

## Geochemical response of a closed-lake basin to 20<sup>th</sup> century recurring droughts/wet intervals in the subtropical Pampean Plains of South America

Eduardo L. PIOVANO\*, Favio E. LARIZZATTI<sup>1)</sup>, Deborah I.T. FÁVARO<sup>1)</sup>, Sonia M.B. OLIVEIRA<sup>2)</sup>, Sandra R. DAMATTO<sup>3)</sup>, Barbara P. MAZZILLI<sup>3)</sup> and Daniel ARIZTEGUI<sup>4)</sup>

Centro de Investigaciones Geoquímicas y Procesos de la Superficie (CIGeS), Universidad Nacional de Córdoba, Av. Velez Sarsfield 1611, X5016GCA – Córdoba, Argentina

<sup>1)</sup>Laboratório de Análise por Ativação Neutrônica (LAN/CRPQ) – IPEN, P.O. Box 11049, CEP: 05422-970 São Paulo, Brazil

<sup>2)</sup>Instituto de Geociências – Universidade de São Paulo, São Paulo, Brazil

<sup>3)</sup>Centro de Metrologia das Radiações – Divisão de Radiometria Ambiental (CMRA) – IPEN, São Paulo, Brazil

<sup>4)</sup>Institute Forel and Dept. of Geology & Paleontology, University of Geneva, CH-1205 Geneva, Switzerland

\*e-mail corresponding author: epiovano@efn.uncor.edu

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### ABSTRACT

*Laguna Mar Chiquita is a highly variable closed saline lake located in the Pampean Plains of central Argentina. Presently is the largest saline lake in South America (~ 6,000 km<sup>2</sup>) and also one of the largest in the world. During the 20<sup>th</sup> century the hydrological balance of the region was characterized by contrasting scenarios. Well-defined wet or dry climatic phases had ruled the lake level fluctuations and the rivers discharge, mainly controlling the geochemical composition of sediments. Sediments accumulated during positive hydrological balances (i.e., high lake level) are mainly composed of allogenic mineral due to higher riverine inputs into the lake. This fluvial-dominated lake phases are recorded as sediments enriched in Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> and in trace elements such as Co, Cr, Cs, Rb, Sc, Hf, Ta, Th as well as rare earth elements (REE). Sediments accumulated during dry phases (i.e., low lake levels and high salinity) are evaporite mineral-rich with elevated concentrations of CaO, MnO, MgO, and P<sub>2</sub>O<sub>5</sub>. High contents of As and U are probably due to a co-precipitation during high evaporative phases. The calibration of the sediment chemical composition of Laguna Mar Chiquita to well-defined water-level fluctuations of the 20<sup>th</sup> century shows that elemental geochemistry can be a useful proxy to study former lake-water fluctuations. It may further provide a comparative model to evaluate past environmental conditions in other saline lacustrine basins.*

*Key words: salt lake, geochemistry, lake sediments, South America, Laguna Mar Chiquita, 20<sup>th</sup> Century*

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### 1. 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, Jellison *et al.* 1996). The chemical composition of saline lake sediments can change drastically in response to fluctuations in the lake water-level, and consequently in salinity. Hence, lake-sediments geochemistry (e.g., Komor 1994; Volkova 1998; Valero-Garcés *et al.* 2000) can provide additional information to study the record of hydrological variations through time.

The 20<sup>th</sup> century hydrological history of southeastern South America was characterized by highly variable water balances (Depetris & Kempe 1990; Depetris *et al.* 1996; García & Vargas 1998; Genta *et al.* 1998; Piovano *et al.* 2002; Piovano *et al.* 2004). The forcing mechanisms behind these changes are not fully understood yet. Thus, it is particularly difficult to discern whether these recent contrasting hydrological situations – i.e. extensive droughts during the 40's or positive hydrological balances since the 70's have been triggered by natural and/or anthropogenic causes. Thus, the analyses of long-term hydro-climatological series dur-

