The palaeohydrological evolution of Lago Chungará (Andean Altiplano, northern Chile) during the Late Glacial and Early Holocene using oxygen isotopes in diatom silica

Armand Hernández,[1*] Roberto Bao,[2] Santiago Giralt,[1] Melanie J. Leng,[3,4] Philip A. Barker,[5] Alberto Sáez,[6] Juan J. Pueyo,[6] Ana Moreno,[7,8] Blas L. Valero-Garcés,[7] Hilary J. Sloane,[3]

[1]Institute of Earth Sciences 'Jaume Almera'-CSIC, C/Lluís Solé i Sabarís s/n, 08028 Barcelona, Spain
[2]Faculty of Sciences, University of A Coruña, Campus da Zapateira s/n, 15701 A Coruña, Spain
[3]NERC Isotope Geosciences Laboratory, British Geological Survey, Nottingham NG12 5GG, UK
[4]School of Geography, University of Nottingham, Nottingham NG7 2RD, UK
[5]Department of Geography, Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK
[6]Faculty of Geology, University of Barcelona, C/ Martí Franquès s/n, 08028 Barcelona, Spain
[7]Pyrenean Institute of Ecology - CSIC, Apdo. 202, 50080 Zaragoza, Spain
[8]Limnologycal Research Center, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, MN 55455, USA

***Correspondence to:** Armand Hernández; Institute of Earth Sciences 'Jaume Almera' (CSIC). C/Lluis Sole i Sabaris s/n. E-08028 Barcelona (Spain).

Phone: +34.934.095.410

Fax: +34.934.110.012

E-mail: ahernandez@ija.csic.es

Abstract

Oxygen isotopes of diatom silica and petrographical characterization of diatomaceous laminated sediments of Lago Chungará (northern Chilean Altiplano), have allowed us to establish its palaeohydrological evolution during the Late Glacial-Early Holocene (*ca* 12,000 – 9400 cal years BP). These laminated sediments are composed of light and dark pluriannual couplets of diatomaceous ooze formed by different processes. Light sediment laminae accumulated during short term diatom blooms whereas dark sediment laminae represent the baseline limnological conditions during several years of deposition. Oxygen isotope analysis of the dark diatom laminae show a general $\delta^{18}O$ enrichment trend from the Late Glacial to the Early Holocene. Comparison of these $\delta^{18}O_{diatom}$ values with the previously published lake level evolution suggest a correlation between $\delta^{18}O_{diatom}$ and the evaporation/precipitation ratio, but also with the evolution of other local hydrological factors as changes in the ground water outflow as well as shifts in the surface area to volume ratio of Lago Chungará.

Keywords: diatom ooze, laminated sediments, oxygen isotopes, rythmites, Holocene, Andean Altiplano

1. Introduction

Oxygen isotopes of diatom silica have been used extensively in palaeoenvironmental reconstructions from lake sediments in the last decade (see Leng and Barker, (2006) for a comprehensive review). Using oxygen isotope ratios in palaeoenvironmental reconstruction is however not easy, because the sedimentary record can be influenced by a wide range of interlinked environmental processes ranging from regional climate change to local hydrology. The oxygen isotopic composition of diatom silica depends on the isotope composition of the water when the skeleton of the siliceous micro-organisms is secreted, and also on the ambient water temperature (Shemesh et al. 1992). Therefore, knowledge of all the environmental factors that may have influenced the isotope composition of the lake water is vital for the interpretation of the $\delta^{18}O_{diatom}$ signal (Leng et al. 2005a). One of these environmental factors is evaporation, which has a major influence on the isotope composition of any standing water body (Leng and Marshall, 2004). The $\delta^{18}O$ record can therefore be used, at least in closed lakes, as an indicator of changes in the precipitation to evaporation ratio (P/E) related to climatic changes (Leng and Marshall, 2004). Yet, before any palaeoclimatic interpretation of the isotope records from a lake is considered, other local palaeohydrological intervening factors from the basin need to be taken into account (Sáez and Cabrera, 2002; Leng et al. 2005a).

The sedimentary records of high-altitude, Andean Altiplano lakes, are good candidates for carrying out oxygen isotope studies to reconstruct the Late Quaternary palaeoclimatology of the region, because they preserve an excellent centennial- to millennial-scale record of effective moisture fluctuations during the Late Glacial and Holocene (Abbot et al. 1997; Argollo and Mourguiart, 2000; Valero-Garcés et al., 2000, 2003; Grosjean et al., 2001; Baker et al., 2001a, 2001b; Tapia et al., 2003; Fritz et al., 2004, 2006). The $\delta^{18}O$ analyses of carbonates, cellulose and biogenic silica have successfully been used to reconstruct the hydrological responses to climate change in different Andean lacustrine systems (Schwalb et al., 1999; Seltzer et al., 2000; Abbott et al., 2000, 2003; Wolfe et al., 2001; Polissar et al., 2006).

Up to now, only stable isotopes in carbonates have been examined in Lago Chungará (Valero-Garcés et al. 2003), although its sedimentary record is made up of rich diatomaceous ooze ideal for diatom silica oxygen isotope studies. Lago Chungará currently behaves as a closed lake, without any surface outlet and evaporation as the dominant water loss process (Herrera et al., 2006); however it has shown a complex depositional history since the Late Glacial (Sáez et al., 2007) and the relative role of other factors (groundwater versus evaporation) should be evaluated.

Here we examine a high resolution $\delta^{18}O$ diatom silica record of three selected sections belonging from the Late Glacial to Early Holocene (c. 12,000 – 9400 cal yrs BP) from Lago Chungará. We emphasise the role that some local factors such as sedimentary infill and palaeohydrology can play on the interpretation of the $\delta^{18}O$ diatom silica record and therefore the need to discriminate between the climatic and local environmental signals.

