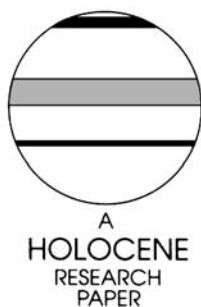


Stable isotopic record of hydrological changes in subtropical Laguna Mar Chiquita (Argentina) over the last 230 years

Eduardo L. Piovano,^{1,2*} Daniel Ariztegui,³ Stefano M. Bernasconi² and Judith A. McKenzie²

(¹Centro de Investigaciones Geoquímicas y de Procesos de Superficie, F.C.E.F. y N., University of Córdoba, Av. Velez Sarsfield 1611, X5016GCA Córdoba, Argentina; ²Geological Institute, ETH-Zentrum, Sonneggstrasse 5, 8092 Zürich, Switzerland; ³Institute Forel and Department of Geology and Paleontology, University of Geneva, Rue des Maraichers 13, 1205 Geneva, Switzerland)

Received 3 December 2001; received manuscript accepted 12 June 2003



Abstract: Laguna Mar Chiquita, a highly variable closed saline lake located in the Pampean plains of central Argentina, is presently the largest saline lake in South America (~6000 km²). The availability of historical, instrumental lake-level and salinity data for the past 100 years allows for the calibration of the isotopic archive recorded in the lake sediments. Prolonged intervals with either negative or positive hydrological balances have severely modified lakewater levels, salinity and primary productivity, and have also controlled the isotopic composition of both the authigenic carbonate ($\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$) and sedimentary organic matter ($\delta^{13}\text{C}_{\text{om}}$). Extensive evaporation during lowstand stages results in an enrichment of ¹⁸O and ¹³C in the lake waters, and is recorded in the sediments as the most positive $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ compositions (0.0‰ and -1.9‰, respectively). Conversely, more negative $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values (-1.8‰ and -3.8‰, respectively) are the result of increasing freshwater input into the lake system. The $\delta^{13}\text{C}_{\text{om}}$ values are related to the isotopic composition of the dissolved inorganic carbon pool and the carbonate equilibrium of the lake water. Relatively low $\delta^{13}\text{C}_{\text{om}}$ values correspond with high lake levels, low salinity, low alkalinity and high lake productivity. High salinity during lowstands diminishes the amount of primary production and the $\delta^{13}\text{C}_{\text{om}}$ value is correspondingly high. The calibrated isotopic model was extrapolated to reconstruct precipitation-evaporation variability from the end of the 'Little Ice Age' (c. AD 1770) to the present. Low water levels predominated until the last quarter of the twentieth century, when a positive hydrological balance without equivalent in the previous history of Laguna Mar Chiquita became dominant.

Key words: Stable isotopes, saline lake, palaeohydrology, 'Little Ice Age', twentieth century, central Argentina.

Introduction

Variations in the hydrological balance of saline lakes drive changes in the primary productivity, mineral precipitation and sedimentation patterns, which can be distinctly preserved in the lacustrine record (Hardie *et al.*, 1978; Last, 1993; Newton, 1994; Jellison *et al.*, 1996). Environmental conditions during sediment deposition can be obtained from many proxies; however, stable oxygen and carbon isotopes, in both

authigenic carbonates and autochthonous organic matter, provide unrivalled information to reconstruct past limnological conditions (Kelts and Talbot, 1990; Talbot, 1990; Johnson *et al.*, 1991; Li and Ku, 1997; Hassan *et al.*, 1997; Meyers and Lallier-Vergès, 1999).

Laguna Mar Chiquita is a shallow saline lake in the subtropical Pampean plains of Argentina (30°54'S–62°51'W; Figure 1). Temporal variability in precipitation and river discharge has produced dramatic lake-level fluctuations,

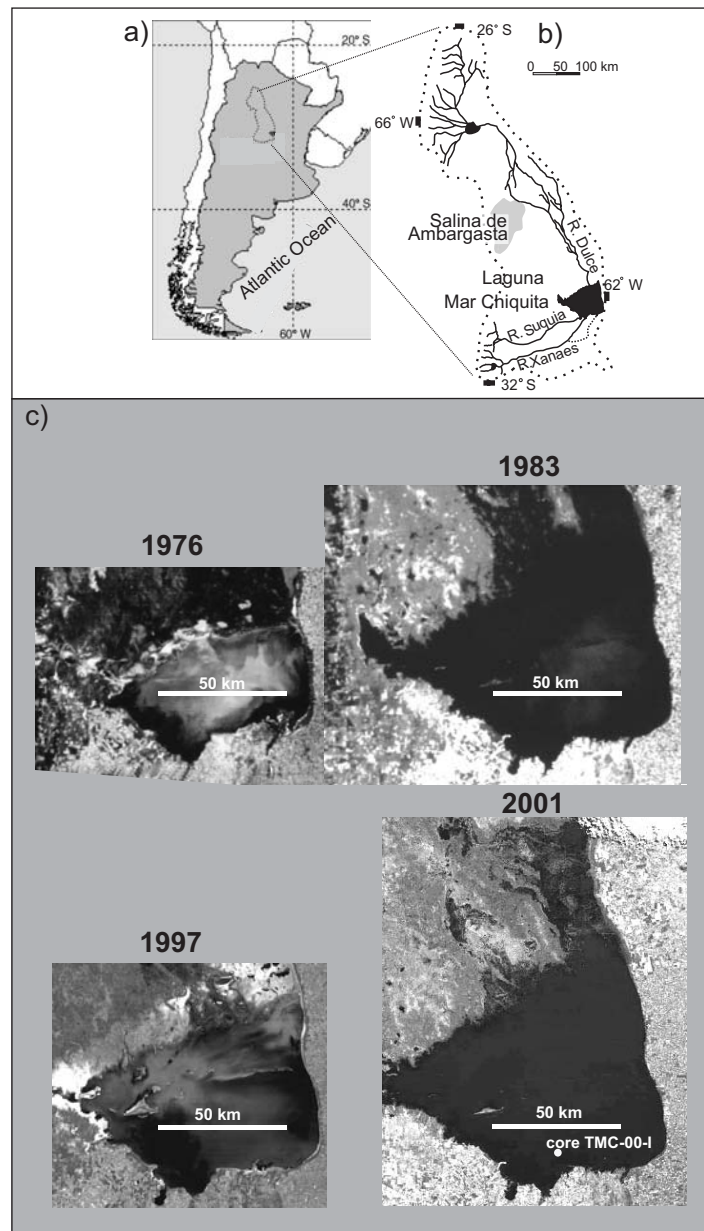


Figure 1 (a) Location map of Laguna Mar Chiquita in central Argentina. (b) Enlargement displaying the lake catchment area of $\sim 37\,500\text{ km}^2$. (c) Satellite images showing the lake-surface variations between 1976 and 2001. The position of the studied sedimentary core is shown in the 2001 satellite image. Satellite images were obtained at <http://conae.gov.ar>.

making Laguna Mar Chiquita a sensitive climatic indicator (Piovano *et al.*, 2002). Historical and instrumental data show that during dry intervals the lake surface was reduced to $\sim 1000\text{ km}^2$, whereas during periods with a positive hydrological balance the lake has covered an area of up to $\sim 6000\text{ km}^2$. During highstands, as at present, Laguna Mar Chiquita becomes not only the largest saline lake in South America but also one of the largest in the world.

