

Climate, catchment runoff and limnological drivers of carbon and oxygen isotope composition of diatom frustules from the central Andean Altiplano during the Lateglacial and Early Holocene

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Abstract

Diatom-based carbon and oxygen isotope analyses ($\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$) were performed on diatom-rich laminated sediments of Lake Chungará (Andean Altiplano, northern Chile) deposited during the Lateglacial and Early Holocene (12,400–8300 cal years BP) to reconstruct climate change and environmental response across this major climate transition. The $\delta^{13}\text{C}_{\text{diatom}}$ data show both centennial-to-millennial scale changes related to fluctuations in lake productivity and CO_2 concentration in the lake water, and variations in carbon sources to the lake through time. The $\delta^{18}\text{O}_{\text{diatom}}$ data reflect changes in lake hydrology and climate. The combination of $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ data reveals interactions between the internal lake processes and its catchment runoff. During wet periods (low $\delta^{18}\text{O}_{\text{diatom}}$ values) $\delta^{13}\text{C}_{\text{diatom}}$ indicates an enhanced contribution of allochthonous carbon, whereas during dry periods (high $\delta^{18}\text{O}_{\text{diatom}}$) $\delta^{13}\text{C}_{\text{diatom}}$ values suggest more autochthonous carbon production and recycling. These decadal-to-centennial oscillations are not recognized after 10,000 cal years BP, possibly as a result of ENSO-like phenomenon weakening. Humid conditions during the Lateglacial–Early Holocene transition (12,400–10,100 cal years BP) were possibly due to the establishment of La Niña-like conditions in the tropical South Pacific. Whereas, dry conditions in the Early Holocene (10,100–9100 cal years BP) may be caused by the northward migration of the ITCZ due to both ENSO-like weakening and an insolation minimum. Finally, a return to humid conditions at the end of the Early Holocene (9100–8300 cal years BP) is coincident with an increase in summer insolation.

Keywords: Carbon isotopes; Oxygen isotopes; Diatoms; Lake productivity; Andean Altiplano; Palaeoclimate

Highlights

- First $\delta^{13}\text{C}_{\text{diatom}}$ record from South America and only the third ever from a lake.
- First to look at decadal scale changes in the lake carbon cycle.
- Adds to growing understanding of $\delta^{13}\text{C}$ in a lake with authigenic carbonate.
- Coupling of carbon cycle to palaeohydrology with links to ENSO.
- Laminated sediments show that carbon supply and demand can change rapidly.

1. Introduction

Lakes play an important role in the contemporary global carbon cycle, potentially affecting regional climate and global change (Cole et al., 2007; Tranvik et al., 2009) and may be expected to have had significant, yet variable influence in the past. Conversely, climate variability is a major driver of the carbon cycle in lakes and operates at a variety of temporal scales. At the millennial scale, climate forcing of landscape processes will dominate (Street-Perrott et al., 2007), whereas at the annual scale ecological variability are expected to be dominant (Cole et al., 2007). Much less is known about the relationship between climate and carbon biogeochemical cycling at the decadal-to-century scale yet this time scale is critical in understanding future global change.

Fundamental information on the carbon cycle of lakes can be derived from long-term studies performed on carbon held within their sedimentary records (e.g. Ficken et al., 1998; Filippi and Talbot, 2005). Shifts in carbon isotope composition of bulk organic matter ($\delta^{13}\text{C}_{\text{bulk}}$) in sediment records have been used to infer past productivity changes (e.g. Brenner et al., 1999). Photosynthetic aquatic organisms preferentially use the lighter ^{12}C and this can become depleted in the water if lake productivity is high, causing a positive shift in $\delta^{13}\text{C}$ carbon pool (Meyers and Lallier-Verges, 1999; O'Reilly et al., 2003). Using $\delta^{13}\text{C}$ to reconstruct aquatic productivity must assume that no change occurred in the type or amount of particulate carbon entering the lake from terrestrial plants (C3 or C4 type), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) from weathering of minerals and catchment soils. However, the stable isotope signature from algae is widely variable between species and habitats (Hecky et al., 1973; Hecky and Hesslein, 1995). In addition, algae

usually have $\delta^{13}\text{C}$ values similar to those of C3 higher plants, making difficult to determine whether changes $\delta^{13}\text{C}_{\text{bulk}}$ are triggered by photosynthetic aquatic productivity or higher plant communities. Thus, $\delta^{13}\text{C}_{\text{bulk}}$ is very much dominated by source effects, to such an extent that the nature of the carbon available to the lower levels of food webs is often masked.

One way to overcome the problem of the heterogeneous nature of sedimentary organic carbon is by investigating it in single ubiquitous photosynthetic organisms such as diatoms (Hurrell et al., 2011). Diatom frustules contain polysaccharides and proteins enclosed within the silica cell wall structure (Kroger and Polusen, 2008). This organic matter (OM) is protected by silica of the diatom frustules against diagenetic processes that might affect the sediments and mixing with the bulk sediment carbon pool (Des Combes et al., 2008). This OM can be analysed for carbon isotopes ($\delta^{13}\text{C}_{\text{diatom}}$) and reflect the original signal taken from dissolved carbon in the water during the diatom cell formation. This method has been used in marine environments (e.g. Singer and Shemesh, 1995; Rosenthal et al., 2000; Crosta and Shemesh, 2002; Schneider-Mor et al., 2005). However, the $\delta^{13}\text{C}_{\text{diatom}}$ is a new technique in lacustrine sediments (Hernández et al., 2011; Hurrell et al., 2011; Barker et al., 2012) where the complexity of sedimentary conditions, such as the existence of different carbon sources and highly dynamic aquatic food webs, raise further questions of interpretation (Hurrell et al., 2011). In lakes, $\delta^{13}\text{C}_{\text{diatom}}$ values should be the balance between the $\delta^{13}\text{C}$ of the source of the carbon used by the diatoms and the consumption of ^{12}C by primary biological producers.

The palaeoenvironmental changes revealed by $\delta^{13}\text{C}_{\text{bulk}}$ in lake sediments are often related to variations in lake hydrology and regional precipitation (Heikkilä et al., 2010) at various

temporal scales. To disentangle the relative importance of these signals it is necessary to use independent proxy data. Variations in the regional precipitation can be revealed from the oxygen isotope composition ($\delta^{18}\text{O}$) of carbonate or diatom silica (Ito, 2001; Leng and Marshall, 2004). In lakes with low carbonate content palaeoclimate information can be obtained from the oxygen isotope composition of diatom silica ($\delta^{18}\text{O}_{\text{diatom}}$). If diatom silica is precipitated in isotope equilibrium with the lake water, then silica–water fractionation equations may be used to estimate variations in past lake water temperatures providing there is no change in the isotope composition of the lake water (Leng and Marshall, 2004). A thorough understanding of the factors that may have influenced the isotope composition of the lake water is necessary to correctly interpret the $\delta^{18}\text{O}$ signal from the analysed diatom silica. The $\delta^{18}\text{O}_{\text{diatom}}$ values in hydrologically-open lakes usually reflect the isotope composition of precipitation, both rain and snowfall, received by the lake; whereas oscillations of $\delta^{18}\text{O}_{\text{diatom}}$ in closed lakes respond predominantly to the precipitation/evaporation balance (P/E) (Leng and Barker, 2006). As a consequence, $\delta^{18}\text{O}_{\text{diatom}}$ studies in lacustrine sediments have increased in recent years (e.g. Hu and Shemesh, 2003; Rosqvist et al., 2004; Swann et al., 2010; Barker et al., 2011). However, palaeoenvironmental reconstructions based on the combined use of $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ are still rare.