2. The Lago Chungará

Geology, climate and limnology

Lago Chungará (18º15'S, 69º10'W, 4520 m a.s.l.) is located at the NE edge of Lauca Basin, in the Chilean Altiplano. It lies in a highly active tectonic and volcanic context (Clavero *et al.*, 2002). The lake sits in the small hydrologically closed Chungará Sub-Basin which was formed as a result of a debris avalanche during the partial collapse of the Parinacota Volcano, damming the former Lauca River (Fig. 1A). Lago Chungará and Lagunas Cotacotani were formed almost immediately. The collapse post-avalanche event has been dated and the ages range between 18,000 cal years BP, using He-exposure techniques (Wörner *et al.*, 2000; Hora et al., 2007), and 11,155 – 13,500 ^{14}C yr BP, employing radiocarbon dating methods (Francis & Wells, 1988; Baied & Wheeler, 1993; Amman *et al.*, 2001). In these cases the authors dated lacustrine sediments from Lagunas Cotacotani. In addition, Clavero *et al.* (2002, 2004) dated palaeosoil horizons by radiocarbon and proposed a maximum age of 8000 ^{14}C yr BP for the collapse.

Lago Chungará is situated in the arid Central Andes, in region dominated by tropical summer moisture (Garreaud *et al.*, 2003). The isotope composition of rainfall (Aravena *et al.*, 1999; Herrera *et al.*, 2006) and the synoptic atmospheric precipitation patterns (Ruttlant and Fuenzalida, 1991) indicate that the main moisture source comes from the Atlantic Ocean via the Amazon Basin. During the summer months (DJFM) weak easterly flow prevails over the

Altiplano as a consequence of the southward migration of the subtropical jet stream and the establishment of the Bolivian high pressure system (Garreaud *et al.*, 2003). This narrow time window defines the wet season in the Altiplano (Valero-Garcés *et al.*, 2003). Mean annual rainfall in the Chungará region is about 350 mm yr^{-1}, but the actual range is variable (100-750 mm yr^{-1}). Mean temperature is 4.2ºC and the potential evaporation was estimated at over 4750 mm yr^{-1} (see references in Valero-Garcés *et al.*, 2000).

A significant fraction of the inter-annual variability of summer precipitation is currently related to the El Niño Southern Oscillation (ENSO) (Vuille, 1999). El Niño years seem to be recorded in the Sajama and Quelcaya ice-cores by significant decreases in snow accumulation (Thompson *et al.*, 1986; Vuille, 1999). Instrumental data from the Chungará region show a reduction of the precipitation during moderate to intense El Niño years. However, there is no direct relationship between the relative El Niño strength and the amount of rainfall reduction (for further details see Valero-Garcés *et al.* 2003).

Rainfall isotope composition in this region is characterised by a large variability in $\delta^{18}O$ (between +1.2 and –21.1‰ SMOW) and of δD (between +22.5 and –160.1‰ SMOW). The origin of the lightest isotope values are the strong kinetic fractionation in the air masses from the Amazon. The altitudinal isotopic gradient of $\delta^{18}O$ in the Chungará region is very high (between +0.76‰/100 m and +2.4‰/100 m) compared with other worldwide regions (Herrera *et al.*, 2006).

Lago Chungará has an irregular shape with a maximum length of 8.75 km, maximum water depth of 40 m, a surface area of 21.5 km^2 and a volume of 400 x 10^6 m^3 (Mühlhauser *et al.*, 1995; Herrera *et al.*, 2006) (Fig. 1B). The western and northern lake margins are steep, formed by the eastern slopes of Ajoya and Parinacota volcanoes. The eastern and southern margins are gentle, formed by the distal fringe of recent alluvial fans and the River Chungará valley (Sáez *et al.*, 2007). 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. The main water outlet is by evaporation (3.10^7 m^3 y^{-1}) but it has been estimated that groundwater outflow from Lago Chungará to Lagunas Cotacotani is about 6-7.10^6 $m^3 y^{-1}$ (Risacher *et al.*, 1999; Dorador *et al.*, 2003). The calculated residence time for the water lake is approximately 15 years (Herrera *et al.*, 2006). The lake is polymictic, oligomesotrophic to meso-eutrophic (Mühlhauser *et al.*, 1995), contains 1.2 g l^{-1} of Total Dissolved Solids, its conductivity ranges between 1500 and 3000 μS cm^{-1} (Dorador et al. 2003) and the water chemistry is of Na-Mg-HCO_3-SO_4 type. Temperature profiles measured in November 2002 showed a gradient from the lake surface (9.1-12.1ºC) to the lake bottom (6.2-6.4ºC at 35 m of water depth), with a thermocline (0.5-0.6ºC) located at about 19 m of water depth. Oxygen ranged from 11.9-12.5 ppm (surface) to 7.6 ppm (bottom) and the pH oscillated between 8.99 (surface) and 9.30 (bottom). Lake water is enriched by evaporation with regard to rainfall and spring waters. The mean values of $\delta^{18}O$ and δD are –1.4‰ SMOW and –43.4‰ SMOW, respectively (Herrera *et al.*, 2006). Primary productivity is mainly governed by diatoms and chlorophyceans (Dorador *et al.*, 2003). Macrophyte communities in the littoral zone form dense patches that contribute to primary productivity. Seasonal measurements of conductivity, nitrate, phosphate and chlorophyll reveal changes in productivity and in the composition of algal communities mainly due to changes in water temperature and salinity (Dorador *et al.*, 2003). The absence of raised lacustrine deposits around the lake margins suggests that the current level of the lake is at its highest since the lake formation (Sáez *et al.*, 2007).

Previous work and sedimentary sequence

In November 2002 fifteen sediment cores (6.6 cm inner diameter and up to 8 m long) were recovered from Lago Chungará using a raft equipped with a Kullenberg system. All cores were cut in 1.5 m sections and physical properties (GRAPE-density, p-wave velocity and magnetic susceptibility) were measured in the laboratory using a GEOTEK™ Multi-Sensor Core Logger (MSCL) at 1 cm intervals. Afterwards, the cores were split in two halves, scanned using a DMT colour scanner, and the textures, colours and sedimentary structures were described. Smear slides were prepared for the description of the sediment composition and to estimate the biogenic, clastic and endogenic mineral content.