Based on a sedimentological model, Piovano *et al.* (2002) reconstructed the hydrological fluctuation of the lake since the end of the 'Little Ice Age' (*c.* AD 1770). This was accomplished through the combination of historical and instrumental lake-level data with an in-depth sedimentological and geochemical study of well-dated cores. Low lake levels with an associated increase in water salinity have promoted the development of gypsum-calcite-halite layers and a substantial decrease in primary productivity, as reflected by the deposition of evaporite mineral-rich and organic matter-poor

sediments. Conversely, high lake levels are recorded as diatomaceous organic matter-rich muds with low carbonate contents. The clear sedimentological and geochemical imprint of lake-level fluctuations encouraged us to analyse the oxygen and carbon stable isotopic composition in both authigenic carbonates and organic matter, and to identify their response to these lake-level variations. In particular, previous lake-level reconstructions, mostly based on sedimentological evidence, can now be improved by using sedimentary organic matter carbon isotope ratios as an additional proxy to quantify both past lake-level and salinity changes.

This paper presents climate data for the last 230 years from an area of the globe where limnogeological studies combining high-resolution geochemical and sedimentological data are still rare. Furthermore, the sediments' calibration with historical data leads to better understanding of the causes and mechanisms associated with isotopic fractionation in highly variable saline lakes.

Methodology

A stable isotopic study of authigenic carbonates and bulk organic matter was undertaken on material from a 1.15 m long sedimentary core. Core TMC-00-I was retrieved in July 2000 from the deepest area of the lake using a hand corer beaker sampler. Figure 1c shows the core location in a 2001 satellite image.

A robust ^{210}Pb chronology for core TMC-00-I allowed us to link the isotopic record to both well-documented twentieth-century lake-level changes and measurements of lakewater salinities. Further information on the dating technique as well as the chronological model and sedimentation rates can be found in Piovano *et al.* (2002).

Historical data such as salinities, shoreline positions and photographs were taken from Von Grumbkow (1890), Doring (1907), Frank (1915), Kanter (1935), Bertoldi de Pomar (1953), Durigneux (1978) and Martínez (1991). Water salinities from AD 1995–2000 were obtained from unpublished reports. The annual river inflow data were standardized using the equation $Q'(Y) = [Q(Y) - Q_M] / Q_M$, where $Q(Y)$ is the annual runoff and Q_M is the mean annual runoff. The gauging data series correspond to a monthly mean (Vörösmarty *et al.*, 1998).

Total organic and inorganic carbon (TOC and TIC, respectively) in sediments were obtained by coulometry (Coulometric Inc). Analytical reproducibility is $\pm 1\%$ for the TIC content. TOC was obtained as the difference between the measured inorganic carbon and total carbon (TC). Analytical reproducibility is $\pm 2\%$ for TC content. Carbonate and organic carbon accumulation rates were calculated according to Niessen *et al.* (1992).

Samples for carbon isotope analysis of sedimentary organic matter and fresh planktonic organisms were decalcified with 1N HCl and then washed in deionized water. They were loaded into tin sample capsules and measured using a Carlo-Erba CNS[®] analyser with autosampler coupled to a Fisons Optima mass spectrometer. Carbon isotope values are reported in the conventional delta notation with respect to VPDB. Analytical reproducibility for $\delta^{13}\text{C}$, determined on repeated analyses of NBS 22 and internal standards, is better than $\pm 0.1\%$. The nitrogen content was determined with the same procedure as above but on bulk untreated samples. Analytical reproducibility is $\pm 0.2\%$ for N content.

For the determination of the isotopic composition of carbonates, the samples were washed in distilled water to remove soluble salts, and then reacted at 90°C with 100% phosphoric acid using an automated carbonate device connected to a VG-Prism mass spectrometer. The results are calibrated against NBS 18, NBS 19 and NBS 20 and reported in the conventional delta notation with reference to VPDB. Analytical reproducibility of the method, based on repeated analysis of standards, is better than $\pm 0.1\%$ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Samples with carbonate contents lower than 2% showed a poor reproducibility, possibly due to sample inhomogeneities or to some contamination. The results presented here are the average of at least three measurements with a reproducibility of $\pm 0.5\%$. The carbonate and organic matter isotope data are given in Table 1.

The oxygen isotopic composition of the lake, rivers and groundwaters was determined by equilibration with CO_2 using an automated Isoprep-18 equilibration device coupled to a Micromass Optima mass spectrometer. Analytical reproducibility based on repeat analysis of internal standards is $\pm 0.05\%$. All oxygen isotope data for the waters are reported in the standard delta notation with respect to Vienna standard mean ocean water (VSMOW).

Site description, climate and hydrology

Laguna Mar Chiquita is a large and shallow saline lake located in a tectonic depression formed during the middle Pleistocene (Kröhling and Iriondo, 1999) in the Pampean plains of Argentina (Figure 1a). The geomorphology of the area and lake biota have been previously described by Kröhling and Iriondo (1999) and Reati *et al.* (1997), respectively.

This subtropical region is characterized by austral summer precipitation and dry winters. The Amazon basin is the principal source of moisture for central South America (Rao *et al.*, 1996) and low-level jets (LLJ) east of the Andes, known as Pampean LLJ, are an important mechanism for the summer poleward transport of the water vapour. LLJ variability largely determines the hydrological balance of the region (Berri and Inzunza, 1993; Nogués-Paegle and Mo, 1997; Saulo *et al.*, 2000). As a consequence of changes in the regional water budget, long dry intervals occurred throughout the first 75 years of the twentieth century, whereas a recent increasing trend in streamflows has been reported in the Río de la Plata basin (Genta *et al.*, 1998; García and Vargas, 1998; Depetris *et al.*, 2004).

Laguna Mar Chiquita is fed mainly by three rivers (Figure 1b), but groundwater seepage is also an important source of inflow. The main river is the Río Dulce with an average annual discharge of 3.0 km^3 , whereas Río Suquia and Río Xanaes both have a total annual discharge of 0.7 km^3 (Reati *et al.*, 1997). The system has no surficial outlet and the loss of water is by evaporation, which is additionally favoured by the panlike shape of the lake. The present-day area is approximately 6000 km^2 with a maximum depth of 10 m. Historical and instrumental records show that water-level fluctuations characterize the twentieth-century history of the lake (Figure 2a), defining low- and highstands (Piovano *et al.*, 2002). A lake-level curve was reconstructed using historical information from 1890 to 1967, whereas continuous instrumental data have been available since 1967. Low and high water stands were defined as below or above the 66.5 m a.s.l. water altitude, respectively (corresponding to the lake level during 1977), and are represented in Figure 2a as negative or positive values in grey and black shading areas, respectively. Lake-level changes are closely associated with rainfall variability. Large rainfall fluctuations in the Mar Chiquita area occurred during the twentieth century, with annual values ranging from a minimum of 303 mm yr^{-1} to a maximum of 1074 mm yr^{-1} . During the interval 1934–72 average annual precipitation was 653 mm yr^{-1} , while the average increased to 810 mm yr^{-1} during the interval 1973–97. This change in precipitation controls the amount of river discharge (Figure 2, b–d) and, consequently, water-level variations in Laguna Mar Chiquita. Dry intervals are synchronous with lowstands and low river discharge (grey areas), and increasing lake levels and river discharges (black areas) have occurred during wet intervals.