Recent palaeoenvironmental studies conducted at Lake Chungará (Andean Altiplano, northern Chile) described the sedimentological and environmental evolution of the lake during the last ca 14,000 cal years BP (Valero-Garcés et al., 2003; Sáez et al., 2007; Moreno et al., 2007; Giralt et al., 2008; Pueyo et al., 2011; Bao et al., submitted for publication). These studies provide supporting data to test hypothesised relationships between $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ signals and biogenic productivity, carbon cycling, and its relationship with the P/E balance in this tropical region of South America during the Lateglacial and Early Holocene (12,400–8300 cal years BP). Studies based on $\delta^{18}\text{O}_{\text{diatom}}$ and some preliminary $\delta^{13}\text{C}_{\text{diatom}}$ analysis, using a lamina by lamina sampling, explored the possibilities that this kind of studies can offer in palaeoenvironmental reconstructions (Hernández, 2010). As a result,

ultra-high resolution environmental and climate reconstructions in the Andean Altiplano during the Lateglacial–Early Holocene transition (12,000–11,500 cal years BP) were established for the pure diatomaceous ooze intervals, also offering insights into processes generating laminated sediments (Hernández et al., 2010, 2011). In addition, a lower resolution study, using $\delta^{18}\text{O}_{\text{diatom}}$, highlighted the importance of reconstructing the different evolutionary stages of lake ontogeny given that climate derived palaeohydrological signals can be distorted by changes in lake basin morphology (Hernández et al., 2008).

Here we discuss and interpret the processes affecting $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ signals on the palaeoenvironmental evolution of this lake. For the first time we analyse the laminated sediments of this lake to understand the interaction of the carbon cycle and the hydrological cycle at decadal resolution as well as longer term trends. In addition, the comparison of $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{bulk}}$ here enables possible biological and environmental controls on $\delta^{13}\text{C}$ to be recognized, further aiding our knowledge of the sedimentary legacy of carbon cycling in lakes.

2. Lake Chungará setting

2.1. Climate and limnology

Lake Chungará (18°15'S, 69°10'W, 4520 m asl) is located at the northeastern edge of Lauca Basin on the Andean Altiplano (Central Andes, northern Chile), in the boundary between Bolivia, Chile and Perú. This basin is the westernmost and highest fluvio-lacustrine basin of the Altiplano and lies in a highly active tectonic and volcanic context (Hora et al., 2007).

The climate around Lake Chungará is dominated by arid conditions due to the influence of the South Pacific Anticyclone. Annual rainfall ranges from 100 to 750 mm year⁻¹ (mean 411 mm year⁻¹) (Valero-Garcés et al., 2000). At present, the seasonal precipitation cycle over South America is dominated in tropical latitudes by the so-called South American Summer Monsoon (SASM) (Zhou and Lau, 1998). Precipitation over the Andean Altiplano originates primarily from the Atlantic Ocean, and humidity is advected into the Amazon Basin by the north-easterly SASM which is associated with the Inter

Tropical Convergence Zone (ITCZ) (Zhou and Lau, 1998; Vuille and Werner, 2005). It is then transported further south along the eastern slopes of the Andes by the South American Low Level Jet. Ultimately, upper-tropospheric easterly anomalies which are modulated by Pacific sea-surface temperatures transport the humidity to the Cordilleras and onto the Altiplano (Garreaud et al., 2003). A significant amount of interannual variability in the Altiplano precipitation is related to the state of the ENSO system (Garreaud and Aceituno, 2001), indeed the instrumental data from the Chungará area shows a trend to dry conditions during the ENSO-like warm phase (El Niño years) and wet conditions during the ENSO-like cold phase (La Niña years) (Valero-Garcés et al., 2003). The isotope composition of rainfall in the Central Andes is characterised by a large variability in $\delta^{18}\text{O}$ (between +1.2 and -21.1‰) and of δD (between +22.5 and -160.1‰). The origin of the lowest oxygen isotope composition of precipitation is the strong fractionation in the air masses from the Amazon and it is directly related to higher rainfall intensity ('amount effect') (Herrera et al., 2006). The oxygen isotope composition of rainfall in the Chungará region oscillates between -14‰ and -20‰, with a mean value of -14.3‰ (Herrera et al., 2006).

The lake has an irregular shape, with a surface area of 21.5 km², maximum water depth of 40 m and a water volume of ca 400 hm³ (Herrera et al., 2006) (Fig. 1). At present, the main inlet to the lake is the Chungará River (300–460 l s⁻¹), although secondary streams enter the lake in the south-western margin. Evaporation is the main water loss ($3 \cdot 10^7$ m³ year⁻¹). There is no surface outlet, but groundwater outflow ($6\text{--}7 \cdot 10^6$ m³ year⁻¹, Dorador et al., 2003) represents about 20% of the total loss. The calculated residence time for the lake's water is approximately 15 years (Herrera et al., 2006). The $\delta^{18}\text{O}$ and δD composition of the lake water diverges from the Global Meteoric Water Line and the Regional Meteoric Line, and is attributed to the enrichment of the lake water by evaporation (Herrera et al., 2006). The mean lake water $\delta^{18}\text{O}$ and δD values are -1.1‰ and -39.2‰, respectively (Herrera et al., 2006; Pueyo et al., 2011).

The atomic C/N ratio of recent biomass in Lake Chungará yields values between 40 and 80 for land plants, between 4 and 25 for aquatic plants, and around 9 for plankton (Pueyo et al., 2011). The carbon isotopic composition of plants yields values of around -25‰ for land plants, between -10 and -4‰ for aquatic plants, and -13‰ for mixed plankton (Pueyo et al., 2011). These latter $\delta^{13}\text{C}$ values are higher than those commonly attributed to plankton (Meyers, 2003) and are related to high DIC- $\delta^{13}\text{C}$ values (+4‰) measured in the recent lake water (Pueyo et al., 2011). The $\delta^{13}\text{C}_{\text{bulk}}$ values from offshore sediments (-17‰ in the more recent to -22‰ in the oldest sediments), together with C/N ratios between 8 and 17 (12.7 in average), reflect the algal contribution to the total organic matter in these sediments (Meyers and Teranes, 2001). Pueyo et al. (2011) considered that organic matter in offshore sediments of Lake Chungará was mainly derived from phytoplankton and $\delta^{13}\text{C}_{\text{bulk}}$ values reflected the organic provenance (phytoplankton vs. macrophytes and land plants) and changes in productivity.