After a detailed lithological correlation of the cores (Sáez *et al.*, 2007), cores 10 and 11 located offshore were selected for conducting the palaeoenvironmental reconstruction. A composite core recording the whole sedimentary infill (minimum thickness of 10 m) of the offshore zone was constructed from the detailed description and correlation of cores 10 and 11. From hereby all core depths are referred to this composite core. From the bottom to the top of the core, two sedimentary units (units 1 and 2) were identified and correlated mainly using tephra keybeds. These lithological units were subdivided in two subunits (subunit 1a, 1b, 2a and 2b). Basal unit 1a ranges between 0.58 m and 2.56 m of thickness and is made up of finely laminated green and whitish diatomaceous ooze. Unit 1b (from 0.62 m to 1.87 m thick) is composed of laminated and massive brown diatomaceous ooze with carbonate rich intervals. Unit 2a (between 1.56 m and 3.44 m thick) is made up of a brown diatomaceous ooze with tephra layers and carbonate-rich intervals. The sediments of the uppermost unit 2b range from 0.86 m to 3 m in thickness and they are composed of dark grey to black diatomaceous ooze with abundant tephra layers (for further details see Moreno *et al.*, 2007 and Sáez *et al.*, 2007).

The cores have been analysed for a number of proxies including X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Total Organic and Inorganic Carbon (TOC and TIC), pollen, diatoms and total biogenic silica (Moreno *et al.*, 2007 and Sáez *et al.*, 2007)

The chronological model for the sedimentary sequence of Lago Chungará is based on 17 AMS ^{14}C dates of bulk organic matter and aquatic plant macrofossils, and one $^{238}U/^{230}Th$ date from carbonates. The radiocarbon dates were performed in the Poznan Radiocarbon Laboratory (Poland), whereas the $^{238}U/^{230}Th$ sample was analysed by high-resolution ICP-IRMS multicollector at the University of Minnesota (Edwards *et al.*, 1987; Cheng *et al.*, 2000; Shen *et al.*, 2002). The present day reservoir effect was determined by dating the dissolved inorganic carbon (DIC) of the lake water at the Beta Analytics Inc. laboratory (USA). The real reservoir effect of the lake was calculated by correcting the DIC radiocarbon date for the effects of the thermonuclear bomb tests (Hua and Barbetti, 2004). The calibration of radiocarbon dates was performed using the CALIB 5.02 software and the INTCAL98 curve (Stuvier *et al.*, 1998; Reimer *et al.*, 2004). The software described in Heegaard *et al.* (2005) was used to construct the final age-depth model (see Moreno *et al.* (2007) and Giralt et al. in press for details).

3. Materials and methods

Three intervals from unit 1 were selected and sampled for thin section study and $\delta^{18}O$ diatom silica analysis. The interval 1 (located at the subunit 1a, between 831 cm and 788 cm of core depth) is made up of the finely laminated green and whitish sediments. Interval 2 (between

605 cm and 622 cm of core depth) is found in the transition between the subunit 1a and the subunit 1b and it is made up of laminated green and pale brown diatomaceous ooze. The interval 3 (located at the subunit 1b, between 537 cm and 574 cm of core depth) is made up of laminated dark brown and white diatomaceous ooze with carbonates.

The chronological model defines the corresponding age of the three intervals. Interval 1 was deposited between 11,990 and 11,530 cal years BP, interval 2 between 10,430 and 10,260 cal years BP and interval 3 between 9,890 and 9,430 cal years BP.

Each interval was continuously covered by thin sections. Thin sections of 120 mm x 35 mm (30 μm in thickness), with an overlapping of 1 cm at each end, were obtained after freeze-drying and balsam-hardening. Detailed petrographical descriptions and lamina thickness measurements were performed with a Zeiss Axioplan 2 Imaging petrographic microscope. Several samples were also selected for observation with a Jeol JSM-840 electron microscope in order to complement the petrographical study.

Each lamina of the three intervals was sampled with a blade for isotope analysis. A total of 190 samples (111 samples from interval 1, 37 samples from interval 2 and 42 samples from interval 3) were obtained. However, a selection of 37 samples were analysed according to its facies composition, level of purification, and stratigraphic position. Analysis of the oxygen isotope composition of diatom silica from these 37 samples requires that the material is almost pure diatomite (Juillet-Leclerc, 1986), so a meticulous protocol involving chemical attack, sieving, settling and laminar flow separation was performed. Specifically our samples were treated following the method proposed by Morley *et al.* (2004) with some variations (Fig. 2A). The first stage (chemical attack) followed the standard method in order to remove the carbonates (10% HCl) and organic matter (hydrogen peroxide) (Battarbee *et al.* 2001), but also included a further step using concentrated HNO_3 in order to remove any remaining organic matter. The second stage (sieving at 125 μm) allowed us to eliminate resistant charcoal and terrigenous particles. The 63 μm and 38 μm sieves allowed us to obtain a fraction of quasi-monospecific diatoms (*Cyclostephanos andinus*) in most of the samples. The third stage was an alternative approach to heavy liquid separation. Gravitational split-flow thin fractionation (SPLITT) was employed in the Lancaster University (UK) (Rings, et al., 2004; Leng and Barker, 2006). The SPLITT technique was only applied to the most problematic samples which contained remaining difficult to separate clay and fine tephra particles. In the final step, the purified diatom samples were dried at 40ºC between 24h and 48h. After the cleaning process six samples were checked with XRD, TC analysis and SEM observations. This checking process revealed that the samples did not contain significant terrigenous matter. The TC values were below 0.5% wt and the terrigenous content (clays or tephra) was less than 1% wt (Fig. 2B). Although a large amount of diatoms were broken during the cleaning process, this does not affect the final isotope data. We therefore assume that the $\delta^{18}O$ values of the purified samples retained climatic and hydrological information (Morley *et al.*, 2004; Leng and Barker, 2006).

Oxygen extraction for isotope analyses followed the classical step-wise fluorination method (Matheney and Knauth, 1989). The method involved three steps. First, the hydrous layer was stripped by outgassing in nickel reaction tubes at room temperature. Second, a prefluorination clean up step involving a stoichiometric deficiency of reagent, bromine pentafluoride (BrF_5), heated at 25ºC for several minutes. The final step was a full reaction at 450ºC for 12 hours with an excess of BrF_5. The oxygen liberated was converted to CO_2 by exposure to hot graphite (following Clayton and Mayeda (1963)). The oxygen yield was monitored, for every sample, by comparison with the calculated theoretical yield for SiO_2. The intervals examined here had mean yields of 69% - 70% of their theoretical yield based on silica. This fact suggests that around 30% of the material, including hydroxyl and loosely bonded water (both OH^- and H_2O), was removed during prefluorination. A random selection of 5 samples were analysed in duplicate giving a 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‰. The CO_2 was analysed for $^{18}O/^{16}O$ using a Finnigan™ Matt 253 mass spectrometer. The results were calibrated versus NBS-28 quartz international standard. Data are reported in the usual delta form (δ) as per mille (‰) deviations from V-SMOW. The fluorination process and the $^{18}O/^{16}O$ ratios measured were carried out at the NERC Isotope Geosciences Laboratory, British Geological Survey (UK).