High salinities of up to 360 g L^{-1} were reported during lowstands in 1911 (Frank, 1915), 251 g L^{-1} in 1951 (Bertoldi de Pomar, 1953) and 270 g L^{-1} in 1970 (Martínez, 1991). The long lowstand during the first 75 years of the twentieth century was interrupted only by short-term pulses of water-level increases in 1915 (Frank, 1915), between ~ 1931 and 1935 (Kanter, 1935) and between 1959 and 1961 as revealed in photographic documents. In the early 1970s the lake level started to rise, reaching a highstand that has prevailed since 1977. Comparatively lower salinities (e.g., 29 g L^{-1} in 1986; 35 g L^{-1} in 1989; Martínez *et al.*, 1994) characterize this latest and ongoing highstand. Within five years, from 1977 to 1982, the maximum depth increased from 4.0 m to 8.6 m, the lake

Table 1 Analytical results of core samples and suspended matter in the rivers and lake (avg = average value, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ = isotope ratios of carbonate, $\delta^{13}\text{C}_{\text{om}}$ = isotope ratio of organic matter)

Sample no.	Position (cm)	$\delta^{13}\text{C}_{\text{carb}}$ (‰)	$\delta^{18}\text{O}_{\text{carb}}$ (‰)	$\delta^{13}\text{C}_{\text{cm}}$ (‰)	C/N
1avg	0.4	-4.4	-1.4	-20.9	10.8
40	1.4	-4.3	-2.6	-20.7	—
2	2.4	-2.9	-1.1	-21.1	—
41avg	3.4	-5.0	-3.1	-21.3	8.7
42	4.4	-2.1	-1.2	-20.2	—
3	5.4	-3.6	-1.4	-21.0	—
43	6.4	-4.1	-0.9	-20.8	8.7
44avg	7.4	-4.6	-3.0	-20.7	—
45	8.4	-3.6	-2.3	-21.1	—
46avg	9.4	-4.3	-2.9	-21.1	—
4	10.9	-3.2	-1.3	-20.7	—
47avg	11.4	-4.2	-3.1	-20.7	9.5
48	12.4	-4.2	-2.3	-20.5	—
49	13.4	-3.7	-0.3	-20.5	—
50	14.4	-4.2	-0.9	-20.9	—
51	15.4	-5.3	-1.3	-21.0	—
5	16.4	-2.8	-0.4	-23.3	—
6	18.4	-2.9	-1.8	-21.3	8.9
7	20.8	-3.5	-2.8	-21.3	8.1
8	22.4	-2.9	-1.5	-21.1	8.0
9	23.4	-1.7	-0.2	-21.1	8.4
52	25.4	-2.5	-1.0	-19.1	9.6
10	26.9	-2.5	-1.0	-18.9	—
53	27.4	-1.9	-0.5	-18.1	6.7
54	29.4	-2.3	-0.2	-17.2	—
11	31.9	-1.8	0.5	-17.2	—
12	33.4	-2.2	0.2	-16.4	27.5
55	35.4	-2.0	0.0	-17.3	6.9
13	36.9	-2.4	-0.2	-17.5	—
14	40.4	-2.6	-0.2	-16.2	10.4
56	44.4	-1.7	0.0	-18.2	9.5
15	47.4	-1.6	0.8	-17.5	—
16	50.9	-2.2	0.1	-17.5	9.9
57	53.4	-1.6	0.3	-17.5	12.7
17	55.4	-1.6	-0.1	-17.3	—
58	57.4	-1.1	-0.2	-17.4	10.2
18	61.2	-1.5	0.4	-16.6	—
19	64.1	-1.7	-0.2	-16.8	11.6
59	66.4	-1.8	0.4	-17.0	15.1
20	70.9	-1.4	0.2	-17.2	—
60	72.0	-0.5	1.7	-17.5	11.0
21	73.9	-0.7	0.3	-17.9	—
22	75.8	-2.7	-0.7	-16.1	10.8
23	78.4	-2.1	-0.5	-16.7	10.7
24	80.4	-2.1	-0.1	-16.2	8.5
61	82.4	-2.1	-0.4	-17.2	11.3
25	84.4	-1.8	0.1	-17.3	—
62	86.4	-1.3	0.6	-17.0	12.2
26	89.4	-1.5	0.2	-17.1	—
63	91.4	-1.5	0.4	-16.7	8.8
27	93.4	-2.1	-0.1	-17.3	—
28	96.6	-1.6	0.4	-16.9	11.3
29	98.9	-2.5	-0.7	-15.8	11.0
37	101.4	-1.5	-0.8	-18.0	11.9
30	102.4	-2.3	-0.4	-16.3	11.9
31	106.4	-1.9	0.7	-16.6	11.8
32	108.4	-2.2	-0.2	-17.0	4.3
38	111.1	-2.7	0.0	-17.2	10.0
64	112.4	-1.8	1.1	-16.5	14.7
34	113.9	-1.9	-0.9	-18.4	13.4
Gastropod avg	0.0	-2.6	1.2	—	—
Gastropod	3.4	-2.5	1.1	—	—
Gastropod	6.4	-4.2	0.5	—	—
Gastropod	13.4	-3.6	2.6	—	—
Gastropod avg	14.4	-3.5	1.7	—	—

Table 1. (continued)

Sample no.	Position (cm)	$\delta^{13}\text{C}_{\text{carb}}$ (‰)	$\delta^{18}\text{O}_{\text{carb}}$ (‰)	$\delta^{13}\text{C}_{\text{cm}}$ (‰)	C/N
Río Suquia-7/99	suspended matter	—	—	-22.8	—
Río Suquia-12/99	suspended matter	—	—	-20.5	—
Río Xanaes-7/99	suspended matter	—	—	-19.3	—
Río Xanaes-12/99	suspended matter	—	—	-21.0	—
Río Dulca-7/99	suspended matter	—	—	-22.9	—
Río Dulca-7/00	suspended matter	—	—	-26.0	—
Lake-3/2000	suspended matter	—	—	-20.9	—
Lake 7/2000	suspended matter	—	—	-20.1	—

surface from 1960 km² to 5770 km² and the volume from 4240 km³ to 21 400 km³ (Reati *et al.*, 1997). This variation as well as the 1997 lake-level drop and a later increase are clearly seen in the satellite images shown in Figure 1c.

Lake waters are alkaline (pH > 8) of Na-Cl-SO₄ type. During lowstands, they are supersaturated with respect to both calcite and gypsum, whereas they remain supersaturated with respect to calcite but only occasionally with respect to gypsum during highstands (Martínez *et al.*, 1994). The shallow depth of the lake, in addition to constant winds, results in a well-mixed water-column. Bottom sediments, however, are under permanent anoxic conditions due to the presence of high quantities of organic matter allowing for the development of sulphate-reducing conditions at the sediment-water interface (Martínez *et al.*, 1994).

The Laguna Mar Chiquita sedimentary model

Using a well-constrained ²¹⁰Pb chronology, Piovano *et al.* (2002) determined the sedimentological response of the lake system to the last 100 years of documented lake-level changes. Two ²¹⁰Pb age profiles in sediment cores from the main water body were used to develop an age model to link the sedimentary record to documented lake-level changes and to estimate sedimentation rates for the different lake-level stands. The last highstand yields sedimentation rates between 0.77 and 1.12 cm yr⁻¹, while sedimentation rates during lowstands are between 0.25 and 0.34 cm yr⁻¹. A long-term average sedimentation rate of 0.45 cm yr⁻¹ was used for dating below 54 cm, the lower limit of ²¹⁰Pb dating.

