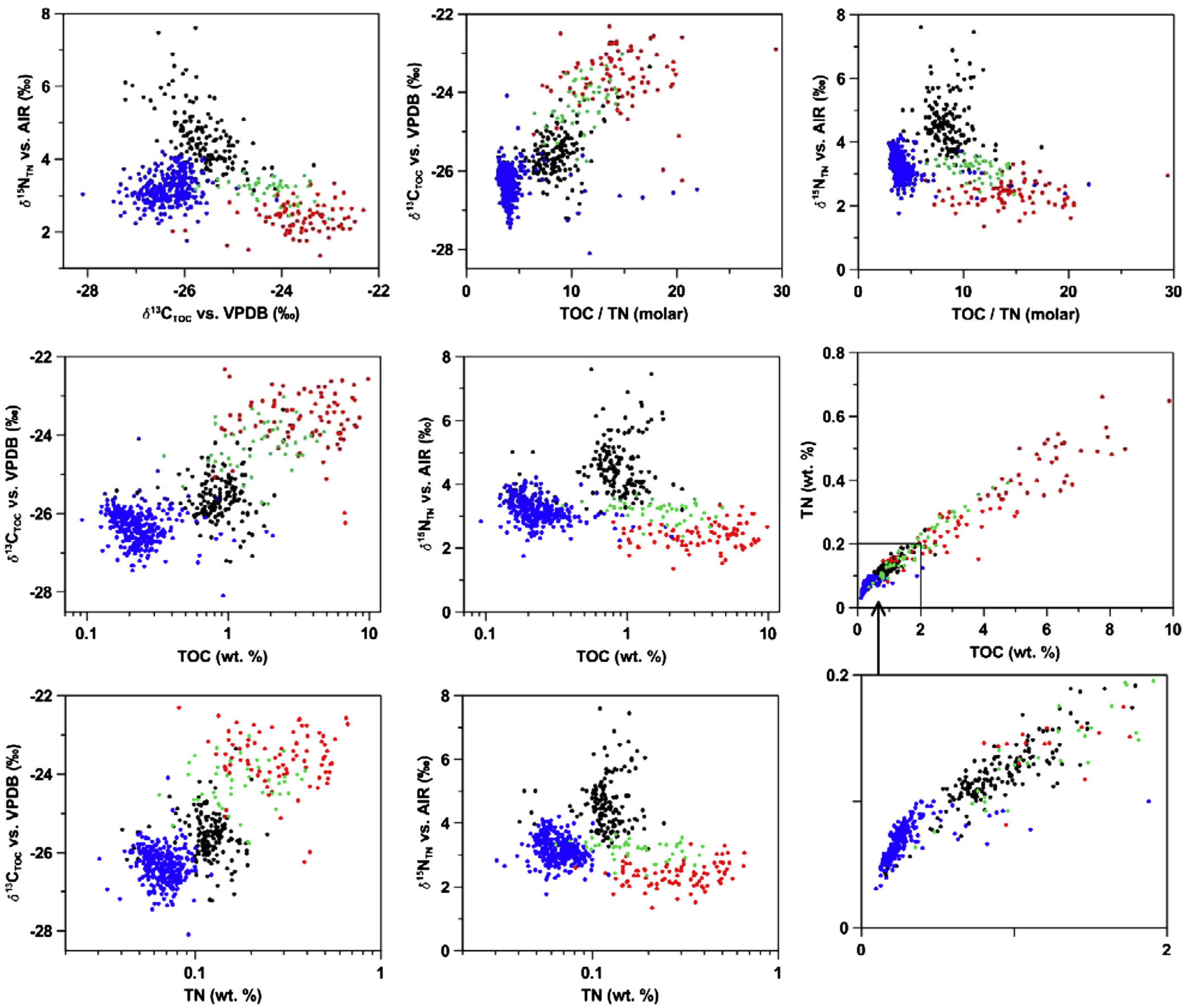

Fig. 5. Cross-plots of the measured proxy parameters for the four main phases (blue: phase 1, 26,075–17,300 cal. years BP; red: phase 2, 17,300–13,000 cal. years BP; green: phase 3, 13,000–10,970 cal. years BP; black: phase 4, 10,970–8400 cal. years BP). Samples from sections of re-deposited sediments are excluded. The cross-plot of TOC and TN is enlarged in the lower right. Low correlations on the intra-phase scale can be observed, however there are visible inter-phase relationships among the proxy parameters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

boundary of 13,000 cal. years BP. The period between around 13,000 and 10,970 cal. years BP seems to be a transition from high to low TOC and TN values with smaller variability but still overall similarity to the period between around 17,300–13,000 cal. years BP (Fig. 4A).