4. Results: Petrography and isotope composition of diatoms

Smear slide, SEM, and several analyses (XRD, TC, biogenic silica) of the lake sediments before they were prepared for isotope analysis showed that the samples were composed of both amorphous and crystalline material. The amorphous fraction comprises biogenic silica (between 47%-58% weight), organic matter and volcanic glass. The crystalline fraction represented <10% of the sediments.

4.1. Interval 1 (11,990 – 11,530 cal years BP)

Diatom concentration range from 108.3 to 633.8 million valves g^{-1}. The interval is dominated by euplanktonic diatoms ranging from 79.1% to 93.9% of the diatom assemblage. The thicknesses of the laminae are between 0.9 and 10.3 mm (Fig. 3A). Smear slide, thin section and SEM observations showed that light laminae were quasi-monospecific layers of large *Cyclostephanos andinus* (diameter > 50 μm). The upper contact of the light laminae with the dark laminae is transitional, showing an increase in diatom diversity with subdominant tychoplanktonic (*Fragilaria* spp.) and benthic diatoms (mainly *Cocconeis* spp., *Achnanthes* spp., *Navicula* spp. and *Nitzschia* spp.) (Fig. 4A) whereas the lower contact is abrupt (Fig. 4C). Diatom valves show good preservation with no preferred orientation in the lower part, but increasingly oriented upwards. The content of the organic matter also increases upwards. Dark laminae comprise a more diverse mixture of diatoms, including the euplanktonic smaller *Cyclostephanos andinus* (diameter < 50 μm) than those found in light laminae, and diatoms of the *Cyclotella stelligera* complex, as well as tychoplanktonic and benthic diatoms. These dark laminae are also enriched in organic matter probably originated by diatoms and other algae groups. The lower contact of dark laminae is transitional whereas the upper one is abrupt. Up to 41 light and dark laminae couplets were defined. The thickness of these couplets ranges between 4.2 mm and 22.5 mm and, according to the chronological model they are pluriannual (mean about 10 years). The rythmite starts with the dominance of light laminae progressively changing to a dominance of dark laminae.

The $\delta^{18}O_{diatom}$ values of the purified diatoms in interval 1 range from +35.5‰ to +39.2‰ (Fig. 3A). Higher $\delta^{18}O_{diatom}$ occur in the lower part of the interval (around 822 cm of core depth). There is an upwards decreasing trend (~1.9‰/100 years) attaining a minimum of +35.5‰

around 803 cm depth. This stretch is followed by an increasing shift of ~2.9‰/100 years towards the upper part of the interval where a relative maximum of +38.8‰ is reached at 793 cm depth. The uppermost two samples show a light depletion. The mean $\delta^{18}O_{diatom}$ value of this interval is +37.8±0.85‰.

4.2. Interval 2 (10,430 – 10,260 cal years BP)

Diatom concentration ranged from 95.2 to 218 million valves g^{-1} in the interval 2. Almost 94% of the diatom assemblages of this interval were made up of euplanktonic diatoms. Benthic taxa show the minimum values for the three analysed intervals. The thickness of diatomaceous ooze laminae ranged from 1.8 mm to 16 mm (Fig. 3B). Light laminae were dominated by large *Cyclostephanos andinus* (diameter > 50 μm) with some tychoplanktonic (*Fragilaria* spp.) and benthic diatoms, as well as minor amounts of siliciclasts and organic matter. Dark laminae are composed of a mixture of small and large *Cyclostephanos andinus* valves, with more abundant tychoplanktonic and benthic diatoms (as well as organic matter) compared to light laminae. Diatom valves are not so well preserved as in interval 1 sometimes showing a high degree of fragmentation and a preferred orientation. The contact between the laminae is similar to those found in interval 1. Clear couplets were only observed in the upper two thirds of the interval and only 10 couplets could be identified (Fig. 3B). They are pluriannual (mean couplet represents about 10 years of sedimentation) and their thicknesses range between 5.5 and 19 mm. Light laminae were more abundant in the upper part of the interval 2, whereas dark laminae are more abundant in the lower part.

The $\delta^{18}O_{diatom}$ curve shows a clear increasing trend during this interval (Fig. 3B). The lowest $\delta^{18}O_{diatom}$ value (+36‰) was recorded at the bottom of the interval (617 cm depth) and the maximum at the two uppermost samples (+39.7‰ and +39.6‰; 606-605 cm of core depth). The magnitude of the increasing trend is much higher between the two lowermost samples (~18.5‰/100 years) than for the rest of the interval (~0.6‰/100 years). The mean $\delta^{18}O_{diatom}$ value of this interval is +38.7±1.4‰.

4.3. Interval 3 (9890 – 9430 cal years BP)

Diatom concentration ranges between 163.8 and 255.8 million valves g^{-1} for interval 3. Euplanktonic diatoms (68.6% - 98.1%) also dominate this interval, and have the minimum $\delta^{18}O_{diatom}$ values for the three intervals. On the contrary, benthic diatoms show moderate values (up to 31.4%), being the highest for the three intervals. Light diatomaceous ooze laminae ranged between 0.9 and 12.3 mm in thickness (Fig. 3C), and they comprise *Cyclostephanos andinus* (diameter > 50 μm) increasing upwards in both taxonomic diversity and organic matter content. The lower contact with dark laminae shows an abrupt change in diatom size whereas the upper one is gradual. Diatom valves show good preservation with no orientation in the lower part but are preferentially oriented upwards. Dark laminae comprise a mixture of smaller *Cyclostephanos andinus* (diameter < 50 μm), with subdominant tychoplanktonic and benthic diatoms, as well as a high organic matter content. The lower contact is gradual whereas the upper one abrupt. Up to 18 light and dark pluriannual couplets were defined (mean couplet represent around 12 years). These couplets are 3 to 18 mm thick. The rythmite starts with light laminae progressively changing to dark laminae.