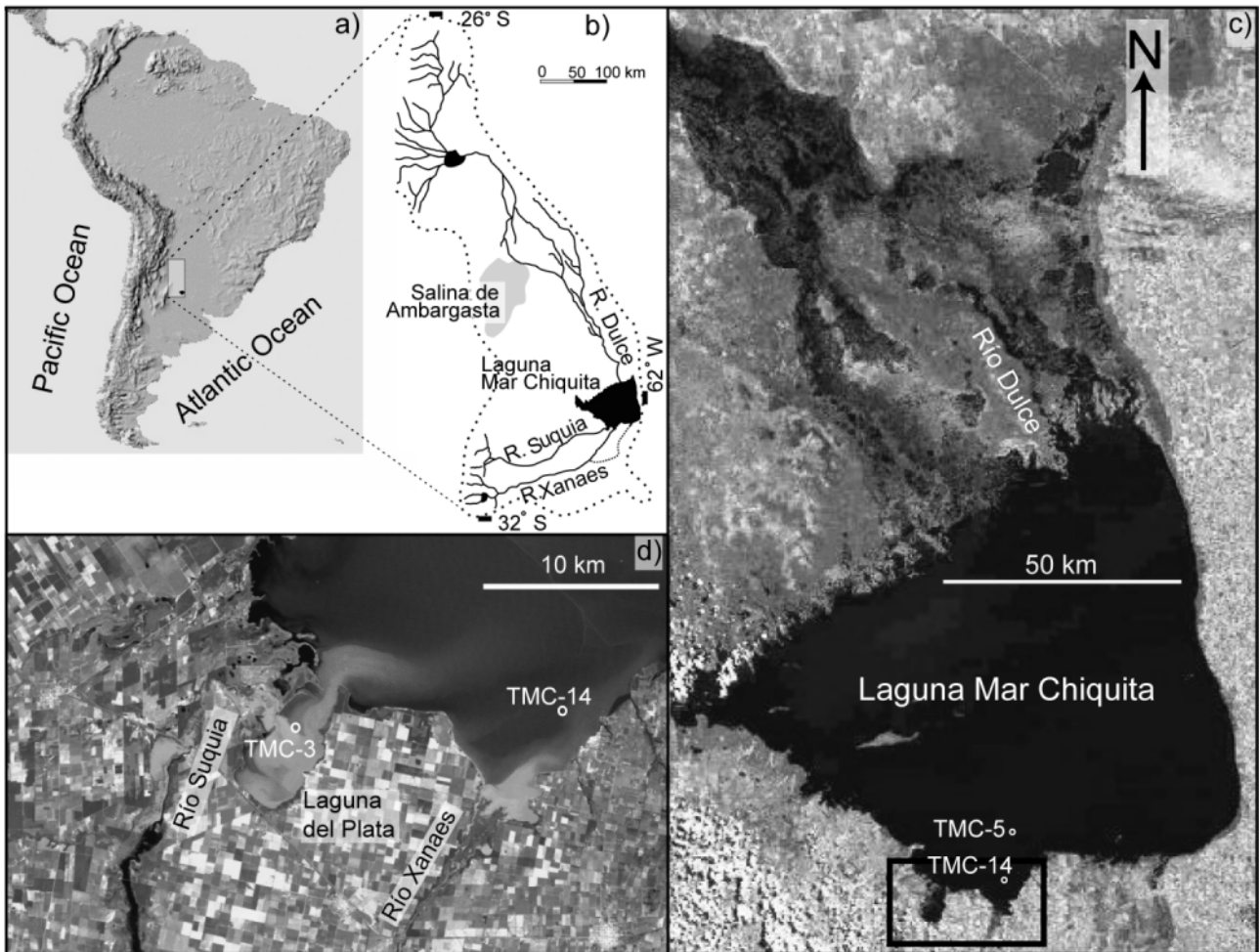
ing times of negligible human impact and beyond the instrumental record are critical for a better understanding of the Earth-system climatic unevenness.