Considering the points outlined above we propose to structure the investigated time window of the Laguna Potrok Aike profile into four characteristic phases (Fig. 6):

4.2.1. Phase 1 (26,075–17,300 cal. years BP)

TOC and TN contents have very low values, mean 0.26 and 0.07% ($n = 323$) for TOC and TN, respectively. Except for several outlier samples, both TOC and TN contents stay more or less on a constant level during this phase. TOC/TN ratios are usually lower than 5 (mean 4.31, $n = 322$). Only several outlier samples show extreme high TOC/TN ratios up to 19. $\delta^{13}C_{TOC}$ values vary in a small range with the mean value of −26.3‰ ($n = 324$). Most $\delta^{15}N_{TN}$ values have a range between 2 and 4‰ with a mean value of 3.2‰ ($n = 323$). Generally there is no clear correlation between all proxy parameters in this phase, apart from the relation of TOC and TN which has, however, a steeper slope compared with the later phases.

4.2.2. Phase 2 (17,300–13,000 cal. years BP)

Around 17,300 cal. years BP, an abrupt und marked shift occurs for all proxy parameters. TOC and TN contents rise to the highest values within the total profile investigated. TOC contents range from 0.80 to 9.87% (mean 4.00%, $n = 85$) and TN contents from 0.08 to 0.66% (mean 0.31%, $n = 85$) in the whole phase. A two step increase at the transition from phase 1 to 2 can be observed in both variables. The first rise of smaller extent within a short time (from 0.20 to 1.50% for TOC, from 0.07 to 0.15% for TN) is followed by a second larger increase (from 1.5 to more than 6% for TOC, from 0.15 to more than 0.4% for TN). TOC/TN ratios also display a two step increase and rise to a mean value of 14.34 ($n = 85$). In comparison to the changes in TOC, the increase in $\delta^{13}C_{TOC}$ values by up to 2.5‰