The $\delta^{18}O_{diatom}$ curve for interval 3 (Fig. 3C) shows an overall continuous increasing trend of ~0.9‰/100 years from +39.1‰ (570 cm of core depth) to +41.3‰ (548 cm of core depth). Superimposed over the general trend are short-term fluctuations. The mean $\delta^{18}O_{diatom}$ value of this interval is +40.1±0.77‰.

The three intervals have different $\delta^{18}O_{diatom}$ averages displaying a progressive low-frequency enrichment from the interval 1 (+37.8±0.85‰) to interval 3 (+40.1±0.77‰). The overall isotopic enrichment is 2.1‰ throughout these intervals.

5. Discussion

5.1. The sedimentary model of diatom rythmites

Laminated diatomaceous oozes in the sedimentary record of Lago Chungará comprise variable thickness couplets of alternating light and dark laminae. These couplets display different features (colour and mean thickness) in the three intervals described here although they exhibit similar diatom assemblages and textural characteristics and therefore it is assumed that their formation is by similar environmental processes. Rythmite types have been established (Fig. 4); light laminae are formed almost exclusively by diatom skeletons of a quasi-monospecific assemblage of *Cyclostephanos andinus,* while dark laminae with a high organic matter content comprise a mixture of a more diverse diatom assemblage including the euplanktonic *Cyclostephanos andinus* although diatoms of the *Cyclotella stelligera* complex are the dominant taxa. Subdominant groups are some tychoplanktonic (*Fragilaria* spp.) and benthic taxa (*Cocconeis* spp., *Achnanthes* spp., *Navicula* spp., *Nitzschia* spp.).

Each couplet was deposited during time intervals ranging from 4 to 24 years according to our chronological model. Couplets are therefore not a product of annual variations in sediment supply but to some kind of pluriannual processes. The good preservation and size of diatom valves in the light laminae suggest accumulation during short-term extraordinary diatom blooms perhaps of only days to weeks in duration. These diatom blooms could have been triggered by climatically driven strong nutrient inputs to the lake and/or to nutrient recycling under extreme turbulent conditions and mixing affecting the whole water column. On the contrary, the baseline conditions are represented by the dark laminae. Each of these laminae is made up of the remains (organic matter and diatom skeletons) of a diverse planktonic community deposited throughout several years under different water column mixing regimes. The preserved remains are therefore a reflection of different stages in the phytoplankton succession throughout several years (Reynolds, 2006).

5.2 Lake level and $\delta^{18}O_{diatom}$ changes

A preliminary lake level reconstruction of Lago Chungará was undertaken employing the variations of euplanktonic diatoms, *Botryoccocus* and macrophyte remains (see Sáez *et al.*, 2007). This reconstruction shows a general deepening trend during the Late Glacial and Early Holocene. This overall increase in lake level is punctuated by one deepening (D1; Fig. 5) and by two shallowing episodes (S1 and S2; Fig. 5). According to this model the three selected intervals described here represent two different lacustrine conditions. Intervals 1 and 3 are likely shallower episodes whereas interval 2 occurred during a period between two shallow intervals, and likely with higher lake level conditions. However, the resolution of the lake level reconstruction provided by Sáez et al (2007) does not preclude the occurrence of other shallowing episodes as those detected. The isotope analyses presented here of these three intervals have allowed us to characterise the hydrological evolution of the lake during three key time windows of the Late Glacial and Early Holocene. Dark laminae were selected for $\delta^{18}O_{diatoms}$ analyses to investigate the baseline hydrological evolution of Lago Chungará. The $\delta^{18}O_{diatom}$ variation can result from a variety of processes (Jones *et al.*, 2004; Leng *et al.*, 2005b) but for closed lakes, particularly in arid regions where water loss is mainly through evaporation, measured $\delta^{18}O$ values are always higher than those of ambient precipitation since the oxygen lighter isotope (^{16}O) is preferentially lost via evaporation. Under these circumstances, the $\delta^{18}O$ record can be used as an indicator of changes in the precipitation to evaporation ratio (P/E) related to climatic changes (Leng and Marshall, 2004).

Lago Chungará is a hydrologically closed lake and its main outflow is currently via evaporation, thus meaning that changes in $\delta^{18}O$ values should be directly related to shifts in the precipitation to evaporation ratio (P/E). The lake level change from the deeper water conditions recorded during the sedimentation of the interval 2 to the shallower conditions occurred during the deposition of the interval 3 according to the Sáez et al. (2007) reconstruction, is compatible with the observed increase in $\delta^{18}O$ values. However, the isotope values and the lake level reconstruction do not agree over the transition from interval 1 to interval 2. The isotope values suggest a reduced P/E (shallower) stage whereas several proxy indicators suggest deeper conditions (Fig. 5). A possible explanation for this could involve shifts in $\delta^{18}O$ related to other environmental circumstances, such as variations in the morphometrical parameters and changes in the groundwater outflow. Changes in the surface to volume ratio and in the groundwater outflow of Lago Chungará from the Late Glacial to Early Holocene are the factors likely to account for most of the shifts found in the $\delta^{18}O$ values.

Besides fluctuations in the evaporation/precipitation ratio, another factor to take into account is the basin morphology. During the lake's evolution the lake's surface to volume ratio would have changed. A tentative palaeobathymetric reconstruction of Lago Chungará based on the lake level curve from Sáez et al. (2007) (Fig. 6) shows that during the Late Glacial the lake only occupied the present central plain area. The rise in the lake level during the Early

Holocene, although punctuated by some oscillations, flooded the extensive eastern and southern lake's shallow margins. Under this situation, the lake underwent a significant increase in its surface area (Fig. 6). Because the eastern margin is much shallower than the central plain (Fig. 1), the whole lake's surface area to volume ratio would have significantly increased, and also concurrently the relative importance of evaporation. So the observed $\delta^{18}O$ high values of the interval 3 could be explained not only by the shallowing trend from interval 2 to interval 3, but also by the increasing of the lake's surface to volume ratio between both intervals.

There are no signs of subaerial exposition in the recovered sediments of the eastern platform, which indicates that lake water level did not drop significantly afterwards. Although lake water depth conditions were deeper during interval 3 than during the interval 1, the mean isotope value is higher during interval 3. This fact could be explained by the increase of the surface to volume ratio and by the reduction of groundwater losses. Hence, the morphology of the lake, and not only water depth, must be considered as a key factor in any interpretation of the $\delta^{18}O_{diatoms}$ in terms of changes in P/E.