The recent history of Laguna Mar Chiquita, a shallow saline lake in Central Argentina (Fig. 1a), is characterized by marked water-level and salinity variations. During highstands, as at present, the lake becomes not only the largest saline lake in South America but also one of the largest in the world. High resolution sedimentological and isotopical results from Laguna Mar Chiquita sediments (Piovano *et al.* 2002, 2004) point toward the high sensitivity of this lake to record past environmental changes.

The aim of this paper is to calibrate the geochemical composition of the 20<sup>th</sup> century sedimentary record of Laguna Mar Chiquita to well-defined water level fluctuations. These results, in conjunction with independent sedimentological and isotopical data, will allow us to constrain past lake level fluctuation and hence, environmental changes beyond both instrumental and historical documentary information.

### 2. GENERAL SETTING

Laguna Mar Chiquita is a large and shallow saline lake located in the subtropical Pampean Plains of central Argentina (30°54'S – 62°51'W; Figs 1a and b). Is a ter-



**Fig. 1.** (a) Geographical map of South America showing the location of Laguna Mar Chiquita in the Pampean plains of Argentina. (b) Detail of the drainage basin. (c) Core location in the satellite image of the lake. (d) Detail of the area indicated in (c) showing the Laguna del Plata with core location.

minimal lake in a catchment area of *ca* 37,500 km<sup>2</sup>. Basin elevations range from *ca* 72 m a.s.l., corresponding to present-day lake water level, up to 5,000 m a.s.l. in the highest portion of Río Dulce upper catchment (Fig. 1b). The geology at the Pampean Plains catchment area is composed of aeolian and fluvial sediments deposited since the Upper Pleistocene (Kröhling & Iriondo 1999). The northernmost area of the lake is covered by wetlands (see Fig. 1c) that are significantly reduced during dry periods. Very low relief and gentle slopes characterize the north, west and south coast of the lake, with the exception of some 0.3 to 4.0 m high isolated cliffs in the south.

Recent variability in precipitation and river discharge has produced dramatic lake-level fluctuations, remarking that Laguna Mar Chiquita is very sensitive to climatic changes (Piovano *et al.* 2002, 2004). Historical and instrumental data show that during dry intervals, the lake surface was reduced to  $\sim$ 1,000 km<sup>2</sup>, whereas during periods with a positive hydrological balance, as at present, the lake covers an area of up to  $\sim$ 6,000 km<sup>2</sup>. The

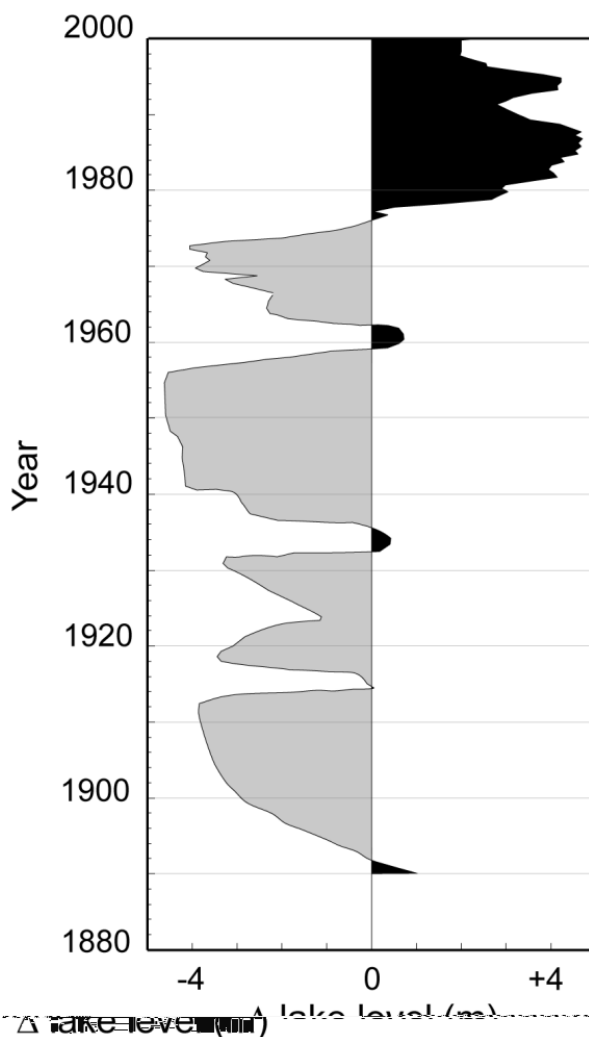
present-day maximum length and width are 120 km and 80 km, respectively, while the maximum water depth is  $\sim$ 10 m.