2.2. Sedimentary record

Stratigraphy and facies associations for the uppermost part of the Lake Chungará sequence were established through fifteen Kullenberg cores and seismic imagery (Sáez et al., 2007; Bao et al., submitted for publication). From the bottom to the top of the core, two sedimentary units (Units 1 and 2) were identified and correlated over the offshore zone of the lake mainly using tephra marker horizons (Fig. 1). Unit 1 is made up of laminated diatomaceous ooze with carbonates and amorphous OM. A petrographical study established a depositional rhythmite type for those sediments where rhythmites are composed of variable-thickness triplets of white, light- and dark-green laminae (Hernández et al., 2011). Unit 2 is composed of brown diatomaceous ooze with abundant tephra layers. Detailed stratigraphical and geochemical data are provided in earlier publications (Moreno et al., 2007; Sáez et al., 2007; Giralt et al., 2008; Pueyo et al., 2011). A lithological correlation of cores 10 and 11 was performed, obtaining a composite core representing the whole sedimentary infill of the offshore zone (minimum thickness of 10 m) (Sáez et al., 2007). From here on, all core depths refer to the composite core. The

chronological model for the complete sedimentary sequence of Lake Chungará is based on 17 AMS ^{14}C dates of bulk OM and aquatic plant macrofossils, and one $^{238}\text{U}/^{230}\text{Th}$ date from carbonates. The studied section included 8 radiocarbon dates (Table 1). All radiocarbon dates were corrected for present-day reservoir effect and calibrated using the INTCAL 98 curve (see Giralt et al. (2008) for further details).

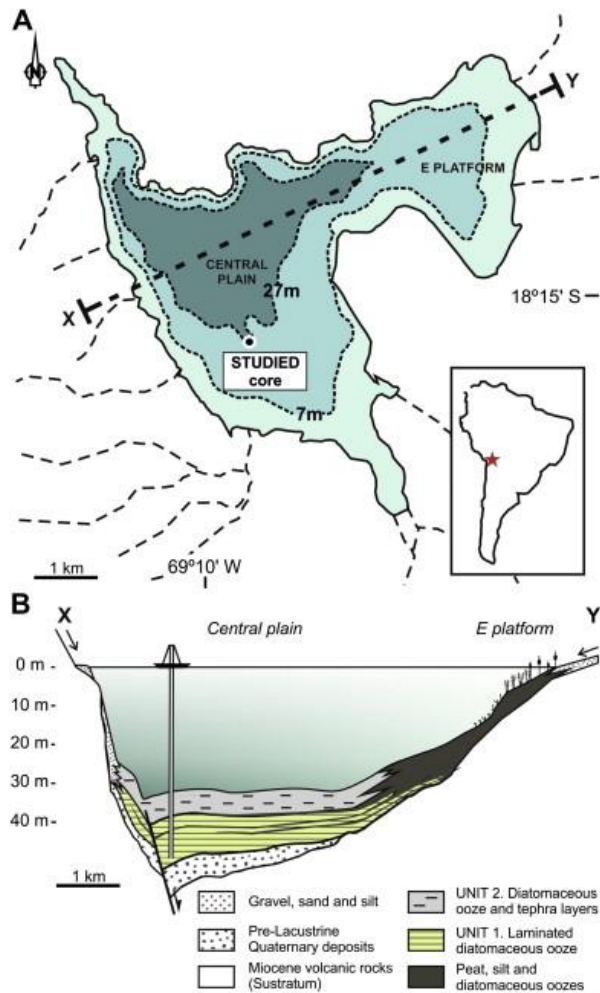


Fig. 1. (A) Bathymetric map of Lake Chungará showing the position of the core. Black dashed line indicates the cross-section throughout the lake. (B) Cross-section of sediment infilling of Lake Chungará. Position of the core is shown; note that the core is projected in its equivalent position at the lake central plain. Arrows indicate major hydrological inputs and sedimentary contributions to the lake. Simplified from Sáez et al. (2007).

3. Materials and methods

This study is based on the laminated sediments from the offshore zone of Lake Chungará (Fig. 1).

Previous $\delta^{18}\text{O}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{diatom}}$ analyses were undertaken on the laminated unit from the same core (Hernández et al., 2008, 2010, 2011) using a lamina by lamina sampling (temporal resolution <10 years). By contrast, the whole core (12,400–1300 cal years BP) was sampled at approximately 10 cm intervals for the present work giving a mean temporal resolution of 125 years. A total of 88 samples with around 100 mg of bulk-dried sediment were processed. Samples were treated following the four clean-up stage method proposed by Morley et al. (2004) with some variations (Hernández et al., 2008). The cleaning process removed small diatom taxa, including the periphytic species, and resulted in monospecific or quasi-monospecific samples dominated by *Cyclotella andina* (diameter 40–60 μm) (Fig. 2). This reduced possible interspecific variability in the isotope data (Leng and Barker, 2006). The purity of the samples was checked using light and scanning electron microscopy, and samples containing <98% of diatom silica were also treated by ignition in air at 550 $^{\circ}\text{C}$ (cf Tyler et al., 2007). Even so, some samples were not deemed pure enough for isotope analysis (Fig. 2). Hence, only samples containing >98% diatom silica ($n = 52$) were analysed and these all came from the laminated unit (Unit 1) representing the Lateglacial and Early Holocene (12,400–8300 cal years BP) with a new mean temporal resolution of 80 years.

Both $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ analysis were undertaken at the NERC Isotope Geosciences Laboratory (UK). Samples containing 1–2 mg of cleaned diatoms were analysed for the carbon isotope composition of occluded OM and %C within the diatom frustules. The analyses were performed using an elemental analyser (Costech ECS4010) interfaced with a VG dual inlet isotope ratio mass spectrometer (see Hurrell et al., 2011 for details). Samples were measured against a within-run laboratory standard (BROC) and $^{13}\text{C}/^{12}\text{C}$ ratios were converted into $\delta^{13}\text{C}$ values versus Vienna Pee Dee Belemnite (VPDB). Replicate analysis of well-mixed samples indicated a precision of $+<0.1\text{‰}$ (1σ) (for $\delta^{13}\text{C}$) and 0.1 (1σ) (for %C).

Table 1.AMS ^{14}C dates from the studied section (Modified from Giralt et al. (2008)).