Furthermore, changes in the groundwater fluxes in Lago Chungará could have been a significant factors for the shifts found in the $\delta^{18}O$ values from the Late Glacial to Early Holocene. The groundwater outflow from the lake during the Late Glacial was probably higher than during the Holocene. This condition would progressively change with the sedimentary infill of the basin. Drainage, through the breccia barrier would progressively become less efficient as the groundwater outflows silted-up (Leng et al., 2005a). Thus, the evaporative outflow would have predominated over groundwater during the Early Holocene. This highlights the fact that stable isotopes would not have, in this case, a direct correspondence with changes in the lake water level.

In summary, the relative increase in evaporation due to the magnification of the lake's surface to volume ratio between the studied intervals would have played a significant role. Superimposed onto this situation, the increase in the $\delta^{18}O$ values from the Late Glacial (when the lake was at its shallowest) to the Early Holocene (when the overall deepening trend started) is also likely to have been related to a change to a predominant evaporative lake as the lake's bottom became more impermeable with the sediment's infilling.

6. Conclusions

The thin section study of the diatomaceous laminated sediments shows that rythmite type is made up of light quasi monospecific lamina of the euplanktonic diatom *Cyclostephanos andinus* and a pluriannual dark lamina rich in organic matter and a mixture of a more diverse diatom assemblage. The formation of light laminae is related to the short term (days to weeks) diatom blooms whereas dark laminae represents the recovery of the baseline conditions lasting several years.

The oxygen isotope record of the dark laminae diatoms of Lago Chungará indicates a progressive $\delta^{18}O$ enrichment from the Late Glacial to Early Holocene. Besides changes in the evaporation/precipitation ratio, two other factors would have governed shifts in the Lago Chungará $\delta^{18}O$ record: the lake's stepped morphology forced the expansion of the lake towards the eastern and southern shallow lake margins during the rising trend. These changes provoked an increase in the lake's surface to volume ratio thus enhancing the evaporation which caused isotope enrichment during the Early Holocene. In addition changes in the groundwater/evaporation outflow ratio and changes in the lake's extend. The hydrology of the lake was modified during the Late Glacial to Early Holocene transition as the lake's groundwater outflow became progressively sealed by sediments, thereby increasing lake water residence time and potential evaporation

Previous work has focused on issues of diagenesis, contamination and host-water interactions that can all influence $\delta^{18}O_{diatom}$ whereas local hydrological factors have been largely neglected. These results point to the complex interplay among the different factors which intervene in the diatom oxygen isotope record of closed lakes and how interpretation needs to be adapted to the different evolutionary stages of the lake's ontogeny. This study highlights the importance of reconstructing local palaeohydrology as this may be only indirectly related to palaeoclimate.

Acknowledgments

The Spanish Ministry of Science and Education funded the research at Lago Chungará through the projects ANDESTER (BTE2001-3225), BTE2001-5257-E, LAVOLTER (CGL2004-00683/BTE) and GEOBILA (CGL2007-60932/BTE). The Limnological Research Center (University of Minnesota, USA) provided the technology and expertise to retrieve the cores. NERC (UK) funded the isotope analysis. We are grateful to CONAF (Chile) for the facilities provided in Chungará. We thank Michael Köhler (GFZ-Potsdam) for the thin sections preparation.

References

Abbott, M.B., Seltzer, G.O., Kelts, K., Southon, J., 1997. Holocene paleohydrology of the tropical Andes from Lake Records. Quaternary Research 47, 70–80.

Abbott, M.B., Wolfe, P.W., Aravena, R., Wolfe, A.P. and Seltzer, G.O. 2000. Holocene hydrological reconstructions from stable isotopes and paleolimnology, Cordillera Real, Bolivia. Quaternary Science Reviews, 19: 1801-1820.

Abbott MB, Wolfe BB, Wolfe AP, Seltzer GO, Aravena R, Mark BG, Polissar PJ, Rodwell DT, Rowe HD, Vuille M. 2003. Holocene paleohydrology and glacial history of the central Andes using multiproxy lake sediment studies. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 194: 123–138. DOI:10.1016/s0031-0182(03)00274-8

Amman C, Jenny B, Kammer K, Messerli B. 2001. Late Quaternary Glacier response to humidity changes in the arid Andes of Chile (18-29°S). *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 172: 313-326.

Aravena R, Suzuki O, Peña H, Pollastri A, Fuenzalida H, Grilli A. 1999. Isotopic composition and origin of the precipitation in northern Chile. *Appl. Geochem*. 14: 411-422.

Argollo, J., Mourguiart, P., 2000. Late Quaternary climate history of the Bolivian Altiplano. Quaternary International 72, 37–51.

Baied CA, Wheeler JC. 1993. Evolution of High Andean Puna ecosystem environment, climate and culture change over the last 12,000 years in the Central Andes. *Mountain Research and Development* 13: 145-156.

Baker, P.A., Seltzer, G.O., Fritz, S.C., Dunbar, R.B., Grove, M.J., Tapia, P.M., Cross, S.L., Rowe, H.D., Broda, J.P., 2001a. The history of South American tropical precipitation for the past 25,000 years. Science 291, 640–643.

Baker, P.A., Rigsby, C.A., Seltzer, G.O., Fritz, S.C., Lowenstein, T.K., Bacher, N.P., Veliz, C., 2001b. Tropical climate changes at millennial and orbital timescales on the Bolivian Altiplano. Nature 409, 698–701.

Battarbee RW, Jones VJ, Flower RJ, Cameron NG, Bennion H, Carvalho L, Juggins S. 2001. *Diatoms.* In: (Eds. Smol J.P., Birks H.J.B. and Last W.M.), *Tracking Environmental Change Using Lake Sediments*. Volume 3: Terrestrial, Algal, and Siliceous Indicators, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 155–202.

Cheng, H., Edwards, R.L., Hoff, J., Gallup, C.D., Richards, D.A. and Asmeron, Y. (2000) The half-lives of uranium-234 and thorium-230. Chemical Geology, 169, 17-33. DOI: 10.1007/s00445-001-0183-0

Clavero, J.E., Sparks, .S.J. and Huppert, H.E. (2002) Geological constraints on the emplacement mechanism of the Parinacota debris avalanche, northern Chile. *Bull. of Volcanology*, 64, 40-54

Clavero, J.E., Sparks, .S.J., Polanco, E. and Pringle, M. (2004) Evolution of Parinacota volcano, Central Andes, Northern Chile. *Rev. Geol. Chile*, 31, 317-347.