Overall, the Laguna Mar Chiquita sedimentary cores comprise two main lithological units, A and B (Figure 3). Unit A, laminated to banded organic carbon-rich muds, present in the uppermost part of the sedimentary record shows a distinctive dark colour associated with organic matter enrichment and low carbonate content. ²¹⁰Pb ages indicate that this unit has accumulated during the most recent ongoing highstand (i.e., since 1977). Unit B banded to laminated muds with evaporites was further subdivided into three subunits: B₁, B₂ and B₃. Subunit B₁ was defined in the transition from the uppermost organic matter-rich sediments (unit A) to evaporite-rich and TOC-poor subunit B₃ (see Figure 3). The age model indicates that the deposition of the uppermost subunit B₁ corresponds to the transition from low to high lake stands between 1972 and 1976 and during the documented short-term rising pulse between 1959 and 1962. This sediment type is additionally present at three different core levels, which correspond to 1878, 1845 and 1803. Subunit B₂ is formed by fine-grained calcite lamina with less abundant gypsum,

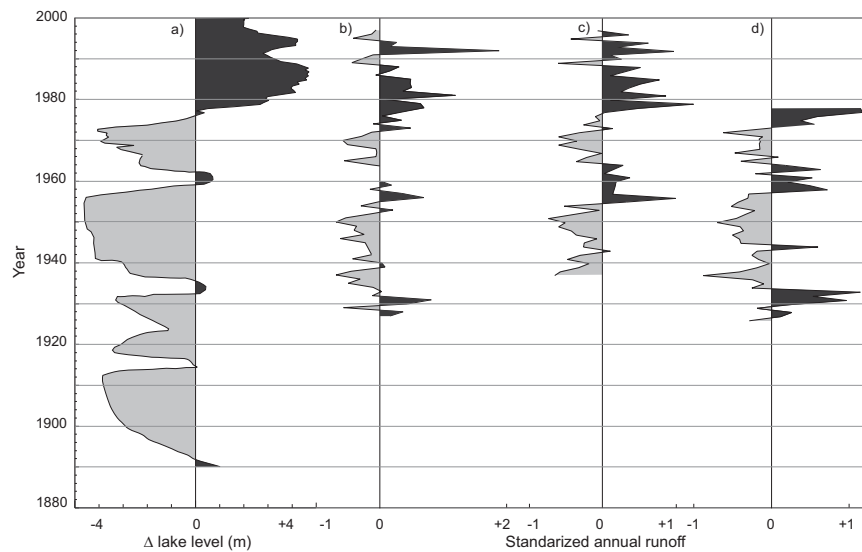


Figure 2 (a) Lake-level curve for Mar Chiquita (after Piovano *et al.*, 2002). Highstands are indicated by black, and lowstands by grey. Standardized runoff of rivers Suquia (b), Xanaes (c) and Dulce (d). Discharges above and below the mean annual runoff are in black and grey, respectively.

interbedded with organic-rich muds. This subunit occurs four times in the lower half of the core, but only the 56–59 cm level (1894) can be linked to the lake-level curve (Figure 2a). This comparison indicates that subunit B₂ sediments correspond to a low to intermediate stage of the lake during short-term lake-level rises. Subunit B₃ is the most abundant lithology and is mainly composed of thin- to thick-banded sediments that contain evaporitic layers up to 2 cm thick, consisting of a calcite-gypsum-halite assemblage. The age model indicates that deposition of subunit B₃ corresponds to reported lowstand intervals of the lake prior to 1972. Furthermore, the evaporitic layers throughout the cores correspond to years of documented extremely low lake levels.

The significant correlation between lithological units and known lake-level changes (since 1894) allowed the formulation of a sedimentary model that reflects the lake fluctuations. The variations in water salinity during lake-level changes controls both the amount of primary producers in the lake and the precipitation of authigenic minerals observed as distinctive organic-rich (unit A) or evaporite-rich (unit B) lacustrine facies at highstands and lowstands respectively. The extrapolation of this sedimentary model to the remainder core, i.e., sediments older than 1894, allowed the reconstruction of a lake-level curve covering the substantial hydrological changes that occurred within and after the end of the ‘Little Ice Age’ as shown in Figure 3.

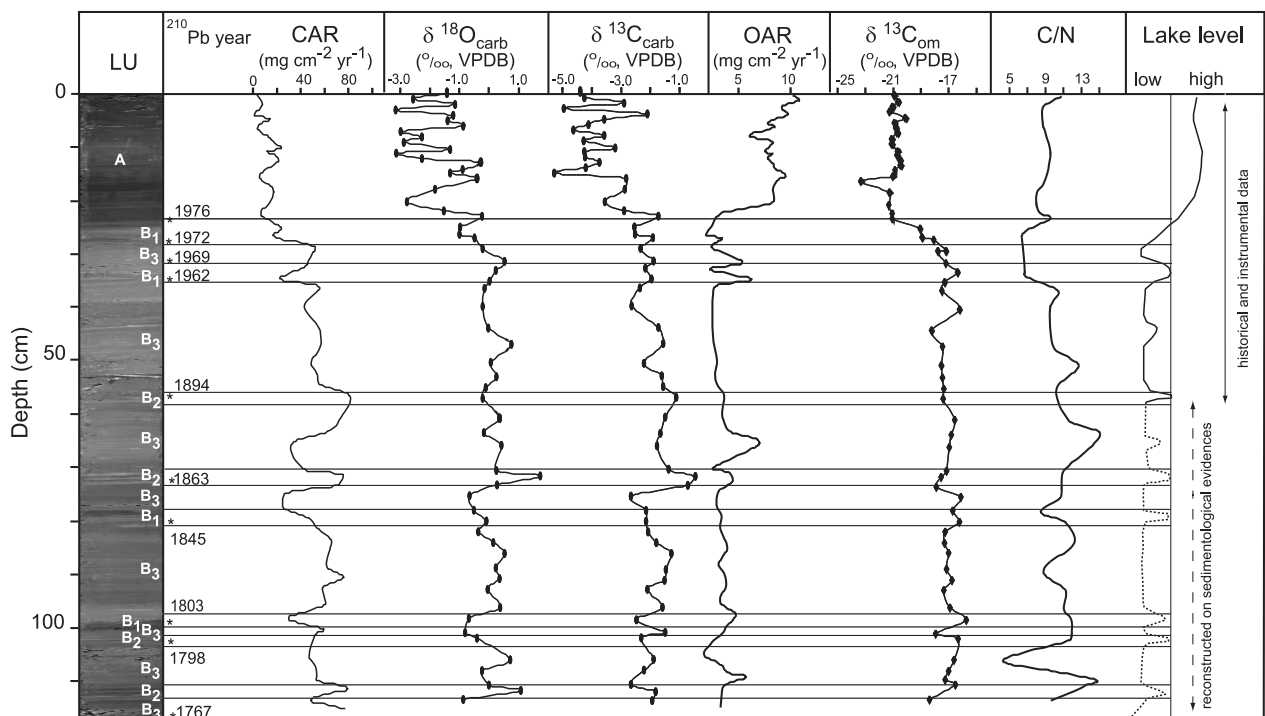


Figure 3 Lithological units (LU), chronologies (AD years; the corresponding level is indicated by *) and lake-level curve are based on sedimentological evidences (modified from Piovano *et al.*, 2002). Carbonate accumulation rate (CAR), organic matter accumulation rate (OAR), isotopic compositions of carbonates and sedimentary organic matter, and C/N ratios are shown.

Results

Figure 3 shows the carbonate and organic carbon accumulation rates (CAR and OAR, respectively), C/N ratios, and the isotopic compositions of both carbonate and organic matter for sedimentary record of the last 230 years. ^{210}Pb chronologies and the reconstructed documented lake-level curve are taken from Piovano *et al.* (2002). Isotopic results are presented in Table 1.

Carbon and oxygen isotopic compositions show an overall decreasing trend from base to top, with some distinctive shifts that can be correlated with lithologic changes. Unit A, the record of the present highstand, is characterized by more negative isotopic compositions for both carbonate and organic matter. Conversely, unit B, the record of low lake levels, shows ^{18}O and ^{13}C enrichment in both carbonate and organic matter relative to unit A.

Isotopes in carbonates and waters

SEM and XRD analyses indicate that Laguna Mar Chiquita carbonates are authigenic and mostly calcite (Piovano *et al.*, 2002). Their $\delta^{18}\text{O}_{\text{carb}}$ values range from -3.1‰ to 1.7‰ , and $\delta^{13}\text{C}_{\text{carb}}$ values range between -5.3‰ and -0.5‰ (Figure 3). Sediments deposited during lowstands (unit B) have $\delta^{18}\text{O}_{\text{carb}}$ values ranging from -1.0‰ to 1.7‰ (average = 0.0‰), whereas $\delta^{18}\text{O}_{\text{carb}}$ values decrease to -3.1‰ (average = -1.7‰) in sediments accumulated during high water levels (unit A).