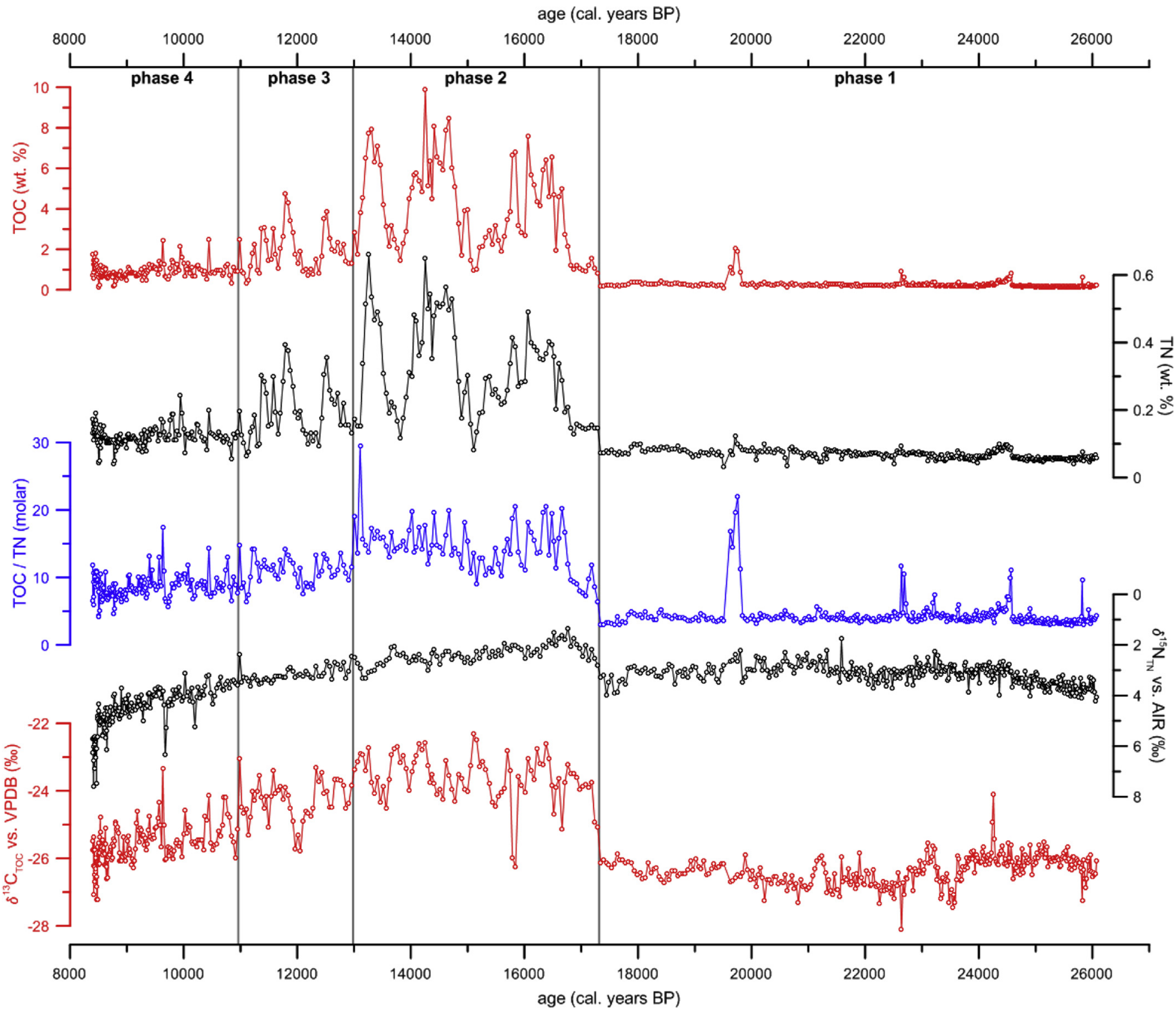

Fig. 6. Proposed four main phases of measured proxy parameters during the investigated last Glacial–Interglacial transition for core 5022-2CP from Laguna Potrok Aike determined by assemblage of two approaches of stratigraphically constrained CONISS cluster analyses (Fig. 4). Grey lines mark the boundaries of the proposed stages. Note inverse scale of $\delta^{15}N_{TN}$ values.

occurs in just one step. During the whole phase the $\delta^{13}C_{TOC}$ values have a high mean value of −23.6‰ ($n = 85$). By contrast with other proxy parameters, the $\delta^{15}N_{TN}$ values decrease at first with about 2.0‰ at the transition from phase 1 to 2. About five hundred years later, the $\delta^{15}N_{TN}$ values begin to rise slightly into the next phase. TOC, TN contents, TOC/TN ratios and $\delta^{13}C_{TOC}$ values exhibit here the highest variability in the total profile investigated.

4.2.3. Phase 3 (13,000–10,970 cal. years BP)

TOC and TN contents decline with reduced variability, ranging from 0.35 to 4.75% (mean 1.89%, $n = 46$) for TOC and from 0.06 to 0.39% (mean 0.19%, $n = 46$) for TN. TOC/TN ratios drops to a mean value of 10.99 ($n = 46$). A decrease in $\delta^{13}C_{TOC}$ values can also be observed having a mean value of −24.3‰ ($n = 46$). The slow and slight increase in the $\delta^{15}N_{TN}$ values continues with little variability like the former phases. This phase can be considered as a transition from phase 2 to 4.

4.2.4. Phase 4 (10,970–8400 cal. years BP)

After 10,970 cal. years BP, both TOC and TN contents decrease to a low level that is nevertheless still higher than in the phase 1. TOC has a range from 0.15 to 2.47% (mean 0.91%, $n = 153$) and TN from 0.04 to 0.24% (mean 0.12%, $n = 153$). TOC/TN ratios decrease down to a mean value of 8.56 ($n = 152$). The $\delta^{13}C_{TOC}$ values with a mean of −25.6‰ ($n = 154$) drop towards the level of the phase 1 with a still higher variability. The $\delta^{15}N_{TN}$ values proceed to rise reaching more than 7.0‰ at the end of this phase. Cross plots reveal a negative correlation between $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ values ($r = -0.6$, $p < 0.0001$) in this phase.

There are no obvious correlations among the proxy parameters, except for the TOC and TN relation (Fig. 5). This behaviour could be seen as an indication of a variety of independent control factors determining the elemental and isotopic values of bulk organic matter looking at the intra-phase scale. However, an inter-phase relation can be found for several parameters (Fig. 5). Phase 1 distinguishes itself from other phases by low values of all proxy parameters and their narrow range of variability. From phases 2 to 4, carbon isotope compositions decrease with the rise of nitrogen isotope compositions, thus showing an overall negative correlation. This trend is accompanied by a reduction in TOC, TN contents and TOC/TN ratios correlating positively with carbon isotope compositions.

5. Discussion and interpretation

5.1. Nitrogen proxies and inorganically bound nitrogen

One of the geochemical proxies frequently used in environmental studies is the nitrogen content, for example to determine the carbon to nitrogen ratio. Nitrogen in aquatic sediments is a constituent of organic matter as well as bound to inorganic matter, mainly clay minerals (Müller, 1977). Normally, their carbon to nitrogen ratio is expressed as the TOC to TN ratio due to difficulties in the separation between the organic and the inorganic fraction of total nitrogen. However, especially in sediments with low organic matter concentrations (TOC < 0.3%), TOC/TN ratios could be reduced due to an elevated proportion of inorganic nitrogen (Meyers, 2003) thus being a poor estimator of the carbon to nitrogen ratio in sedimentary organic matter.