Clayton, R.N. and Mayeda, T.K. (1963). The use of bromine pentafluoride in the extraction of oxygen from oxide and silicates for isotope analysis. *Geochim. Cosmochim. Acta*.27: 43–52.

Dorador, C., Pardo, R. and Vila, I. (2003). Variaciones temporales de parámetros físicos, químicos y biológicos de un lago de altura: el caso del Lago Chungará. *Revista Chilena de Historia Natural* 76, 15-22.

Edwards, R.L., Chen, J.H. and Wasserburg, G.J. (1987) ^{238}U-^{234}U-^{230}Th-^{232}Th systematics and the precise measurement of time over the past 500,000 years. *Earth and Planet. Sci. Lett.,* 81, 175-192.

Francis, P.W. and Wells, G. (1988) Landsat thematic mapper observations of debris avalanche deposits in the Central Andes. *Bull. Volcanol*., 50, 258-278

Fritz S. C., Baker, P. A., Lowenstein, T. K., Seltzer , G. O., Rigsby, C. A., Dwyer G. S., Tapia P. M., Arnold K. K., Ku, T-L and Luo, S. 2004. Hydrologic variation during the last 170,000 years in the southern hemisphere tropics of South America. Quaternary Research, 61: 95-104. DOI: 10.1016/j.yqres.2003.08.007

Fritz, S.C., Baker, P.A., Tapia, P., and Garland, J., Spatial and temporal variation in cores from Lake Titicaca, Bolivia/Peru during the last 13,000 years, Quaternary International, 2006: 23-29. DOI:10.1016/j.quaint.2006.05.014

Garreaud, R. D., Vuille, M. and Clement, A. C. (2003). The climate of the Altiplano: observed current conditions and mechanisms of past changes. *Palaeogeography, Palaeoclimatology, Palaeoecology* 194, 5-22. DOI: 10.1016/S0031-0182(03)00269-4

Giralt, S., Moreno, A., Bao, R., Sáez,.A., Prego, R., Valero, B.L., Pueyo, J.J., González-Sampériz, P., Taberner, C. (In press). A Statistical approach to distangle environmental forcings in a lacustrine record: the Lago Chungará case (Chilean Altiplano). J. of Palaeolimnology.

Grosjean, M., van Leeuwen, J.F.N., van der Knaap, W.O., Geyh, M.A., Ammann, B., Tanner, W., Messerli, B., Núñez, L., Valero-Garcés, B.L., Veit, H., 2001. A 22,000 14C year BP sediment and pollen record of climate change from Laguna Miscanti (231S), northern Chile.Global and Planetary Change 28, 35–51.

Heegaard, E., Birks, H. J. B. and Telford, R. J. (2005). Relationships between calibrated ages and depth in stratigraphical sequences: an estimation procedure by mixed-effect regression. *The Holocene* 15, 612-618.

Herrera, C., Pueyo, J.J., Sáez, A. and Valero-Garcés, B.L. (2006). Relación de aguas superficiales y subterráneas en el área del lago Chungará y lagunas de Cotacotani, norte de Chile: un estudio isotópico. *Revista Geológica de Chile*, 33 (2), 299-325.

Hora, J., Singer, B., Wörner, G. (2007). Volcan eruption and evaporative flux on the thick curst of the Andean Central Volcanic Zone: 40Ar/39Ar constrains from Volcán Parinacota, Chile. *Geological Survey of American bulletin* 119, 343-362.

Hua, Q. and Barbetti, M. (2004), Review of tropospheric bomb C-14 data for carbon cycle modeling and age calibration purposes, *Radiocarbon*, 46 (3) 1273-1298

Jones, V., Leng, M.J., Solovieva, N., Sloane, H. and Tarasov, P. (2004). Holocene climate on the Kola Peninsula; evidence from the oxygen isotope record of diatom silica. *Quaternary Science Reviews* 23, 833–839. DOI:10.1016/j.quascirev.2003.06.014

Juillet-Leclerc A. (1986). Cleaning process for diatomaceous samples. In: (Ed. Ricard M.) *8th Diatom Symposium*, Koeltz Scientific Books, Koenigstein, pp. 733–736.

Leng, M.J. and Barker, P.A. (2006). A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction. *Earth Sci. Rev.* 75,5–27. DOI: 10.1016/j.earscirev.2005.10.001

Leng MJ, Lamb AL, Heaton THE, Marshall JD, Wolfe BB, Jones MD, Holmes JA, Arrowsmith C (2005a) Isotopes in lake sediments. In: Leng MJ (ed), Isotopes in palaeoenvironmental research. Springer, Dordrecht, The Netherlands, pp 147–184

Leng, M.J., Metcalfe, S.E. and Davies, S.J. (2005b). Investigating late Holocene climate variability in Central Mexico using carbon isotope ratios in organic materials and oxygen isotope ratios from diatom silica within lacustrine sediments. *J. of Palaeolimnol*. 34, 413– 431. DOI: 10.1007/s10933-005-6748-8

Leng, M.J. and Marshall, J.D. (2004). Palaeoclimate interpretation of stable isotope data from lake sediment archives. *Quaternary Science Reviews* 23, 811 – 831. DOI: 10.1016/j.quascirev.2003.06.012

Matheney, R.K. and Knauth, L.P. (1989). Oxygen-isotope fractionation between marine biogenic silica and seawater. *Geochimica et Cosmochimica Acta* 53, 3207–3214.

Moreno, A., Giralt, S., Valero-Garcés, B.L., Sáez, A., Bao, R., Prego, R., Pueyo, J.J., González-Sampériz P. and Taberner, C. (2007). A 13 kyr high-resolution record from the tropical Andes: The Chungará Lake sequence (18 °S, northern Chilean Altiplano). *Quaternary Internacional* 161, 4-21. DOI: 10.1016/j.quaint.2006.10.020

Morley, D.W., Leng, M.J., Mackay, A.W., Sloane, H.J., Rioual, P. and Battarbee, R.W. (2004) Cleaning of lake sediment samples for diatom oxygen isotope analysis. *J. Paleolimnol*. 31,391–401.