The human impact in the region started as far back as the end of the 19th century, and it mainly comprises intensive deforestation and agricultural activities. At present, livestock rising and agriculture are the prevailing land uses of the region.

The lake is fed by three major rivers (Fig. 1b) and receives in addition, a substantial groundwater input. The main tributary is the Río Dulce with an average annual discharge of 3.0 km<sup>3</sup>, whereas Río Suquia and Río Xanaes both have a total annual discharge of 0.7 km<sup>3</sup> (Reati *et al.* 1997). The Río Suquia mouths in a small satellite lake, Laguna del Plata (Fig. 1d), which is connected to the main lake only during highstands. The system as a whole has no surficial outlet and the loss of water is through evaporation, which is additionally favored by the pan-like shape of the lake.

This subtropical region is characterized by austral summer precipitation and dry winters. The Amazon ba-

sin 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 vapor. LLJ variability largely determines the hydrological balance of the region (Berri & Inzunza 1993; Nogués-Paegle & Mo 1997; Saulo *et al.* 2000). Large rainfall fluctuations in the Mar Chiquita area occurred during the 20<sup>th</sup> century, with annual values ranging from a minimum of 303 mm y<sup>-1</sup> to a maximum of 1074 mm y<sup>-1</sup>. During the interval 1934-72, average annual precipitation was 653 mm y<sup>-1</sup>, while the average increased to 810 mm y<sup>-1</sup> during the interval 1973-97.



**Fig. 2.** Lake level fluctuations during the 20<sup>th</sup> century.  $\Delta$  lake level = 0 is an intermediate lake-level stage with a 66.5 m a.s.l. shoreline elevation. Positive values represent highstands (black) and negative values indicate lowstands (gray areas; modified from Piovano *et al.* 2002).

The 20<sup>th</sup> century hydrology of the lake was characterized by intermittent low and highstands accompanied with substantial changes in lake water volume, and therefore water salinity. Large rainfall fluctuations in

the catchment area control river discharges and, consequently, lake water-level. Documented dry intervals are synchronous with low river discharge and lake lowstands whereas an increasing in both river discharge and lake levels has occurred during wet intervals (Piovano *et al.* 2004). Low and high water stands were defined as below or above the 66.5 m a.s.l. water altitude (average value), respectively, and are represented as negative or positive values in gray and black shading areas, respectively (Fig. 2). Low lake levels characterized almost the entire first 75 years of the 20<sup>th</sup> century, with salinities up to 360 g l<sup>-1</sup> in A.D. 1911 (Frank 1915) and 270 g l<sup>-1</sup> in A.D. 1970 (Martinez 1991). The lake level started to rise in A.D. 1972 and an increasing highstand dominates since A.D. 1977 to the present. Comparatively lower salinities (e.g. 29 g l<sup>-1</sup> in 1986; 35 g l<sup>-1</sup> in 1989) were reported during this last highstand (Martinez *et al.* 1994).

The recorded variations in the Laguna Mar Chiquita hydrological balance during the 20<sup>th</sup> century are synchronous with other hydrological changes observed in the discharge rate of south-eastern South American rivers. Long dry intervals throughout the first ¾ of the 20<sup>th</sup> century and a recent increasing trend in streamflows have been reported in the Río de la Plata basin (Depetris & Kempe 1990; Depetris *et al.* 1996; García & Vargas 1998; Genta *et al.* 1998).