For Laguna Potrok Aike a gross estimation of the portion of inorganic nitrogen (IN) in TN (e.g. Talbot, 2001; Lücke and Brauer, 2004) seems insufficient, as no simple linear relation exists between TOC and TN (Fig. 5 lower right) thus excluding a straightforward estimation of IN. Comparably low TOC/TN ratios as in phase 1 of Laguna Potrok Aike have been observed in modern sediments of Lake Ohrid (Vogel et al., 2010) and were also reported by Melles et al. (2007) for Lake El'gygytgyn and by Watanabe et al. (2004) for Lake Baikal. The steeper slope of the TOC versus TN regression line of phase 1 compared to those of phases 2–4 (Fig. 5, lower right) and TOC/TN ratios below 5 might be interpreted as contribution of IN downward of 20.18 m (cd). However, there are several other factors including soil or source rock organic matter input, organic matter decomposition/degradation or grain size distribution that might cause low sedimentary TOC/TN ratios beside inorganically bound nitrogen. This issue is of broader importance as it also affects the interpretation of stable nitrogen isotopes as well as their relation to the respective stable carbon isotope signature.

Measurements reported by Mayr et al. (2009) for recent soils from the catchment of Laguna Potrok Aike cannot explain the very low glacial TOC/TN ratios of the record. A summary of carbon and nitrogen content of soils by Batjes (1996) shows that TOC/TN ratios generally range around 10 and do not fall below 7. Nevertheless a decline of TOC/TN ratios with depth and age, i.e. in the course of decomposition of soil humus was detectable (Batjes, 1996) – a process that might reduce the TOC/TN ratios of fossil soils further than observed in modern soils. Low TOC/TN ratios at around 3 were also found in the samples of rocks beneath soils in the catchment of Lake Holzmaar (Lücke et al. unpublished data). The TOC/TN ratios of such organic matter incorporated into rocks are dependent on the origin of its source rocks. Low sedimentary TOC/TN ratios might be influenced by source rock organic matter originating from the catchment of Laguna Potrok Aike.

Decomposition experiments describe an initial increase in TOC/TN followed by a less significant reduction under oxic conditions (Lehmann et al., 2002). Successive decomposition within a 50 cm long marine core was also found to cause a gradual reduction of TOC/TN ratios in a study by Freudenthal et al. (2001) where the IN content was determined explicitly. The authors attribute this to an increasing importance of inorganically bound nitrogen as decomposition of organic matter proceeds in oligotrophic, organic matter poor sediments. As the $\delta^{15}N$ of IN is depleted in ^{15}N compared to organic nitrogen (Freudenthal et al., 2001; Kienast et al., 2005), a higher portion of IN to TN in the sediments of Laguna Potrok Aike below 20.18 m (cd) would lead to an underestimation of the $\delta^{15}N$ signature of organic nitrogen by the respective bulk nitrogen isotope signature. Kienast et al. (2005) has reported considerable differences of 1–2‰ in the $\delta^{15}N$ of bulk sediment separated into different size fractions. In their study heavier isotope values seem to be associated with the finer sediment fractions whereas coarser fractions seem to become increasingly isotopically lighter. However, our elemental and $\delta^{15}N$ data of size fractions do not indicate such a dependence on grain size distribution for both lithostratigraphic units (Fig. 3).

In short, the issue of IN and its likely influence on TOC/TN and $\delta^{15}N_{TN}$ values in the glacial sediments of Laguna Potrok Aike cannot be decided on the available data. The low TOC/TN ratios of phase 1 sediments seem to imply an overestimation of IN, while the potential bias of IN during phases 2–4 is strongly restricted due to the high organic matter content.

5.2. Phase 1 (26,075–17,300 cal. years BP)

Studies on Patagonian glacier fluctuations have shown that full glacial conditions should dominate the climate in southern South Patagonia prior to around 17,500 cal. years BP (e.g. McCulloch et al., 2005; Sugden et al., 2005; Kaplan et al., 2008). A study of glacial moraines from Kilian et al. (2007) has suggested the start of deglaciation at Gran Campo Nevado, located about 200 km southwestern from Laguna Potrok Aike, at around 18,000 cal. years BP.

These dates coincide well with the end of phase 1 as inferred from our organic geochemical dataset (Fig. 6). During phase 1, the origin of low TOC/TN ratios around 4, as discussed in the Section 5.1, remains unclear but could imply that sedimentary organic matter predominantly stemmed from phytoplankton production as the algae produce organic matter which has lower TOC/TN ratios of 4–10 than those from mosses and vascular-plants with 20 and greater (Meyers, 2003). The samples with distinct spikes of high TOC/TN ratios contain usually high amounts of aquatic moss debris that could affect the analyzed bulk fraction (<200 μm), as suggested by the TOC/TN ratios of sieve fractions (Fig. 3B).