$\delta^{13}\text{C}_{\text{carb}}$ values vary from -2.7‰ to -0.5‰ (average = -1.9‰) in evaporite-rich sediments (unit B), whereas the organic matter-rich sediments (unit A) have values ranging between -5.3‰ and -2.1‰ (average = -3.8‰). The most positive excursions in both $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values occur in levels associated with evaporites within subunit B₃ ($\delta^{18}\text{O}_{\text{carb}} = 0.8\text{‰}$ and $\delta^{13}\text{C}_{\text{carb}} = -1.3\text{‰}$) and in the thinly laminated calcite in subunit B₂ ($\delta^{18}\text{O}_{\text{carb}} = 1.7\text{‰}$ and $\delta^{13}\text{C}_{\text{carb}} = -0.5\text{‰}$). Intermediate isotope values between those found in units A and B are found in subunit B₁ ($\delta^{18}\text{O}_{\text{carb}} = -1.0\text{‰}$ and $\delta^{13}\text{C}_{\text{carb}} = -2.5\text{‰}$). The entire data set exhibits covariance between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values (Figure 4a; $r = 0.8$).

The $\delta^{18}\text{O}$ values from Laguna Mar Chiquita surface waters in year 2000 are 1.15‰ and 1.10‰ for summer samples, decreasing to 0.44‰ and 0.45‰ during winter. Average $\delta^{18}\text{O}$ values in inflowing groundwater and river waters are -6.4‰ and -5.2‰ , respectively, indicating strong evaporative enrichment.

C/N ratios and $\delta^{13}\text{C}$ in organic matter

The C/N ratio of the sedimentary organic matter in the core ranges from 4.3 to 15.1 with an average value of 10.2 (Figure 3). The average C/N ratios for organic carbon-rich muds (unit A) and evaporite-rich sediments (unit B) are 9.0 and 10.6, respectively. The record of $\delta^{13}\text{C}_{\text{om}}$ varies from -15.8‰ to -23.3‰ showing two distinct patterns closely associated with the lithological units. The evaporite-rich muds correlate with ^{13}C -enriched organic matter with values ranging from -19.1‰ to -16.2‰ (average = -17.2‰). Intermediate values in the $\delta^{13}\text{C}_{\text{om}}$ are observed in the uppermost portion of unit B in the transition to unit A between 23.4 and 27.4 cm in the core (Table 1). The organic matter-rich unit A exhibits the lowest $\delta^{13}\text{C}_{\text{om}}$ values ranging between -23.3‰ and -20.2‰ (average = -21.0‰).

Fresh planktonic organic matter sampled at the end of austral summer has a $\delta^{13}\text{C}_{\text{om}}$ value of -20.9‰ and in winter -20.1‰ . The $\delta^{13}\text{C}_{\text{om}}$ value of suspended organic matter in the rivers that feed the lake ranges from -19.3‰ to -22.9‰ , with a minimum of -26.0‰ in one sample (see Table 1).

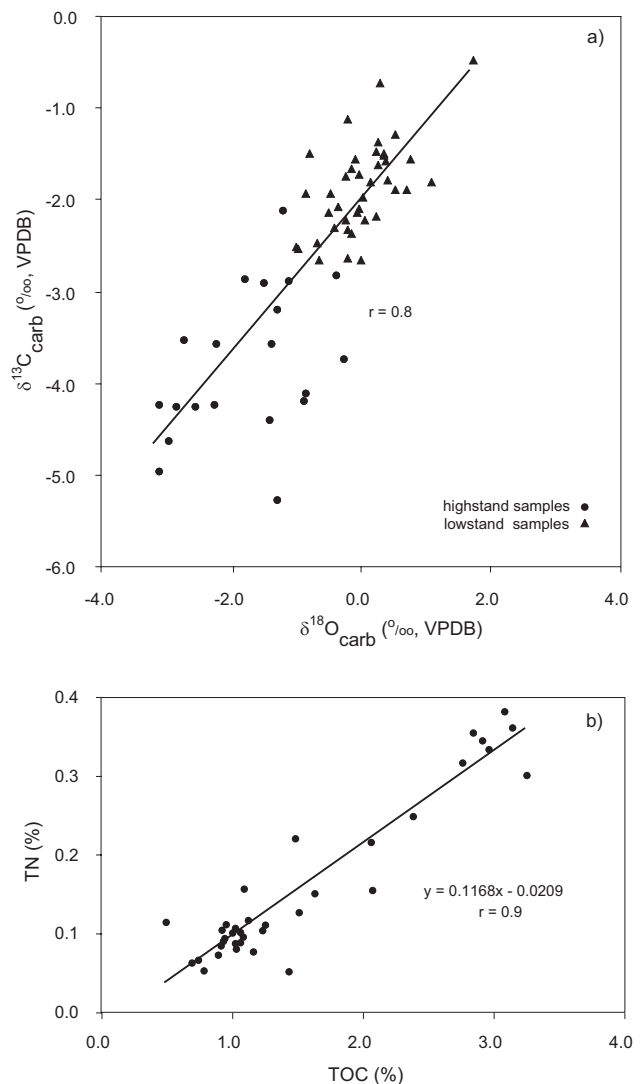


Figure 4 (a) The O and C isotopic compositions of authigenic calcite show a clear co-variance. Symbols indicate different stages of the lake during carbonate precipitation. (b) Linear correlation between TOC and total nitrogen (TN) percentages indicating a relatively uniform source of OM throughout the sediments. The zero x-intercept of the regression line indicates the lack of inorganic nitrogen contribution.

The isotopic response as a proxy for fluctuations of the precipitation-evaporation (P-E) ratio

The substantial correlation between documented water-level fluctuations, sedimentary facies and the stable isotopic composition of lacustrine carbonate and sedimentary organic matter (Figure 3) indicate that stable isotopes composition of lake water is sensitive to changing P-E ratio in Laguna Mar Chiquita. Thus, the isotopic signal can be used as a fingerprint of palaeohydrological changes, which trigger fluctuations in the lake level, water salinity, the dissolved inorganic carbon (DIC) pool, and primary productivity.

The carbonate response

Carbonate precipitation generally occurs close to isotopic equilibrium with lake waters (Stuiver, 1970; McKenzie, 1985; Talbot, 1990; Teranes *et al.*, 1999, Teranes and McKenzie, 2001) and the co-variance between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ in

closed basins has been interpreted as an indicator of water-level fluctuations and P-E ratio variability (Talbot, 1990; Kelts and Talbot, 1990; Li and Ku, 1997). We have assessed the temperature-dependent isotopic equilibrium of analysed carbonates using the equation of Epstein *et al.* (1953). Comparing the measured lakewater isotope composition with the uppermost 2.4 cm of the $\delta^{18}\text{O}_{\text{carb}}$ record, we calculated a range of water temperature between 26 and 30°C, which is in the range of measured lakewater temperatures. Thus, we propose that the linear covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ($r = 0.8$; Figure 4a) in the carbonate isotopic data set from Laguna Mar Chiquita reflects precipitation from waters with varying isotopic composition, which is the consequence of varying P-E ratios (i.e., high river discharge and precipitation versus high evaporation and low to null river discharge). Prolonged periods with negative water balances produce a preferential evaporation of ^{16}O -rich H_2O and outgassing of ^{12}C -rich CO_2 resulting in an enrichment of ^{18}O and ^{13}C in lake waters during lowstands (Stiller *et al.*, 1985; Talbot and Kelts, 1990; Li and Ku, 1997). Increases in the ionic concentrations of the lake water during negative P-E ratios (i.e., 360 g L^{-1} in 1911; 251 g L^{-1} in 1951, 270 g L^{-1} in 1970; see Table 2) are associated with increases in alkalinity, as shown by high carbonate accumulation rates ($\text{CAR} = 20\text{--}300 \text{ mg cm}^{-2} \text{ yr}^{-1}$; Figure 3). Evaporite-rich muds (unit B) accumulated during intervals of negative P-E ratios are characterized by high $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values averaging 0.0‰ and -1.9‰ , respectively. The most positive excursions in both $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values occur in the calcite-gypsum-halite layers of subunit B₃, which were precipitated at very low lake levels, and in the thinly laminated calcite in subunit B₂. Discrete lamina of calcite (in subunit B₂) associated with gypsum are indicating precipitation at high ionic lakewater concentration after pulses of short-term lake level rise.