Composite depth (cm)	Lab ID	Sample reference	Sample material	Uncalibrated ^{14}C (years BP)	Calibrated age ^a (calendar years BP)	Calibrated age ^b (calendar years BP)	$\delta^{13}\text{C}$ (‰PDB)
490.9	Poz-7170	11 A-3, 123	Bulk organic remains	8570 ± 50	7705 ± 1230	9900 ± 950	-16.8 ± 0.1
550.5	Poz-8647	11 A-4, 10	Bulk organic remains	9860 ± 60	7940 ± 1260	11,290 ± 1080	-14.1 ± 0.3
615.2	Poz-7171	11 A-4, 63	Bulk organic remains	11,070 ± 70	8270 ± 1400	12,490 ± 910	-13.6 ± 0.2
665	AA56905	15 A-5, 77	Aquatic plants	4385 ± 101	–	–	–
675	Poz-8725	13 A-4, 66	Bulk organic remains	8810 ± 50	–	–	-22.9 ± 0.1
696.2	Poz-11891	11 A-4, 145.5	Bulk organic remains	11,460 ± 60	8765 ± 1420	13,120 ± 930	-16.2 ± 0.4
744.2	Poz-13032	11 A-5, 41	Bulk organic remains	10,950 ± 80	9080 ± 1540	13,290 ± 910	-22.7 ± 2.3
785.2	Poz-11982	11 A-5, 84	Bulk organic remains	11,180 ± 70	9400 ± 1740	13,605 ± 880	-28.7 ± 3.7
827.2	Poz-13033	11 A-6, 41	Bulk organic remains	12,120 ± 80	9730 ± 2090	14,155 ± 1390	-19.6 ± 1.7
865.2	Poz-7169	11 A-6, 79	Bulk organic remains	13,100 ± 80	10,040 ± 2640	14,795 ± 1760	-23.1 ± 0.2

Bolded radiocarbon dates were not taken into account in the construction of the chronological framework in Giralt et al. (2008).

a Constant reservoir effect of 3260 years throughout all the sequence.

b No reservoir effect correction for the radiocarbon dates of lithological Unit 1.

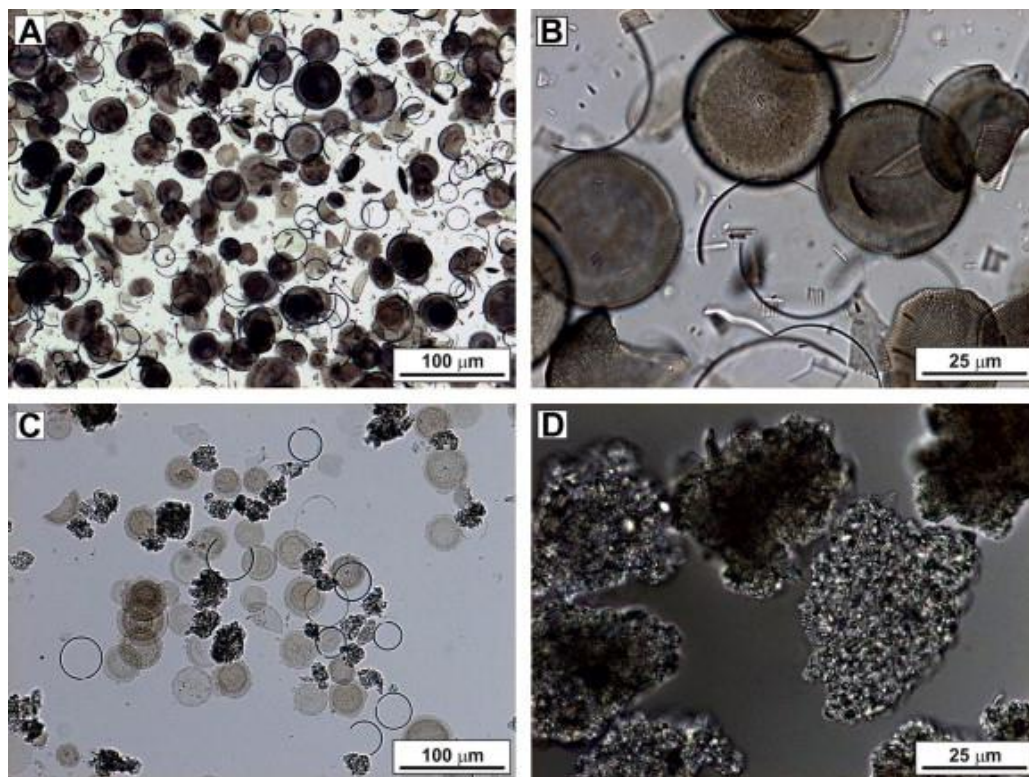


Fig. 2. (A) and (B) Light microscope images of cleaned samples from the laminated unit (Unit 1). The images show valves of *Cyclostephanos andinus* as a unique component at 100× and 400×, respectively. (C) Light microscope image (100×) of a cleaned sample from the non-laminated unit (Unit 2). Note the presence not only of valves of *C. andinus*, but also tephra, organic matter and diatom frustule aggregates. (D) Light microscope image (400×) of tephra, organic matter and diatom frustules aggregates of cleaned sample from the non-laminated unit (Unit 2).

Table 2.
 $\delta^{18}\text{O}_{\text{diatom}}$, $\delta^{13}\text{C}_{\text{diatom}}$ and $\%C_{\text{diatom}}$ data from Lake
 Chungará record. n/a = not analysed.

Sample number	Depth	Age	$\delta^{18}\text{O}_{\text{diatom}}$	$\delta^{13}\text{C}_{\text{diatom}}$	$\%C$
3-095	453.2	8.354	+36.3	-24.6	0.54
3-100	460.7	8.444	+36.7	-25.3	0.42
3-110	473.5	8.595	+38.7	-26.5	0.17
3-115	479.9	8.671	+37.5	-26.2	0.24
3-120	486.3	8.747	+38.8	-25.5	0.29
3-130	499.1	8.913	+38.6	-25.8	0.26
3-135	506.0	9.008	+39.4	-26.4	0.07
3-140	513.0	9.103	+39.0	-24.3	0.44
3-145	521.0	9.211	+39.5	-29.8	0.08
3-149	527.4	9.298	+39.3	-24.3	0.41
4-001	531.0	9.348	+39.6	-24.5	0.22
4-005	539.2	9.459	+39.2	-26.0	0.17
4-010	549.5	9.598	+39.7	-26.7	0.26
4-015	559.7	9.720	+39.8	-27.5	0.09
4-020	569.9	9.842	+40.2	-25.7	0.17
4-025	576.0	9.915	+40.0	-24.0	0.19
4-030	582.1	9.987	+40.1	-23.6	0.27
4-040	592.3	10.108	+40.1	-23.3	0.23
4-045	597.4	10.168	+39.7	-22.6	0.29
4-050	602.5	10.228	+38.3	-22.9	0.42
4-060	612.6	10.349	+39.1	-25.7	0.24
4-070	622.8	10.432	+37.6	-26.8	0.20
4-080	633.0	10.502	+38.2	-27.1	0.20
4-085	638.0	10.538	+38.6	-26.8	0.26
4-090	643.1	10.573	+38.5	-25.9	0.16
4-100	653.3	10.643	+35.8	-24.5	0.24
4-110	663.5	10.714	+37.7	-27.7	0.21
4-120	673.6	10.784	+35.5	-26.8	0.37
4-130	683.8	10.855	+34.7	-27.3	0.37
4-140	693.9	10.925	+37.8	-27.3	0.18
4-147	701.1	10.966	+38.0	-28.0	0.10
5-001	705.1	10.988	+38.0	-25.4	0.21
5-010	714.3	11.037	+39.3	-27.0	0.08
5-015	719.4	11.064	+38.9	-26.0	0.25
5-020	724.4	11.091	+38.0	-26.5	0.24
5-030	734.6	11.145	+37.0	-28.6	0.21
5-040	744.8	11.205	+36.9	-27.9	0.06
5-050	754.9	11.279	+38.1	-26.8	0.04
5-060	765.1	11.354	+37.7	-27.7	0.02
5-070	774.2	11.422	+37.6	-27.3	0.08
5-080	775.3	11.429	+37.9	-26.7	0.08
6-001	790.5	11.558	+35.2	-28.9	0.19
6-002	791.7	11.568	+37.6	-26.6	0.09
6-010	799.7	11.654	+36.9	-26.9	0.07
6-020	809.8	11.760	+38.6	-27.1	0.08
6-030	820.0	11.867	+38.6	-27.2	0.07
6-040	830.2	11.986	n/a	n/a	n/a
6-050	840.3	12.105	+38.2	-27.5	0.02
6-060	850.5	12.232	+38.0	-27.4	0.30
6-062	852.5	12.257	+38.0	-28.6	0.01
6-070	860.7	12.359	+36.9	-30.3	0.16
6-076	863.7	12.396	+37.2	-29.6	0.04