Simulation models of Hulton et al. (2002) suggest a decline in temperature of 6 °C compared to the present values during the LGM in southern South Patagonia. At that time the area of Laguna Potrok Aike was climatically more continental than it is now because of the sea level lowering of up to 150 m below present on the Argentine Shelf (Guilderson et al., 2000).

Under such cold and dry climatic conditions, a tundra-like vegetation and thin soil layers with low nitrogen mineralization rate can be expected in the lake catchment. During the long winter period the lake was likely ice covered with little snow and stratified. Algal production can be maintained under the lake ice cover as reported by many studies (e.g. Spaulding et al., 1993; McKnight et al., 2000). Low air and water temperatures could, however, induce low lake algal productivity as suggested by the low TOC, TN contents and by low $\delta^{13}C_{TOC}$ values (Fig. 6). Although respiration and decomposition would be low due to the low primary production, dissolved CO_2 from internal respiration in the lake could be a main carbon source for algal assimilation during periods with ice cover. This re-utilized CO_2 is depleted in ^{13}C and could contribute to the low $\delta^{13}C$ values. Sediments with low organic carbon contents are characteristic of glacial-age lake sediments in temperate climate zones (Meyers and Lallier-Vergès, 1999). The narrow range of changes in total nitrogen isotope composition may reflect little changes in the lacustrine nitrogen cycle during that time.

5.3. Phase 2 (17,300–13,000 cal. years BP)

The abrupt increase in $\delta^{13}C_{TOC}$ values around 17,300 cal. years BP is interpreted as a fast and persistent increase in lake primary productivity triggered by deglacial warming which caused extended growing seasons, high growth rates and consequent fast consumption and probably lowering of dissolved CO_2 concentrations. Photosynthetic processes use preferentially ^{12}C and lead to organic matter production enriched in ^{12}C and dissolved inorganic carbon (DIC) of surface waters enriched in ^{13}C. Progressively, newly produced organic matter then becomes enriched in ^{13}C by assimilation of isotopically heavier DIC. This effect can also be intensified by a depletion of the dissolved CO_2 concentration as the result of high primary productivity, because a low CO_2 concentration in the photic zone diminishes discrimination against ^{13}C during photosynthesis (O'Leary, 1988; Hollander and McKenzie, 1991). These processes of isotopic fractionation are especially active during phases of lake stratification in the often productive summer season with high carbon demand for photosynthesis but low carbon replenishment from the hypolimnion. Isotopically heavier organic matter can also be produced by increased growth rate of phytoplankton because of declined isotopic fractionation (Laws et al., 1995; Burkhardt et al., 1999). An influence of atmospheric pCO_2 and carbon isotope composition of atmospheric CO_2 can be ruled out (Leuenberger et al., 1992; Monnin et al., 2001), because the small variation observed in ice cores around that time cannot account for the abrupt change in $\delta^{13}C_{TOC}$ values within 150 years in Laguna Potrok Aike. Nevertheless, increased carbon replenishment from the atmospheric CO_2 due to the extended ice-free summer season should be taken into account as an additional more ^{13}C enriched carbon source compared to the re-utilized CO_2 derived by respiration.

The positive shift in $\delta^{13}C_{TOC}$ values of bulk sediment could have been caused, however, also by an increased contribution of aquatic macrophytes which are able to use HCO_3^- as inorganic carbon source thus showing high $\delta^{13}C_{TOC}$ values of about −13‰ to −15‰ (Mayr et al., 2009; Zhu et al. unpublished data). This argument is supported by the massive occurrence of pollen from the aquatic macrophyte *Myriophyllum* in Laguna Potrok Aike within this time window (Wille et al., 2007). A simultaneous drastic rise in TOC/TN above 15 also adds to the argument of a massive increase in organic matter sources from aquatic macrophytes. The abundance of aquatic macrophytes in the lake could be favoured by calm wind conditions during that period, because strong wind-induced currents and waves would strongly hamper or even destroy macrophytes growing in the littoral zone. Comparably calm or absent winds would, in combination with the warming, also permit thermal stratification of the lake during summer months favouring not only macrophyte but also phytoplankton growth. According to Talbot and Lærdal (2000), TOC/TN data would also react on restrictions in the availability of dissolved nitrogen for photosynthesis. It could thus not be ruled out that nitrogen deficiency might partly cause the high TOC/TN ratios of algal organic matter (Healey and Hendzel, 1980), considering nitrate as the probable limiting factor in present Laguna Potrok Aike (Zolitschka et al., 2006).