During intervals of positive P-E ratios, a higher input of freshwater leads to highstands (Figure 2, b–d) decreasing both the salinity ($\text{TDS} < 60 \text{ g L}^{-1}$) and precipitation rate of carbonates ($\text{CAR} = 1\text{--}38 \text{ mg cm}^{-2} \text{ yr}^{-1}$, Figure 3). Low $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values in the uppermost organic carbon-rich muds (unit A; -1.8‰ and -3.8‰ , respectively) reflect precipitation from isotopically lighter lake water due to the increased

inflow of river and meteoric waters. The presence of calcite throughout all the lithologic units is due to the permanent calcite supersaturation of lake waters with $\text{pH} > 8.3$ even during the most dilute stages of the lake.

The $\delta^{18}\text{O}$ value of the lake waters is greater by 5 to 6‰ than the inflowing rivers and groundwaters. In the lake, evaporation reaches a maximal during summer months producing a more ^{18}O -enriched water (average $\delta^{18}\text{O} = 1.12\text{‰}$), than in winter (average $\delta^{18}\text{O} = 0.44\text{‰}$). This small isotopic change (0.68‰) from summer to winter is most probably the result of a well-mixed water-column throughout the year due to the combination of constant wind and shallow waters.

The organic matter response

The average C/N ratio (10.2) indicates that aquatic organisms (i.e., blue-green and green algae) are the main source of the sedimentary organic matter (i.e., Meyers and Lallier-Vergès, 1999). The C/N ratio ranges from 4.3 to 15.1 (Figure 3) and, together with the good correlation between TOC and total nitrogen (TN) ($r = 0.94$), implies a relatively uniform source of OM throughout the sequence, even during intervals of contrasting river discharge. No inorganic nitrogen contribution to the measured total N is indicated by the zero x-intercept of the regression line on the TN versus TOC diagram (Figure 4b).

Water-salinity fluctuations severely regulate the lake biodiversity. Under hypersaline conditions, there is a very limited number of higher-order organisms, whereas they increase at lower salinities during highstands (Reati *et al.*, 1997). Less productive phases recorded in unit B are characterized by a low organic carbon accumulation rate (OAR, $3.28 \text{ mg cm}^{-2} \text{ yr}^{-1}$) and high CARs ($20\text{--}300 \text{ mg cm}^{-2} \text{ yr}^{-1}$), combined with more ^{13}C -enriched organic matter (-19.1‰ to -16.2‰). Low salinities during highstands result in the highest primary productivity as shown by high OARs (6.1 to $10.9 \text{ mg cm}^{-2} \text{ yr}^{-1}$) and low CARs ($1\text{--}38 \text{ mg cm}^{-2} \text{ yr}^{-1}$), associated with more negative $\delta^{13}\text{C}_{\text{om}}$ values (-23.3‰ and -20.2‰) in unit A. Figure 5 shows the carbon isotope composition of sedimentary organic matter from highstands (low salinity) and lowstands (high salinity) plotted against OAR and CAR. The close relationship between lake productivity (OAR) and the isotope composition of organic matter is evident in Figure 5a.

As with the lacustrine carbonates, the C-isotope composition of sedimentary organic matter reflects the isotopic variability of the DIC pool. However, the carbonate equilibrium of the lake water, as well as the type of organisms at different lake salinity, can additionally control the $\delta^{13}\text{C}_{\text{om}}$. The changes in $\delta^{13}\text{C}_{\text{om}}$ in the lake's DIC pool are recorded as similar shifts in both organic matter and carbonates. As a consequence, we conclude that the combined effect of extensive evaporative phases (^{13}C enrichment of lake waters) and the greater amount of inflowing water during intervals with a positive P-E ratio (high input of ^{12}C -rich waters) is the main control on the carbon isotopic composition of organic matter.

Changes in lakewater alkalinity may have an additional effect on the organic matter isotopic composition. The variation of the $\delta^{13}\text{C}_{\text{om}}$ value with alkalinity is illustrated in Figure 5b, which shows a distinct covariance between carbonate accumulation rates (CAR), a proxy for alkalinity, and $\delta^{13}\text{C}_{\text{om}}$ values. Hence, the lowest lake productivity during lowstands is fingerprinted as more positive $\delta^{13}\text{C}_{\text{om}}$ values (Figure 5a) that are associated with comparatively high alkalinities as shown by high CAR (Figure 5b). Alkaline waters with a pH greater than 8.3, as in Laguna Mar Chiquita, have more than 99% of DIC as HCO_3^- (Hassan *et al.*, 1997). Dissolved CO_2 concentrations below $10 \mu\text{mol/L}$ may force organisms to use bicarbonate as a source of carbon (Hollander and McKenzie,

Table 2 Total dissolved solids: TDS in g/L and documented level changes from year 1900 to 2000. Δ lake level = 0 corresponds to 66.5 m a.s.l. lakewater elevation. $\delta^{13}\text{C}_{\text{om}}$ (‰): isotope ratio of sedimentary organic matter from samples accumulated during the same year of measured salinity and documented lake level

Year	TDS (g/L)	Δ Lake level (m)	$\delta^{13}\text{C}_{\text{om}}$ (‰)
2000	40	3.4	-21.0
1997	58	2.2	-20.2
1996	60	2.6	-21.1
1995	37	3.8	-20.7
1985	29	5.0	-20.5
1984	29	4.2	-21.0
1983	30	4.3	-23.3
1981	33	3.6	-21.3
1978	50	2.7	-21.3
1976	80	-0.4	-21.1
1973	218	-2.0	-19.1
1972	270	-4.1	-17.2
1970	270	-3.6	-17.2
1969	272	-3.8	-16.4
1951	251	-4.5	-16.2
1925	186	-1.1	-18.2
1911	360	-3.8	-17.5
1900	223	-2.9	-17.3

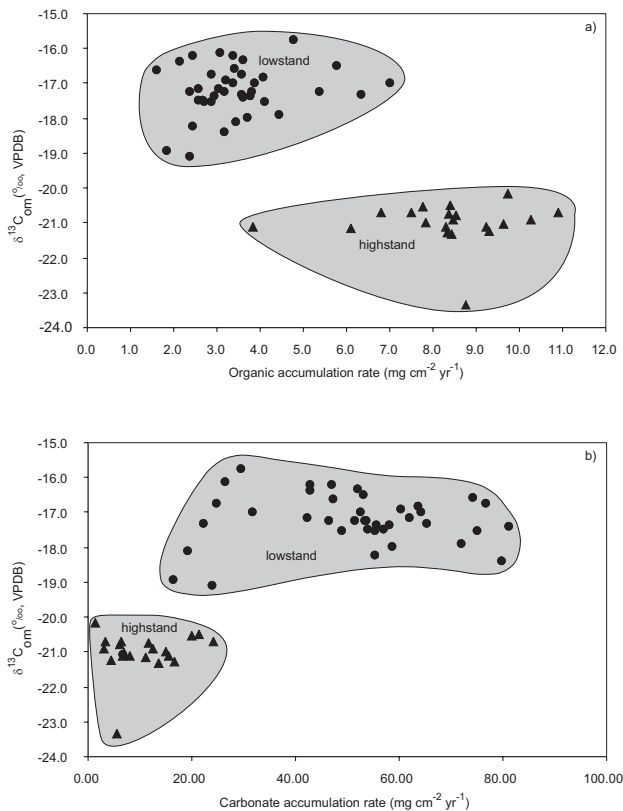


Figure 5 (a) Carbon isotopic composition of organic matter versus organic carbon accumulation rate. (b) Carbon isotopic composition of organic matter versus carbonate accumulation rate.