Muhlhauser, H., Hrepic, N., Mladinic, P., Montecino, V. and Cabrera, S. (1995) Water-quality and limnological features of a high-altitude andean lake, Chungará in northern chile. *Rev. Chilena de Hist. Nat.,* 68, 341-349.

Polissar PJ, Abbott MB, Shemesh A, Wolfe AP, Bradley RS. 2006. Holocene hydrologic balance of tropical South America from oxygen isotopes of lake sediment opal, Venezuelan Andes. Earth and Planetary Science Letters 242. 375–389. DOI: 10.1016/j.epsl.2005.12.024

Reimer, P. J., Baillie, M. G. L., Bard, E., Bayliss, A., Beck, J. W., Bertrand, C. J. H., Blackwell, P. G., Buck, C. E., Burr, G. S., Cutler, K. B., Damon, P. E., Edwards, R. L., Fairbanks, R. G., Friedrich, M., Guilderson, T. P., Hogg, A. G., Hughen, K. A., Kromer, B., McCormac, G., Manning, S., Ramsey, C. B., Reimer, R. W., Remmele, S., Southon, J. R., Stuiver, M., Talamo, S., Taylor, F. W., van der Plicht, J. and Weyhenmeyer, C. E. (2004). IntCal04 Terrestrial Radiocarbon Age Calibration, 0–26 Cal Kyr BP. *Radiocarbon* 46, 1029-1058.

Reynolds, C.S. 2006. The Ecology of Phytoplankton. Cambridge University Press, Cambridge, 535 pp.

Rings, A., Lucke, A., Schleser, G.H., 2004. A new method for the quantitative separation of diatom frustules from lake sediments. Limnology and Oceanography: Methods 2, 25– 34.

Risacher, F., Alonso, H. and Salazar, C. (1999) *Geoquímica de las aguas en las cuencas de cerradas: I, II Regiones de Chile*. Vol II. Convenio de Cooperación DGA, UCN e IRD. Internal report. 141 pp.

Ruttlant, J., Fuenzalida, H., 1991. Synoptic aspects of the central Chile rainfall variability associated with the Southern Oscillation. Int. J. Climatol. 111, 63-76.

Sáez, A. and Cabrera, L. (2002) Sedimentological and palaeohydrological responses to tectonics and climate in a small, closed, lacustrine system: Oligocene As Pontes Basin (Spain). *Sedimentology* 49, 1073–1094.

Sáez, A., Valero-Garcés, B. L., Moreno, A., Bao, R., Pueyo, J. J., González-Sampériz, P., Giralt, S., Taberner, C., Herrera, C. and Gibert, R. O. (2007). Volcanic controls on lacustrine sedimentation: The late Quaternary depositional evolution of lake Chungará (Northern Chile). *Sedimentology*, in press. DOI: 10.1111/j.1365-3091.2007.00878.x

Seltzer, G.O., Rodbell, D.T., Burns, S., 2000. Isotopic evidence for late Quaternary climatic change in tropical South America.Geology 28, 35-38.

Schwalb, A., Burns, S.J. and Kelts, K. 1999. Holocene environments from stable isotope stratigraphy of ostracods and authigenic carbonate in Chilean Altiplano lakes. Palaeogeography, Palaeoclimatology, Palaeoecology, 148: 153-168.

Shemesh, A., Charles, C.D., Fairbanks, R.G., 1992. Oxygen isotopes in biogenic silica: global changes in ocean temperature and isotopic composition. Science 256, 1434–1436.

Shen, C.C., Edwards, R.L., Cheng, H., Dorale, J.A., Thomas, R.B., Moran, S.B. and Edmonds, H.N. (2002) Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. *Chem. Geol.,* 185, 165-178.

Stuiver, M., Reimer, P. J., Bard, E., Beck, J. W., Burr, G. S., Hughen, K. A., Kromer, B., McCormac, G., van der Plicht, J. and Spurk, M. (1998). INTCAL98 Radiocarbon Age Calibration, 24000-0 cal BP. *Radiocarbon* 40, 1041-1083.

Tapia, P.M., Fritz, S.C., Baker, P.A., Seltzer, G.O., and Dunbar, R.B., 2003, A late Quaternary diatom record of tropical climatic history from Lake Titicaca (Bolivia/Peru) Palaeogeography, Palaeoclimatology, and Palaeoecology, 194, 139–164.

Thompson, L.G., Mosley-Thompson, E., Dansgaard, W. and Grootes, P.M. (1986). The Little Ice Age as recorded in the stratigraphy of the tropical Quelccaya Ice Cap. *Science* 234, 361-364.

Valero-Garces, B.L., Grosjean, M., Schwalb, A., Schreir, H., Kelts, K. and Messerli, B. (2000). Late Quaternary lacustrine deposition in the Chilean Altiplano (18º-28ºS). In: *Lake Basins through Space and Time.* (Eds. Gierlowski-Kordech, E., Kelts, K.). *Am. Assoc. Petr. Geol. Studies in Geology.* 46, pp. 625-636.

Valero-Garcés, B.L., Delgado-Huertas, A., Navas, A., Edwards, L., Schwalb, A. and Ratto, N. (2003) Patterns of regional hydrological variability in central-southern Altiplano (18º-26ºS) lakes during the last 500 years. *Palaeogeogr., Palaeoclimatol., Palaeoecol.,* 194, 319-338.

Vuille, M. (1999). Atmospheric circulation over the Bolivian altiplano during dry and wet periods and extreme phases of the Southern Oscillation. *International Journal of Climatology* 19, 1579-1600.

Wolfe, B.B., Aravena, R., Abbott, M.B., Seltzer, G.O. and Gibson, J.J. 2001. Reconstruction of paleohydrology and paleohumidity from oxygen isotope records in the Bolivian Andes. Palaeogeography, Palaeoclimatology, Palaeoecology, 176: 177-192.

Wörner, G., Hammerschmidt, K., Henjes-Kunst, F. and Wilke, H. (2000). Geochronology (40Ar/39Ar, K-Ar and He-exposure ages) of Cenozoic magmatic rocks from northern Chile (18-22ºS): implications for magmatism and tectonic evolution of the central Andes. *Revista Geológica de Chile* 27, 205-240.