For oxygen isotope analysis, a stepwise fluorination method was applied to 5–10 mg of the purified diatoms (see Leng and Sloane, 2008 for further details). The isotopes were measured on a Finnigan MAT 253 mass spectrometer. Samples were measured against a within-run laboratory standard (BFC) and $^{18}\text{O}/^{16}\text{O}$ ratios converted into $\delta^{18}\text{O}$ values versus VSMOW. A random selection between all the treated samples was analysed in duplicate and (in some cases) in triplicate giving a sample reproducibility between 0.01‰ and 0.6‰ (1σ). The standard laboratory quartz and a diatomite control sample (BFC) had a mean reproducibility over the period of analysis of 0.2‰ and are comparable to other laboratories (Chapligin et al., 2011).

4. Results

Values of $\delta^{13}\text{C}_{\text{diatom}}$ record range from -30.3‰ to -22.6‰ and $\delta^{18}\text{O}_{\text{diatom}}$ values from between +34.7 and +40.2‰ (Table 2). Both proxies show centennial-to-millennial trends punctuated by decadal-to-centennial oscillations between 12,400 and 10,000 cal years BP, whereas since 10,000 cal years BP only long-term trends are present (Fig. 3B).

The $\delta^{13}\text{C}_{\text{diatom}}$ record displays a major positive trend (+8‰) during the Lateglacial–Early Holocene transition (12,400–10,000 cal years BP), however this millennial scale trend shows considerable fluctuations with excursions (mean -2.3‰) to lighter values at ca 12,400, 11,600, 11,200, 10,900 and 10,300 cal years BP (Fig. 3). After 10,000 cal years BP the decadal-to-centennial scale oscillations are no longer present and the record exhibits a long-term decreasing trend (-5‰), from 10,000 to 9600 cal years BP, and a subsequent increasing trend (+3‰) from 9600 to 8300 cal years BP. This increase is however interrupted by a very large reversal (-5‰) at 9200 cal years BP that corresponds to an outlier as it is constituted by only one sample (Fig. 3B). The $\%C_{\text{diatom}}$ values show values of up to 0.54%, with the lowest values occurring at the bottom of the core and slightly increasing towards the top (Table 2).