1991), producing enrichment in the ^{13}C content of the organic matter (Stuiver, 1975; Hollander and McKenzie, 1991; Hassan *et al.*, 1997). In Laguna Mar Chiquita a 1.3 m water-level drop from 1986 to 1989 led to increased salinity (*c.* 29 g L^{-1} to 35 g L^{-1}) and pH (8.3 to 8.5), while the average dissolved CO_2 decreased from $14\text{ }\mu\text{mol/L}$ to $5.4\text{ }\mu\text{mol/L}$ in the water-column. Thus, increases in water alkalinity and decreases in dissolved CO_2 concentrations can intensify the ^{13}C enrichment of organic matter during lowstand phases. The observed $\delta^{13}\text{C}_{\text{om}}$ values in lowstand sediments (average = -17.2‰) are within the range found for plankton uptake of dissolved HCO_3^- (e.g., Stuiver, 1975). Conversely, the more negative organic matter isotopic composition of organic matter-rich muds mainly represents a less ^{13}C -enriched pool of DIC during intervals with a positive hydrological balance. The average $\delta^{13}\text{C}_{\text{om}}$ value (-21.0‰) of the most recent sediments in unit A is very close to the average of living plankton (-20.5‰).

In hypersaline Laguna Mar Chiquita, changes in the lake volume and salinity control carbonate precipitation and lake productivity showing a differing isotope response to those lacustrine systems where the carbon isotope composition of the DIC pool is primarily controlled by the annual photosynthesis-respiration cycle (e.g., McKenzie, 1985). In the latter case, seasonal algal blooms can deplete the CO_2 content of the surface water leading toward calcite supersaturation. This process leads, in turn, to carbon isotope fractionation as the ^{12}C is preferentially assimilated into organic matter resulting in an enrichment of ^{13}C in the remaining DIC, which is recorded by simultaneously precipitated calcium carbonate. In contrast, in Laguna Mar Chiquita as a result of the P-E ratio control on primary productivity and carbonate precipitation, both the isotopic composition of authigenic carbonates and organic matter are ^{13}C -depleted during the highest

productive intervals, while ^{13}C -rich isotopic compositions reflect low rates of productivity.

$\delta^{13}\text{C}_{\text{om}}$ as an index of palaeosalinity and palaeolake levels

Our ^{210}Pb age model allows us to link the isotope stratigraphy developed for the Laguna Mar Chiquita core with the historical record of salinity (Frank, 1915; Kanter, 1935; Bertoldi de Pomar, 1953; Durigneux, 1978; Martinez, 1991) and with the documented water-level fluctuations during the twentieth century (Table 2).

Although both carbonate and sedimentary organic matter isotopic compositions record lake-level fluctuations, the $\delta^{13}\text{C}_{\text{om}}$ yields the best fit in the statistical analyses between isotope ratios and instrumental data. There is a significant co-variation between the $\delta^{13}\text{C}_{\text{om}}$ fluctuations and the instrumental and historical twentieth-century lake-level data (Figure 6, a and b). The more negative $\delta^{13}\text{C}_{\text{om}}$ than -20‰ are associated with comparatively low salinities (i.e., highstand). Intermediate salinities, such as during the transition from the last lowstand to the current highstand interval, correspond to $\delta^{13}\text{C}_{\text{om}}$ values ranging between -18‰ and -19‰ . High salinities, and thus lowstands, are reflected by $\delta^{13}\text{C}_{\text{om}}$ values more positive than -18‰ .

$\delta^{13}\text{C}_{\text{om}}$ values were plotted versus the corresponding measured TDS. The data were fitted to a linear function (Figure 6a) that allows us to calculate TDS values for intervals prior to instrumental data availability (Figure 7). The least squares regression is:

$$\text{TDS (g L}^{-1}\text{)} = 49.008 \times \delta^{13}\text{C}_{\text{om}} + 1093.5 \quad (1)$$

Past Δ lake levels (Figure 7) were calculated using the linear equation derived from the data plotted in Figure 6b:

$$\Delta \text{ lake levels (m)} = (-1.5181 \times \delta^{13}\text{C}_{\text{om}}) - 29.266 \quad (2)$$

The noticeable gap displayed in the middle range isotopic values of the sedimentary organic matter is an artifact due to the lack of samples covering the interval from 1973 to 1976. A dramatic change in water salinity from 218 g L^{-1} to 80 g L^{-1} is reported for this timespan, which is in turn recorded as a shift of 2‰ towards more negative values in the organic matter isotope composition (see Table 2). High correlation coefficients (Figure 6, a and b) are significant at $p < 0.05$, thus satisfying the assumed linear relationship between variables. In this linear model, the $\delta^{13}\text{C}_{\text{om}}$ is a good predictor of salinities or lake levels explaining 82% and 83% of the respective variances. The comparison of instrumental values with calculated data (Figure 6, c and d) indicates that the $\delta^{13}\text{C}_{\text{om}}$ is a semi-accurate proxy to quantify the past lake scenarios. Consequently, the proposed model allows us to improve the lake-level reconstruction, which was previously based mostly on sedimentological features (Piovano *et al.*, 2002; Figure 3). It should be noticed that a $\delta^{13}\text{C}_{\text{om}}$ lower than -22‰ results in negative salinity which is a constraint of our equation (i.e., sample 5; $\delta^{13}\text{C}_{\text{om}} = -23.3\text{‰}$).

Palaeoenvironmental implications

Figure 7 shows that high salinities and low lake levels dominated the hydrological balance of Laguna Mar Chiquita from the 'Little Ice Age' until the beginning of the last quarter of the twentieth century. Within this generally dry interval, more humid conditions can be inferred through a drop in the salinity curve and a rise in the calculated lake level for the end of the