Lake waters are alkaline (pH > 8) of Na-Cl-SO<sub>4</sub> type (Martínez 1991). During lowstands, they become supersaturated with respect to both calcite and gypsum, remaining supersaturated with respect to calcite but only occasionally with respect to gypsum during highstands intervals (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 amounts of organic matter allowing for the development of sulfate-reducing conditions at the sediment-water interface (Martínez *et al.* 1994).

### 3. THE LAGUNA MAR CHIQUITA SEDIMENTARY AND ISOTOPE MODELS

Using a well-constrained <sup>210</sup>Pb chronology, Piovano *et al.* (2002, 2004) calibrated the sedimentary and isotope responses of the lake system to the last 100 years of documented lake levels changes. Details on age-model and the <sup>210</sup>Pb dating technique are given in Piovano *et al.* (2002). Laguna Mar Chiquita sedimentary record comprises two characteristic lithological units. Laminated to banded organic-carbon rich muds are present in the uppermost part of the sedimentary record (Unit A) showing a distinctive dark color due to the organic matter enrichment (total organic carbon, TOC: 1.8–3.2%) and low carbonate content (total inorganic carbon, TIC: 0.4–6.6%). This unit is characterized by low oxygen and carbon isotopic compositions for both carbonate and organic matter. Pb-210 age model indicates that this unit is recording the most recent high-

stand (i.e., after 1976). The banded to laminated muds with evaporites of Unit B were subdivided in: a) B<sub>1</sub> defined in the transition from low to high lake stands (TOC: 1.3-2.4%; TIC: 5.6-13.3%); b) B<sub>2</sub> during short-term lake level rises (TOC up to 2.1%; TIC up to 17%); and c) B<sub>3</sub> is the most abundant and is composed of thin to thick-banded sediments hosting evaporites that correspond to years of documented extremely low lake levels (TOC: 0.5-1.6%; TIC: 10-25%). Unit B is comparatively richer in <sup>18</sup>O and <sup>13</sup>C than Unit A in both carbonate and organic matter fractions.

The correlation between lithological units, the geochemical record and documented lake-level changes allowed us to formulate well-calibrated sedimentary and isotope models. Prolonged intervals with either negative or positive hydrological balances have severely modified lake-water levels, salinity and primary productivity, and have also controlled the isotopic composition of both the authigenic carbonate and sedimentary organic matter. Lake level drops and concurrent increases in salinity promoted the development of gypsum-calcite-halite layers and a marked decrease in primary productivity. The deposits of dry phases are evaporite-bearing sediments with low organic matter content and the most positive isotopic excursions. Conversely, increased inflow of river and meteoric waters that leads to high-stands and low salinities, are recorded as diatomaceous organic matter-rich muds, low contents of carbonates

and the most negative isotopic ratios both in carbonates and organic matter.

#### 4. MATERIAL AND METHODS

Three short cores (~2 m length) were retrieved in November 1997 using a hand corer beaker sampler. Core TMC-97-5 and core TMC-97-14 were collected in the deepest area of the lake at *ca* 7-8 m water depth, whereas core TMC-97-3 was retrieved in Laguna del Plata at 3 m water depth (Figs 1c and d).

**Tab. 1.** Average (avg) and standard deviation (st.dev.) of major element oxides concentration (weight %) analyzed by XRF; n: number of samples used to calculate the average value.