Compared to the large one-step increase in $\delta^{13}C_{TOC}$ values at around 17,300 cal. years BP, TOC as well as TN contents responded to deglacial warming in two steps. The first steep rise occurs concurrent with the $\delta^{13}C_{TOC}$ increase, however, after about 500 years, at around 16,800 cal. years BP, a second steep rise in TOC and TN values took place. In view of the relatively smooth changes in sedimentation rates during the transition from phase 1 to phase 2 indicated by the applied age–depth model (Kliem et al., 2013b), the shift in TOC and TN contents should be mainly controlled by the amount of deposited and preserved organic matter itself. The $\delta^{13}C_{TOC}$ values record the immediate response of lake primary productivity to the improvement of growth conditions in the lake which however may not simultaneously generate a proportional high amount of buried sedimentary organic matter. Lehmann et al. (2004a) have shown that $\delta^{13}C_{TOC}$ values are more coupled with lake primary productivity per water volume and not necessarily correlate with total primary production. According to that, increased algal productivity and accompanying more biomass per water volume can result in a thinning of the trophogenic zone due to a reduction in light penetration. Thus, there could be a still relatively low level of total algal production during this time. After several hundred years, continuous lake algal production combined with increased contribution of aquatic macrophytes could cause increased organic matter accumulation and cause the high sedimentary TOC and TN contents.

The declined $\delta^{15}N_{TN}$ values on the onset of phase 2 appear to contrast with enhanced lake primary productivity and accompanying high nitrate utilization with progressively enrichment of ^{15}N in the organic matter (Teranes and Bernasconi, 2000). However, Hodell and Schelske (1998) have reported that on the seasonal scale a decrease in $\delta^{15}N$ values is associated with phytoplankton blooms and coincides with an increase in $\delta^{13}C_{TOC}$ values. Furthermore, nitrogen isotope composition of bulk organic matter in lake sediments is also controlled by other factors like $\delta^{15}N$ values of dissolved inorganic nitrogen (internal and external source), change in algal assemblages and selective preservation of isotopically distinct fractions of organic matter (Talbot and Lærdal, 2000; Talbot, 2001; Lehmann et al., 2004b). A depletion of ^{15}N observed for anaerobic incubations has been attributed to the selective loss of ^{15}N-enriched organic matter and possible addition from ^{15}N-depleted bacterial biomass (Lehmann et al., 2002). However, a geomicrobiological study of Laguna Potrok Aike sediments shows that such microbial processes have mainly secondary effects without distorting paleoenvironmental signals contained in organic proxies of bulk sediments (Vuillemin et al., in review). Abruptly increased lake productivity since around 17,300 cal. years BP could cause anaerobic hypolimnic conditions in the deep basin for several months, while the extensive wind-generated circulation might still be absent due to ice cover. The increased assimilation of isotopically light ammonium (NH_4^+) derived from organic matter degradation can be another reason for the reduction in the nitrogen isotope composition of bulk organic matter at the beginning of phase 2. Since 16,800 cal. years BP bulk organic matter became slowly enriched in ^{15}N indicating probably declined assimilation of isotopically light nitrogen and/or better preservation of ^{15}N-enriched organic matter.

A previous study of Laguna Potrok Aike sediments based on an isotopic mixing model has inferred that at a depth comparable to the onset of phase 2 cyanobacteria were dominant in bulk sediment organic matter with about 52% (Mayr et al., 2009). Regarding this interpretation, the decrease in $\delta^{15}N$ values, increase in $\delta^{13}C_{TOC}$ values and, in particular, the still relatively low TOC/TN ratios between 17,300 and 16,800 cal. years BP could also be explained by cyanobacterial organic matter which shows a mean carbon and nitrogen isotope composition of −21.8‰ and −0.3‰, respectively, in recent samples (Mayr et al., 2009). The dominance of cyanobacteria can be attributed to the ability to fix molecular nitrogen (nitrogen-fixing species) in lakes with nitrogen limitation and the competitive ability to uptake ammonium-nitrogen (non-nitrogen-fixing species) in lakes with nitrate depletion (Blomqvist et al., 1994). Since phosphorous supply might be unlimited in Laguna Potrok Aike due to the characteristics of the regional geology (Zolitschka et al., 2006), the high phosphorous concentration in lake water could favour the occurrence of cyanobacteria (Downing et al., 2001; Wagner and Adrian, 2009). Probably decreased nitrate availability being concurrent with abruptly increased primary productivity might then promote cyanobacteria species using ammonium-nitrogen. Considering our present isotopic data and TOC/TN ratios, however, the proportion of cyanobacterial organic matter with about 52% estimated by the isotopic mixing model in Mayr et al. (2009) appears to be high. Because the factors causing the dominance of cyanobacteria in lakes can be diverse and depend also on the respective environment and the species involved (Dokulil and Teubner, 2000), a better understanding of cyanobacteria development in Laguna Potrok Aike needs further investigations.