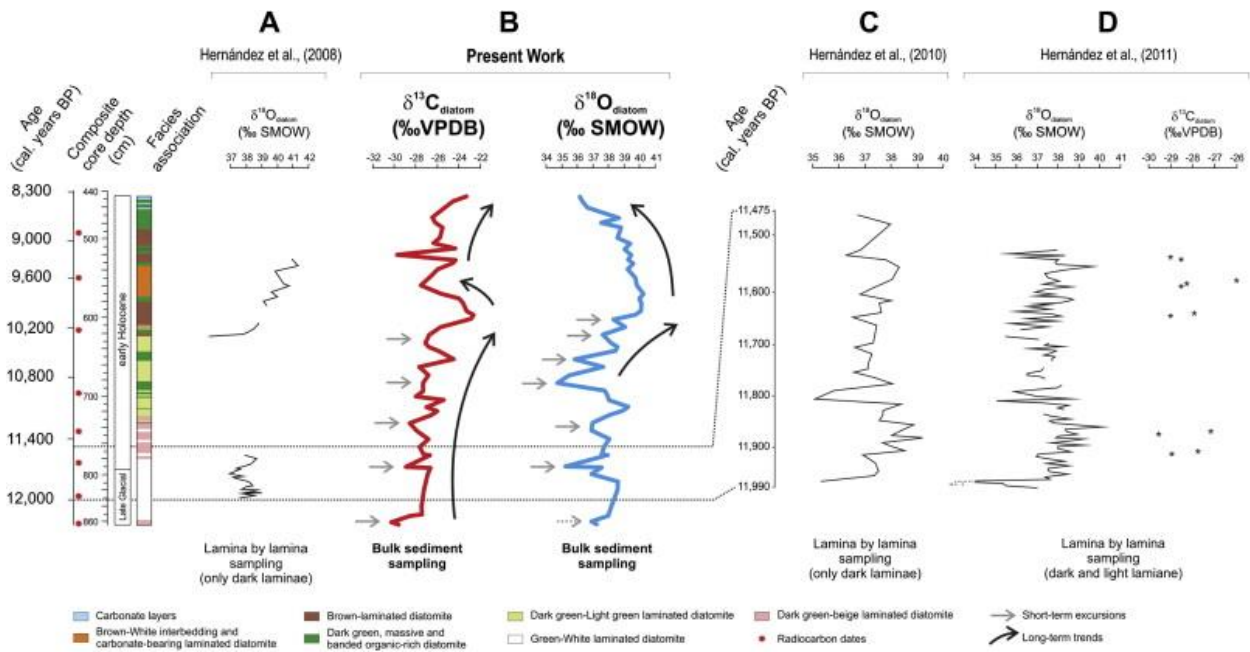


Fig. 3. Facies associations, $\delta^{18}\text{O}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{diatom}}$ data from Lake Chungará laminated sediments. (A) Lago Chungará $\delta^{18}\text{O}_{\text{diatom}}$ data of the green laminae from three intervals representing different hydrological conditions during the Lateglacial and Early Holocene (12,300–9500 cal years BP). These data were obtained from diatoms by lamina by lamina sampling and used to establish the major changes in palaeohydrological evolution of the lake (Hernández et al., 2008). (B) New $\delta^{18}\text{O}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{diatom}}$ records for the period 12,400–8300 cal years BP from the Lake Chungará sedimentary sequence. Black arrows show the main long-term (centennial-to-millennial) trends. Grey arrows indicate the main short-term (decadal-to-centennial) oscillations. Note the absence of short-term variations after 10,000 cal years BP. Data obtained from diatom analysis of bulk sediment sampling are used to show the interaction between in-lake vs runoff and climate processes at a regional scale and at decadal resolution, as well as longer term trends. Data from A and B are plotted against age and depth. (C) $\delta^{18}\text{O}_{\text{diatom}}$ data of all the green laminae from the Lateglacial–Early Holocene transition (12,000–11,500 cal years BP). Data were obtained from diatom analysis by lamina by lamina sampling used to document the moisture balance in the region for this period (Hernández et al., 2010). (D) $\delta^{18}\text{O}_{\text{diatom}}$ data of all laminae (green and white) from the Lateglacial–Early Holocene transition (12,000–11,500 cal years BP). Data obtained from diatom analysis by lamina by lamina sampling used to reveal the biogeochemical processes involved in the laminae formation (Hernández et al., 2011). Data from C and D are plotted against age. Red stars indicate radiocarbon-dated levels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The $\delta^{18}\text{O}_{\text{diatom}}$ values show a long-term increasing trend and up to 6 short-term excursions during the two first millennia (12,400–10,000 cal years BP) which agrees with a previous $\delta^{18}\text{O}_{\text{diatom}}$ study performed in Lake Chungará (Hernandez et al., 2008) (Fig. 3A and B). From 12,400 to 11,000 cal years BP there is no clear long-term trend, but there are two major short-term decreases of -3.4 and -1.2 ‰ in 200 and 70 years, respectively (Fig. 3B). This interval partially coincides with previous higher resolution studies (Hernández et al., 2010, 2011), however the different resolution and sampling methods preclude any possible comparison (Fig. 3B–D). After this, a strong short-term decrease of -4.6 ‰ in 200 years is followed by

a sharp increase ($+5.4$ ‰) during the following 1000 years (11,000–10,000 cal years BP). This trend is punctuated by 3 minor depletions (-2 ‰, -1.4 ‰ and -0.8 ‰) at 10,700, 10,400 and 10,200 cal years BP. As in the $\delta^{13}\text{C}_{\text{diatom}}$ record, short-term oscillations disappear after 10,000 cal years BP, but in the $\delta^{18}\text{O}_{\text{diatom}}$ data, values only unveil a long-term decreasing trend (-2.8 ‰) towards the top of the record (8300 cal years BP) (Fig. 3B).

5. Parameters governing Lake Chungará isotopic composition

Lake Chungará is a high-altitude effectively hydrologically closed lake (Herrera et al., 2006) and

in this type of lake the effects of evaporation are usually more significant than other forcings on $\delta^{18}\text{O}$ (Leng and Barker, 2006). Previous $\delta^{18}\text{O}_{\text{diatom}}$ studies on Lake Chungará revealed that oscillations in oxygen isotopes of the lake water were most likely related to variations in the P/E ratio than to changes in the temperature or isotope composition of rainfall (Hernández et al., 2008, 2010, 2011). However, non-climate effects such as shifts in the water residence time of the lake caused by variations in basin hydrology or in groundwater fluxes are also thought to influence the long-term changes in $\delta^{18}\text{O}_{\text{diatom}}$ values in Lake Chungará (Hernández et al., 2008).

Long-term trends in the $\delta^{13}\text{C}_{\text{diatom}}$ record roughly follow the BSi flux record (Bao et al., 2010) (Fig. 4B), an indicator of past biosiliceous productivity conditions (Conley and Schelske, 2001; Bao et al., submitted for publication). In contrast, decadal-to-centennial $\delta^{13}\text{C}_{\text{diatom}}$ decreases are mostly coincident with $\delta^{18}\text{O}_{\text{diatom}}$ decreases, which are thought to indicate wet events (Fig. 4D). These enhanced rainfall conditions would enable increased terrestrial OM inputs into the lake water from runoff. Isotope values from Lake Chungará catchment inputs of terrestrial plants have $\delta^{13}\text{C}$ which range between -26 and -23‰ , whereas planktonic algae $\delta^{13}\text{C}$ are heavier than -15‰ (See Section 2.1). Thus, even small external loadings could produce significant negative excursions in $\delta^{13}\text{C}_{\text{diatom}}$ values. However, both the slope of the long-term trends and the magnitude of the decadal-to-centennial oscillations in $\delta^{13}\text{C}_{\text{diatom}}$ record are modulated by the water column mixing regime reconstructed from the multivariate statistical analysis of the diatom assemblages (Bao et al., submitted for publication) (Fig. 4A). When mixing intensifies, isotopically depleted dissolved carbon is released from the hypolimnion increasing the $\text{CO}_{2(\text{aq})}$ concentration and provoking the consequent relaxation of the $\delta^{13}\text{C}_{\text{diatom}}$ increase.

These observations suggest that millennial-to-centennial scale changes in $\delta^{13}\text{C}_{\text{diatom}}$ are mainly related to changes in primary productivity, whereas decadal-to-centennial variations are directly influenced by the OM associated with the external loadings to the lake. In addition, CO_2 release from

the hypolimnion can also influence the $\delta^{13}\text{C}_{\text{diatom}}$ variability at both time scales.

6. Palaeoenvironmental reconstruction in Lake Chungará

6.1. Lateglacial–Early Holocene transition humid period (12,400–10,200 cal years BP)

Many continental records indicate that the Lateglacial–Early Holocene transition in the Andean Altiplano was a humid period (e.g. Baker et al., 2001a; Abbott et al., 2003; Giralt et al., 2008) coeval with the Coipasa humid phase established from several palaeorecords on the Andean Altiplano (i.e. Lake Titicaca by Baker et al., 2001b; Lake Paco Cocha by Abbott et al., 2003; Salar de Uyuni by Placzek et al., 2006).

During the first part of this period (12,400–11,000 cal years BP), $\delta^{18}\text{O}_{\text{diatom}}$ values are relatively stable and low (mean $+37.5\text{‰}$), but punctuated by some short-term excursions towards minimum values ($+35.2\text{‰}$). Between 10,800 and 10,200 cal years BP there is a significant enrichment trend with some low spikes ($+5.4\text{‰}/1000$ years) (Fig. 4D). The overall increasing trend is likely a result of enhanced evaporation. Periods of high evaporation have previously been interpreted in terms of flooding of the shallow eastern and southern margins after ca 11,000 cal years BP (Hernández et al., 2008), when the surface area to volume ratio (S/V) of the lake significantly increased because these flooded margins were much shallower than the central plain (Fig. 1). As a result, the relative importance of evaporation was enhanced.