		Core TMC-97-3		Core TMC-97-14		Core TMC-97-5	
		Unit A	Unit B	Unit A	Unit B	Unit A	Unit B
SiO <sub>2</sub>	avg	54.58	53.65	44.32	40.19	41.45	38.32
	st.dev.	2.34	3.07	2.72	4.48	1.58	1.39
Al <sub>2</sub> O <sub>3</sub>	avg	15.11	14.93	11.87	10.24	10.89	9.96
	st.dev.	0.65	0.55	0.98	1.01	0.59	0.43
MnO	avg	0.09	0.1	0.1	0.12	0.14	0.14
	st.dev.	0.01	0.01	0.02	0.01	0.01	0.01
MgO	avg	2.36	2.98	3.46	4.05	3.77	4.21
	st.dev.	0.13	0.53	0.33	0.79	0.04	0.32
CaO	avg	3.13	3.51	6.06	11.02	11.49	14.64
	st.dev.	0.24	0.65	2.15	2.16	2.31	2.12
Na <sub>2</sub> O	avg	4.99	4.42	8.54	7.41	5.5	4.92
	st.dev.	1.11	0.75	1.84	1.51	0.58	0.63
K <sub>2</sub> O	avg	2.92	3.05	2.65	2.32	2.52	2.33
	st.dev.	0.14	0.14	0.18	0.17	0.14	0.09
TiO <sub>2</sub>	avg	0.75	0.74	0.58	0.51	0.54	0.49
	st.dev.	0.05	0.02	0.05	0.05	0.03	0.02
P <sub>2</sub> O <sub>5</sub>	avg	0.22	0.21	0.25	0.25	0.28	0.27
	st.dev.	0.01	0.02	0.02	0.01	0.01	0.02
Fe <sub>2</sub> O <sub>3</sub>	avg	5.94	6.02	4.89	4.05	4.61	4.22
	st.dev.	0.43	0.53	0.52	0.29	0.29	0.22
LOI	avg	9.85	9.63	17.54	20.53	19.44	20.66
	st.dev.	2.18	2.33	2.02	2.67	1.49	0.95
n		3	9	7	8	3	10

1994). Trace elemental concentrations were determined in 90 continuous samples (taken every 2 cm along all the cores) and in reference materials and synthetic standards. Samples were accurately weighted and sealed in pre-cleaned double polyethylene bags for irradiation. Single and multielement synthetic standards were prepared by pipetting aliquots of standard solutions (SPEX CERTIPREP) onto Whatman N° 41 membranes. Sediment samples, reference materials and synthetic standards were irradiated for 16 hours, under a thermal neutron flux of  $10^{12}$  n cm<sup>-1</sup> s<sup>-1</sup> in the IEA-R1m nuclear reactor at IPEN - Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil. Two series of countings were made: the first after one week decay and the second after 15-20 days. The counting time was 2 hours for each sample and reference materials, and 30 minutes for each synthetic standard. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for <sup>57</sup>Co and <sup>60</sup>Co, respectively. The analysis of the data was made using the VISPECT program to identify the gamma-ray peaks and the ESPECTRO program to calculate the concentrations. Both programs were developed at the Radiochemistry Division, IPEN. The elements analyzed were As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Se, Ta, Th, U, Zn, Zr and REE (Ce, La, Nd, Sm, Eu, Tb, Yb, Lu). Validation was done by measuring the reference material Buffalo River sediment (National Institute of Standards and Technology, NIST SRM 2704, USA) and Soil 7 (International Atomic Energy Agency). Results obtained in standard reference materials analysis are reported in Larizzatti *et al.* (2001).

## 5. RESULTS

The mineralogy of sediments include both allocthenic (quartz, feldspars, tourmaline, biotite, muscovite, clay minerals and goethite) and authigenic components (calcite, halite and gypsum). Clastic minerals are more abundant in Unit A reaching up to 50% of the sediments components. Conversely, Unit B is rich in authigenic minerals whereas clastic components can be as low as 15% (Piovano *et al.* 2002).

Major-element oxides concentrations are summarized in table 1 as average values of each lithological unit. The standard deviation, as well as the number of samples used to calculate average values is additionally listed. Concentrations of major-element down cores are plotted in figure 3. Changes in the chemical composition of the sediments become evident according to the core location and lithological unit. Decreasing Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, K<sub>2</sub>O, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> concentrations are evident - both in unit A and B- from core TMC-97-3 and TMC-97-14 to core TMC-97-5. Conversely, MnO, MgO, CaO percentages increase from proximal to more distal cores and from Unit A to unit B. Na<sub>2</sub>O exhibits more fluctuating values, specially in core TMC-97-14 and P<sub>2</sub>O<sub>5</sub> shows small variability.