Beginning with a shift of all proxy parameters, the lake reached a new state with the warming-induced increase in lacustrine primary productivity. However, the water of Laguna Potrok Aike in the late Glacial was still cool, clear and fresh, as inferred by the microfossil record showing the abundance of the diatom *Cyclostephanos patagonicus* and the chlorophyte *Pediastrum kawraiskyi* (Wille et al., 2007;; Massaferro et al., 2013). Although additional nutrient supply may be low due to the still sparse vegetation cover in the catchment, a lake with long-term low primary productivity under full glacial conditions could retain a certain nutrient reservoir being probably sufficient for such warming-induced blooms of algae with low nutrient demand. It is, however, unclear, if the general high algal productivity during phase 2 is linked to the improved nutrient supply from the catchment (increased terrestrial productivity and nutrients leaching through soil columns because of permafrost thawing) and/or to enhanced recycling in the lake (shortened ice cover period).

Besides two samples at around 15,800 cal. years BP that may contain moss debris, TOC, TN contents and TOC/TN ratios tend to decrease from 16,000 to 15,000 cal. years BP. The onset of this shift is simultaneous with the occurrence of an about 1.5 m thick Reclús tephra layer. It is well known that a strong volcanic eruption event has climatic impact on an annual scale (Litt et al., 2003). Considering the decadal resolution of the samples and the duration of the decrease (about 1000 years), it is unlikely that the Reclús eruption caused this development. A similar large reduction in TOC and TN contents also occurs within the period from 14,200 to 13,500 cal. years BP, however, without an obvious decline in TOC/TN ratios. Because of the independent change in carbon isotope compositions (Fig. 6), both large reductions in TOC and TN contents may not be mainly caused by changes in lacustrine primary productivity, but could be controlled by variations in redox and preservation conditions in bottom waters (e.g. Melles et al., 2007). Nevertheless, it seems to be unlikely that the large TOC variation of up to 8% is only derived from a shift in the oxic-anoxic conditions. The concentration of organic matter in lake sediments is also determined by the proportion of the clastic fraction which can dilute the organic fraction in weight percentage (e.g. Veres et al., 2009). During the periods from 16,000 to 15,000 cal. years BP and from 14,200 to 13,500 cal. years BP such a dilution effect may be the case. XRF data by Jouve et al. (2013) show relatively high Si contents (kcps), interpreted as an indicator of detrital input, in both periods, but low Si values in the adjacent periods with high concentrations of organic matter.

5.4. Phase 3 (13,000–10,970 cal. years BP)

Decreasing TOC/TN ratios in phase 3 are likely caused by a reduced proportion of aquatic macrophyte organic matter probably suggesting increasing wind-induced waves on the lake. The progressive decline in $\delta^{13}C_{TOC}$ values could give another indication of the resulting decrease in gross lake algal productivity. However, strong waves in the lake can decrease resistance of CO_2 diffusion and encourage discrimination against ^{13}C in aquatic plants which in turn would lead to organic matter more depleted in ^{13}C than during calm phases (Osmond et al., 1981; O'Leary, 1988; Keeley and Sandquist, 1992). In addition, strong mixing and continuous upwelling of ^{13}C depleted CO_2 to the photic zone can replenish the DIC pool of surface water and prevent enrichment in ^{13}C of lacustrine produced organic matter. Similar effects would be induced by increasing the input of dissolved remineralized ^{13}C depleted soil carbon dioxide, as respiration processes in the catchment intensify due to increased terrestrial productivity over the course of deglaciation warming. The hypothesis about the decrease in lake primary productivity of both algae and aquatic macrophytes can be partly supported by the decline in TOC and TN contents, although a dilution effect by clastic material can still be effective as inferred from contemporaneously elevated Si contents (kcps) (Jouve et al., 2013).

Based on the tendency and variation range of TOC, TN, TOC/TN and $\delta^{13}C_{TOC}$ values, similarities with phase 2 are high and phase 3 may be merely seen as a prolonged transition to the next phase 4, when the lake reaches a reduced nutrient level after the maximum of lacustrine productivity in the early phase of the late Glacial.

5.5. Phase 4 (10,970–8400 cal. years BP)

Lower TOC/TN ratios below 10 may reflect predominant organic matter origin from algae. The absence of the signature of aquatic macrophytes can suggest the persistence of strong wind conditions since phase 3. Lower $\delta^{13}C_{TOC}$ values could be induced by the rapid and continuous replenishment of the DIC pool due to strong mixing of the whole water column preventing enrichment in ^{13}C of algal organic matter. Accompanied by the low TOC and TN contents, ^{13}C depleted algal organic matter could indicate low primary productivity of the lake during this phase. Strong mixing occurring in the whole water column can also give rise to fast degradation of organic matter resulting in the low concentration of organic fraction in sediments. Increased $\delta^{15}N_{TN}$ values since the last phase could be caused by limitations in nitrate availability (Hodell and Schelske, 1998; Jones et al., 2004) which might have been exhausted during the early bloom phase of the lake. Extremely high $\delta^{15}N_{TN}$ values at round 8400 years BP can be the consequence from the high input of ^{15}N enriched soil organic matter during a period with a very low lake level (Haberzettl et al., 2007; Mayr et al., 2009; Kliem et al., 2013a).