This interpretation agrees with a previous reconstruction of the effective moisture balance of the lake based on independent proxy data (Giralt et al., 2008) (Fig. 4E). This moisture balance reconstruction shows a good agreement with a humid period between 12,400 and 10,800 cal years BP, and with a transition towards drier conditions for the following ca 500 years. There is a general consensus that millennial scale shifts in moisture conditions in tropical South America are orbitally-induced by changes in the insolation rate (e.g. Baker et al., 2001a), although long-term changes in ENSO-like conditions also play a major role

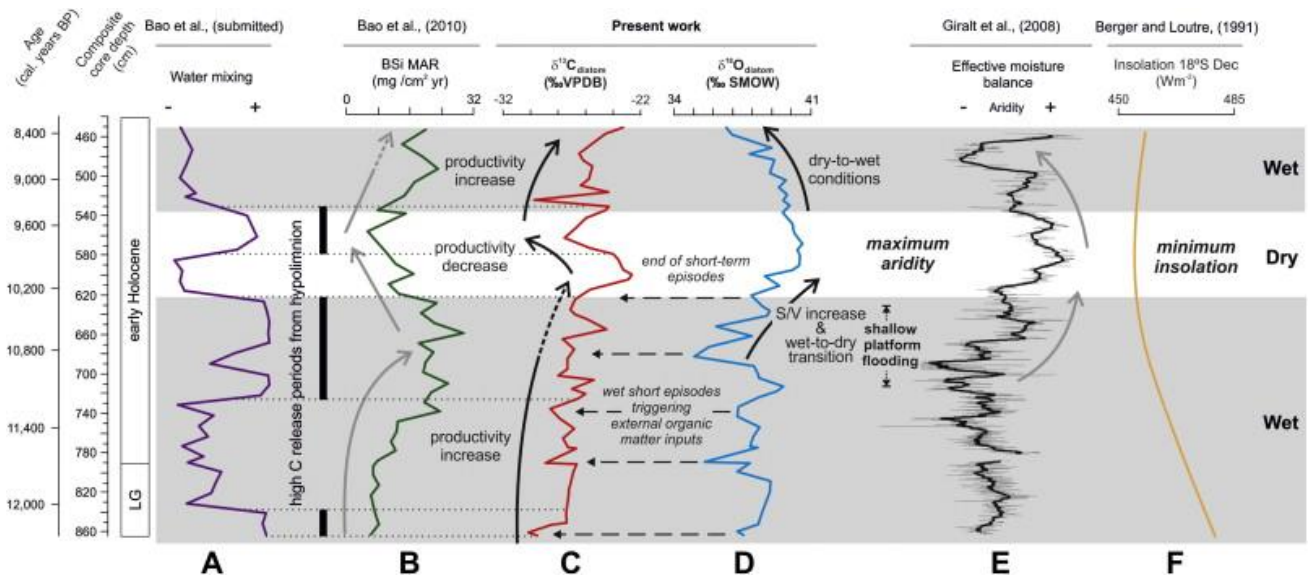


Fig. 4. Palaeoenvironmental reconstruction based on Lake Chungará sedimentary sequence. Comparison between: (A) mixing intensity in the lake water column as deduced by the multivariate analysis of diatom assemblages (Bao et al., submitted for publication); (B) data on Biogenic Silica (BSi) mass accumulation rates in the sediments (Bao et al., 2010); (C) $\delta^{13}\text{C}_{\text{diatom}}$ record (present work); (D) $\delta^{18}\text{O}_{\text{diatom}}$ record (present work); (E) effective moisture balance derived from the second eigenvector of Principal Component Analysis (PCA) on magnetic susceptibility, X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Total Carbon and Total Organic Carbon (TC and TOC), and Biogenic Silica (BSi) for the laminated unit of Lake Chungará (Giralt et al., 2008); and (F) insolation curve in austral summer at 18°S for this period (Berger and Loutre, 1991). All data are plotted against age and depth.

(e.g. Rowe et al., 2002; Abbott et al., 2003). Previously performed spectral analyses of the $\delta^{18}\text{O}_{\text{diatom}}$ values (Hernández et al., 2010) suggest that decadal-to-centennial cycles and events during the Lateglacial–Early Holocene transition (11,990–11,450 cal years BP) could have been triggered by both ENSO-like variability and solar activity. Time-frequency analysis showed that although solar and ENSO forcings were present at the onset of the Holocene, they were more intense during the Lateglacial–Early Holocene transition. This transition might have been mainly governed by La Niña-like conditions that correspond to a wet situation over the Andean Altiplano (Hernández et al., 2010, 2011). In consequence, the most plausible explanation for this humid period would be the establishment of long-term La Niña-like conditions in the tropical Pacific (Betancourt et al., 2000; Koutavas et al., 2002), giving rise to enhanced moisture and several short-term (decadal-to-centennial) oscillations over the Altiplano during the Early Holocene.

$\delta^{13}\text{C}_{\text{diatom}}$ values show an overall millennial scale increasing trend (+7‰) with several negative shifts

in this period. The $\delta^{13}\text{C}_{\text{diatom}}$ record shows a correspondence with the increased BSi flux to the sediments. This trend might be interpreted as a reduction of the available ^{12}C due to enhanced productivity and hence heavier values of $\delta^{13}\text{C}_{\text{diatom}}$. However, BSi flux values increase abruptly at 11,400 cal years BP, concurrently with enhanced mixing conditions. The latter would have released isotopically depleted CO_2 from the hypolimnion having the opposite effect on the $\delta^{13}\text{C}_{\text{diatom}}$ values. As a consequence, the magnitude of the $\delta^{13}\text{C}_{\text{diatom}}$ millennial-to-centennial scales changes did not keep pace with the increase in productivity. However, decadal-to-centennial negative excursions in $\delta^{13}\text{C}_{\text{diatom}}$ coincide with reductions in $\delta^{18}\text{O}_{\text{diatom}}$ suggesting that increased runoff favoured OM inputs from terrestrial plants or mineralised materials from soils and the subsequent carbon isotope depletion (Fig. 4).

In summary, relatively low values of $\delta^{18}\text{O}_{\text{diatom}}$ in this period record humid conditions during the Lateglacial–Early Holocene transition in Lake Chungará, being interrupted by several oscillations at decadal-to-centennial time scales, probably

induced by La Niña-like variability (Hernández et al., 2010). For the same period, $\delta^{13}\text{C}_{\text{diatom}}$ values suggest a long-term increase of in-lake productivity. Although to a lesser extent, this isotope signal is also influenced by the mixing of the water column. Overall, decadal-to-centennial time scale oscillations in $\delta^{13}\text{C}_{\text{diatom}}$ values most likely suggest carbon delivery from the catchment related to enhanced rainfall conditions in the lake region.