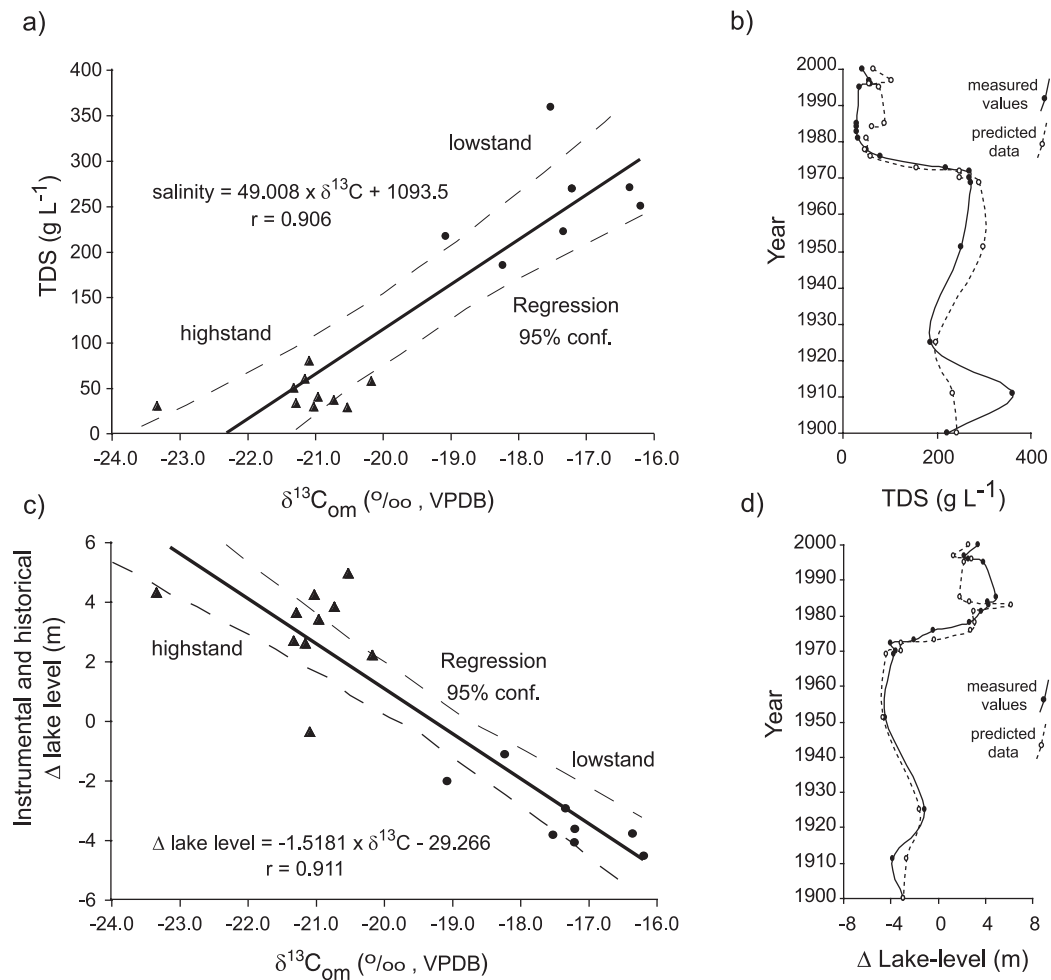


Figure 6 (a) Linear regression between carbon isotopic compositions of organic matter and instrumentally obtained salinities (TDS). (b) Linear regression between carbon isotopic compositions of organic matter and documented lake-level fluctuations. The dashed lines are the 95% confidence bands for the regression lines. (c and d) Comparison of measured salinity and lake-level values with calculated data using the respective linear equations.

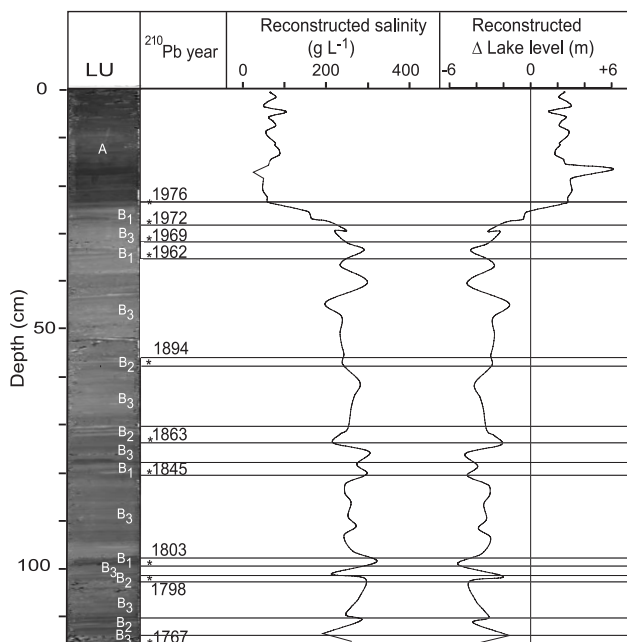


Figure 7 Reconstructed palaeosalinities and Δ lake levels based on linear equations, for the last 230 years. For LU and chronology, see Figure 3.

eighteenth century (below 100 cm in Figure 7). This was followed by negative hydrological budgets in particular during the first half of the nineteenth century, whereas a comparatively more positive hydrological budget can be proposed based on the shifts in both curves around 1863. This interpretation is supported by dendrochronological records from the nearby upper catchment of the Rio Dulce, with slow tree growth during the early nineteenth century followed by a more positive trend in growth until 1860 (Villalba *et al.*, 1998), as well as historical data from the 'Little Ice Age' (Cioccale, 1999). Thus, these two independent reconstructions indicate a similar sequence and magnitude of events. Further tree-ring and glacial evidences for the 'Little Ice Age' in southern South America were presented by Villalba (1994).

As a result of wetter conditions, substantial lake-level rise and low salinities characterize the last quarter of the twentieth century. The triggering mechanism of the most recent increase in precipitation (i.e., since the 1970s) in the low plains of southern South America is not, as yet, well understood. It has been suggested that the increase in precipitation in the subtropical area of Argentina may be caused by the enlargement of the meridional transport of humidity from the tropics to the south (Villalba *et al.*, 1998); additionally, there is evidence that the increasing trend of discharges in the Río de la Plata basin is associated with anomalies in sea surface temperatures of global extent (Robertson and Mechoso, 1998).

Conclusions

Geochemical evidence combined with historical and instrumental data indicate that the hydrological balance determines the oxygen and carbon isotopic composition of both carbonate and organic matter in Laguna Mar Chiquita. The isotopic record of the lake sediments reflects, therefore, the recent P-E variability in the subtropical lowplains of South America.

The carbon isotope signature from Laguna Mar Chiquita differs from other lacustrine basins because the carbon isotope budget is not a direct function of primary productivity (e.g., Lake Greifen; McKenzie, 1985). It is more likely controlled by the P-E ratio impacting the oxygen and carbon isotope budget. Primary productivity is a function of lakewater salinity and is high in the most diluted lake waters during positive P-E ratios. This highest stage of the lake is represented by the most negative $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values. Prolonged negative P-E ratios through time lead to increasing salinity, triggering a higher carbonate accumulation rate associated with a decrease in primary productivity. These evaporative phases of the lake system are recorded by the most positive $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ value.

The carbon isotope composition of the organic matter is the most sensitive to twentieth-century changes in the Laguna Mar Chiquita hydrology and salinity. The most recent variability in the $\delta^{13}\text{C}_{\text{om}}$ mirrors the instrumental and historical record of lake-level variations and, therefore, can be used to infer both lake water salinities and Δ levels from the 'Little Ice Age' until the present. High salinities and low lake levels dominated from the 'Little Ice Age' until the early 1970s. Short pulses indicating comparatively positive water balances at the end of the eighteenth and in the second half of the nineteenth centuries occurred within this generally dry interval. This scenario agrees with previous dendrochronological evidence from the Río Dulce area (Villalba *et al.*, 1998), as well as hydrological data from the Río de La Plata basin (Depetris *et al.*, 2004), pointing towards the regional scale of the reconstructed palaeohydrologic changes. Although not conclusive, our results show that the instrumentally recorded wetter conditions that characterize the last quarter of the twentieth century have no equivalent in the preceding 200-year history of Laguna Mar Chiquita. Thus, its sedimentary record has the potential to identify the frequency of hydrological changes at longer timescales, affording the opportunity to gain insight into palaeocirculation dynamics in subtropical South America during the Holocene.

Acknowledgements

Different aspects of the results presented herein have been carried out at CIGES (Universidad Nacional de Córdoba, Argentina), ETH-Zürich and the University of Geneva (Switzerland). CONICET (Argentina) provided the financial support for this work (FONCYTs PICT 07-08524) and a postdoctoral fellowship at ETH-Zürich to the first author. We would like to kindly thank H. Paul, M. Lehmann and M. Andres for their assistance in the Stable Isotope Laboratory (ETH-Z). We acknowledge P. Depetris, D. Gaiero, A. Mangeaud and C. Vasconcelos for their insightful discussions. We thank A. Schwalb, B. Wolfe and an anonymous reviewer for helpful comments on an earlier draft of this paper.

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