5.6. Inter-phase relations

Phase 1 with low productivity under LGM conditions is clearly distinct from the later phases with high and variable productivity (Fig. 5). Deglacial warming and improved growth conditions led to a distinct and large shift of lake productivity of both algae and aquatic macrophytes from phase 1 to phase 2 as there was possibly a relatively sufficient nutrient reserve in Laguna Potrok Aike directly after the glacial phase with little consumption. The primary productivity in Laguna Potrok Aike reached its maximum at around 14,000 cal. years BP during phase 2 (Fig. 6). Simultaneously, nutrient availability, particularly nitrate, could likely start to become reduced with persistent enhancement in the primary productivity. After phase 2, lake primary productivity declined progressively documented by the overall positive relation between $\delta^{13}C_{TOC}$ values and elemental parameters like TOC, TN contents and TOC/TN ratios (Fig. 5). Under conditions of nitrate limitation, diminished discrimination against ^{15}N by algal assimilation can result in ^{15}N enriched algal organic matter. This factor may explain the negative relation between carbon and nitrogen isotope compositions over the course of the late Glacial and the early Holocene (Fig. 5, upper left).

5.7. Regional and global context

The timing of the onset of the last deglacial warming in the southern hemisphere is illustrated in Antarctic ice cores and Southern Ocean sediments at around 17,000–19,000 cal. years BP (Sachs et al., 2001; EPICA, 2006; Jouzel et al., 2007; Lamy et al., 2007). Moraine records (e.g. McCulloch et al., 2005; Sugden et al., 2005; Kilian et al., 2007; Kaplan et al., 2008) and palynological evidences from peat bog records in South Patagonia (e.g. McCulloch and Davies, 2001; Markgraf and Huber, 2010) have confirmed the terrestrial response to the initial warming signal that also caused an increase in bio-productivity and the shift from phase 1 to phase 2 in Laguna Potrok Aike. McCulloch et al. (2000) suggested two steps of deglacial warming influencing southern South America at 17,600 and 11,400 cal. years BP. Since in southern Patagonia temperature changes primarily control effective moisture (Markgraf and Huber, 2010), which has in turn large impact on the lake-system, both steps can be associated with changes in primary productivity in Laguna Potrok Aike at the onset of phase 2 and phase 4, respectively. A warming induced poleward shift of the southern westerlies could take several thousand years to reach their latitudes of the present day centered on 50° S (McCulloch et al., 2000), thus causing the windier conditions since 13,000 cal. years BP in the Laguna Potrok Aike area. The Antarctic Cold Reversal that is well recorded in Antarctic ice cores (e.g. Stenni et al., 2011) is not evident in our lake sediment geochemical archive. The algal productivity in late-Glacial Laguna Potrok Aike appears to be mainly controlled by nutrient availability as long as temperature was not low enough to influence the primary producers substantially. However, more investigations particularly comparisons with other proxies in Laguna Potrok Aike are needed to gain a better understanding, especially of the connection between the lake response and the Antarctic signal.

6. Conclusions

Based on high-resolution measurements of the TOC, TN contents, TOC/TN ratios, $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ values from bulk sediments (<200 μm) of Laguna Potrok Aike, insights into the paleoenvironment in southern Patagonia during the last Glacial–Interglacial transition are provided. Under full glacial conditions, from ca 26,000 to 17,300 cal. years BP, the lake had a very low primary productivity with a dominant organic matter source from lake algae. At around 17,300 cal. years BP, the lake underwent a rapid reorganization and lacustrine primary productivity increased and remained high during most of the deglaciation until 13,000 cal. years BP as the nutrient supply was still high. The main causes for this development were interpreted as improved growing conditions for primary producers in the lake because of deglacial warming and possible calm wind conditions that might have led to partial thermal summer stratification of Laguna Potrok Aike. This favoured the growth and production of aquatic macrophytes that would have made an important contribution to the sedimentary organic matter. The variations of most proxy parameters are obviously larger during deglaciation than in the LGM suggesting lake and environment instability during this transitional period. Since around 13,000 cal. years BP, the lake appeared to approach a new state with deteriorated growing conditions for all primary producers. This development was likely caused by windier conditions and insufficient nutrient (nitrate) availability probably due to the low regeneration of nutrients in the lake after its exhaustion during the early phase with high primary productivity. This tendency continued into the early Holocene and primary productivity was comparably low but remained on a stable level until around 8400 cal. years BP.

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