6.2. Early Holocene dry period (10,200–9400 cal years BP)

This period shows the highest values of $\delta^{18}\text{O}_{\text{diatom}}$, with no decadal-to-centennial oscillations, suggesting that this phase is the most arid. There are several lines of evidence for low lake levels during this period: the facies are a carbonate-rich brown-white laminated diatomite (Fig. 3), there is a decrease in the relative abundance of planktonic diatoms (Sáez et al., 2007; Bao et al., submitted for publication), and a moisture balance reconstruction based on magnetic susceptibility, X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Total Carbon and Total Organic Carbon (TC and TOC), Biogenic Silica (BSi) and grey-colour curve of the sediment data (Giralt et al., 2008) all show a decrease in the water availability in the lake (Fig. 4E).

Although this dry period seems to follow heterogeneous regional spatial and temporal patterns, it is present in most of the records from the Andean Altiplano (e.g. Seltzer et al., 2000; Baker et al., 2001a; Abbott et al., 2003; Hillyer et al., 2009). It coincides with the minimum values of the summer insolation curve driven by orbital precession (Berger and Loutre, 1991) (Fig. 4F), which could promote much drier conditions than those prevailing during the Lateglacial and thus the lowest lake levels in the region throughout the Holocene (i.e. Hillyer et al., 2009). Thus, this part of the Holocene is likely to have been one of the most arid in the Andean Altiplano region (Hillyer et al., 2009). Moreover, ENSO-like reconstructions also show minimum intensity values for this period (Moy et al., 2002; Rodó and Rodríguez-Arias, 2004; Hernández et al., 2011). The absence or the minimum values of ENSO-like phenomena could

have been responsible for the cessation of the short-term oscillations.

The $\delta^{13}\text{C}_{\text{diatom}}$ record shows contrasting high and low values for this period, when the BSi flux to the sediments experiences a clear decreasing trend (Fig. 4B and C). Under this scenario, high $\delta^{13}\text{C}_{\text{diatom}}$ values, between 10,200 and 10,000 cal years BP, must be explained by drivers other than productivity. The absence of mixing and external inputs during this very dry period (Fig. 4B–D) is likely the main factor responsible for the reduction of ^{12}C availability and the subsequent $\delta^{13}\text{C}_{\text{diatom}}$ values increase. In addition, the carbonate-rich sediments of this period might suggest higher HCO_3^- concentration in the lake water. It is known that diatoms can sometimes use bicarbonate if dissolved CO_2 is limited (Johnston et al., 2001). The utilisation of HCO_3^- would result in increased $\delta^{13}\text{C}_{\text{diatom}}$ values compared to those from species which can only use $\text{CO}_{2(\text{aq})}$ (Fry, 1996).

The maximum $\delta^{13}\text{C}_{\text{diatom}}$ values are followed by a fall of 5‰ between 10,000 and 9600 cal years BP. This decreasing trend in $\delta^{13}\text{C}_{\text{diatom}}$ may be the result of the continuous decrease in productivity coupled with an increase in the dissolved $\text{CO}_{2(\text{aq})}$ concentration. High $\delta^{13}\text{C}_{\text{diatom}}$ values recorded immediately before this shift (10,200–10,000 cal years BP) were perhaps unaffected by the decrease in productivity due to the prevalence of stratified conditions in the water column and low ^{12}C availability. In contrast, the combined effects of enhanced mixing conditions (Fig. 4A) that would have released the $\text{CO}_{2(\text{aq})}$ available in the hypolimnion, and low biogenic productivity (Fig. 4B), would have depleted the carbon pool and the $\delta^{13}\text{C}_{\text{diatom}}$ values. This demonstrates the complexity of factors affecting the $\delta^{13}\text{C}_{\text{diatom}}$ signal, highlighting that more than one factor is usually responsible for the $\delta^{13}\text{C}_{\text{diatom}}$ changes.

6.3. Early Holocene dry-to-wet transition phase (9400–8300 cal years BP)

After 9400 cal years BP the $\delta^{18}\text{O}_{\text{diatom}}$ record shows a slight decreasing upwards trend interpreted as a transition towards moister conditions. Wetter conditions between 9000 and 8300 cal years BP are consistent with the increase in summer insolation (Berger and Loutre, 1991) which led to a rise in the

effective regional moisture (Giralt et al., 2008) (Fig. 4E and F). This humid phase is well established elsewhere over the Andean Altiplano (e.g. Baker et al., 2001a; Hillyer et al., 2009).

$\delta^{13}\text{C}_{\text{diatom}}$ values display a slight enrichment trend through this period, whereas $\delta^{18}\text{O}_{\text{diatom}}$ suggest a gradual increase in humidity. $\delta^{13}\text{C}_{\text{diatom}}$ follow, in general terms, the increased flux of BSi to the sediments (Fig. 4B and C) suggesting a productivity increase. The transition to more humid conditions from the previous Early Holocene severe drought situation (10,200–9400 cal years BP), when vegetation coverage of the catchment was sparse, surely reduced external OM inputs to the lake. This would have limited the carbon pool, resulting in the subsequent $\delta^{13}\text{C}_{\text{diatom}}$ enrichment during this enhanced productivity period. Furthermore, the intensification of the water stratification conditions (Fig. 4A) prevented the release of $\text{CO}_{2(\text{aq})}$ from the hypolimnion to surface waters, thereby stimulating a further $\delta^{13}\text{C}_{\text{diatom}}$ enrichment.

7. Conclusions

This study shows that the combined use of $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ records in lake sediments is a useful proxy for understanding the interaction between in-lake vs climate and runoff from catchment processes at a regional scale. In Lake Chungará, the interpretation of the $\delta^{18}\text{O}_{\text{diatom}}$ record is based on the hydrological balance of the lake, which is modulated by changes in the S/V ratio of the lake water. In contrast, the $\delta^{13}\text{C}_{\text{diatom}}$ record is related to changes in primary productivity, although OM associated with the external loadings and changes in CO_2 release from the hypolimnion also influence the $\delta^{13}\text{C}_{\text{diatom}}$ variability. The combination of $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ shows that during wet events the relative contribution of external carbon loadings significantly enriched the carbon pool (depleting $\delta^{13}\text{C}_{\text{diatom}}$), whereas dry periods favoured lacustrine carbon recycling and the subsequent enrichment of the $\delta^{13}\text{C}_{\text{diatom}}$ values. Combined $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ analyses in the sedimentary record can therefore help us to gain a better understanding of the climate influence on the lake carbon cycle through time and its role in the context of global change.

Both $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ show centennial-to-millennial scale trends throughout the record. These major trends are related to within-lake processes (biogenic productivity and water column mixing) and lake hydrology (regional moisture balance and hydrogeology), respectively. In addition, decadal-to-centennial scale oscillations in both proxies reflect wet episodes and the associated terrestrial OM inputs from the lake catchment. These oscillations are however restricted to the Lateglacial–Early Holocene transition (12,400–10,000 cal years BP), probably as a consequence of a minimum intensity of the ENSO-like after this period. Changes in summer insolation and in ENSO-like strength seem to be the main climate drivers of $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{18}\text{O}_{\text{diatom}}$ oscillations at different time scales.

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