In table 2, trace element data are presented as average values of each lithological unit. Individual data grouped as lithological units are plotted on upper continental crust-normalized graphs (Taylor & McLennan 1995; Fig. 4). Table 2 and figure 5 show that the average concentration of trace elements changes with the lithological units, and to a lesser extent with the loca-

**Tab. 2.** Average (avg) and standard deviation (st.dev.) of elemental concentration (ppm) analyzed by INAA; n: number of analyzed samples.

		Core TMC-97-3		Core TMC-97-14		Core TMC-97-5	
		Unit A	Unit B	Unit A	Unit B	Unit A	Unit B
As	avg	13.2	29.02	37.15	56.09	32.49	59.51
	st.dev.	1.34	11.45	13.9	12.28	10.38	20.04
Ce	avg	70.15	71.49	55.06	46.93	53.48	46.77
	st.dev.	3.09	13.95	1.99	4.25	3.75	2.69
Co	avg	13.43	12.98	11.48	10.08	12.1	10.53
	st.dev.	0.6	1.61	0.73	0.74	0.76	0.52
Cr	avg	48.5	43.24	33.13	28.17	29.93	27.57
	st.dev.	3.77	5.07	2.45	2.59	10.49	1.54
Cs	avg	9.29	9.15	8.14	6.96	8.55	7.22
	st.dev.	0.48	1.06	0.65	0.56	0.82	0.37
Eu	avg	1.16	1.09	0.88	0.75	0.84	0.74
	st.dev.	0.06	0.09	0.05	0.08	0.04	0.05
Hf	avg	4.94	4.56	3.14	2.84	3.08	2.59
	st.dev.	0.54	0.77	0.15	0.48	0.15	0.21
La	avg	29.25	27.83	22.41	18.61	22.27	18.58
	st.dev.	1.27	2.08	1.05	2.26	1.5	1.96
Lu	avg	0.37	0.36	0.3	0.29	0.32	0.31
	st.dev.	0.11	0.04	0.05	0.07	0.07	0.05
Nd	avg	36.5	31.28	28.11	27.79	26.23	24.7
	st.dev.	5.64	2.99	5.38	4.75	2.98	2.41
Rb	avg	133.69	128.62	101.56	85.58	103.56	87.45
	st.dev.	8.98	15.03	6.12	7.6	11.03	6.78
Sc	avg	13.26	13.17	10.64	8.68	10.51	8.89
	st.dev.	0.42	1.43	0.81	0.82	1	0.5
Sm	avg	6.38	6.01	4.69	3.94	4.96	4.11
	st.dev.	0.78	0.41	0.26	0.58	0.46	0.35
Ta	avg	1.41	1.18	0.95	0.87	0.89	0.82
	st.dev.	0.1	0.16	0.13	0.19	0.13	0.1
Tb	avg	0.83	0.76	0.61	0.54	0.65	0.53
	st.dev.	0.16	0.11	0.16	0.07	0.08	0.09
Th	avg	12.22	11.36	9.15	7.62	9.03	8.06
	st.dev.	0.81	1.06	0.55	0.69	0.72	0.89
U	avg	5.27	10.27	12.86	15.04	13.97	14.4
	st.dev.	1.77	4.79	4.85	4.8	3.02	3.73
Yb	avg	2.47	2.21	1.74	1.48	1.71	1.47
	st.dev.	0.11	0.15	0.12	0.17	0.17	0.1
n		7	23	12	18	10	20

tion of the analyzed core. Unit B and distal cores are more enriched both in As and U, while the remaining elements are more abundant in Unit A and in the most proximal core (i.e., TMC-97-3).

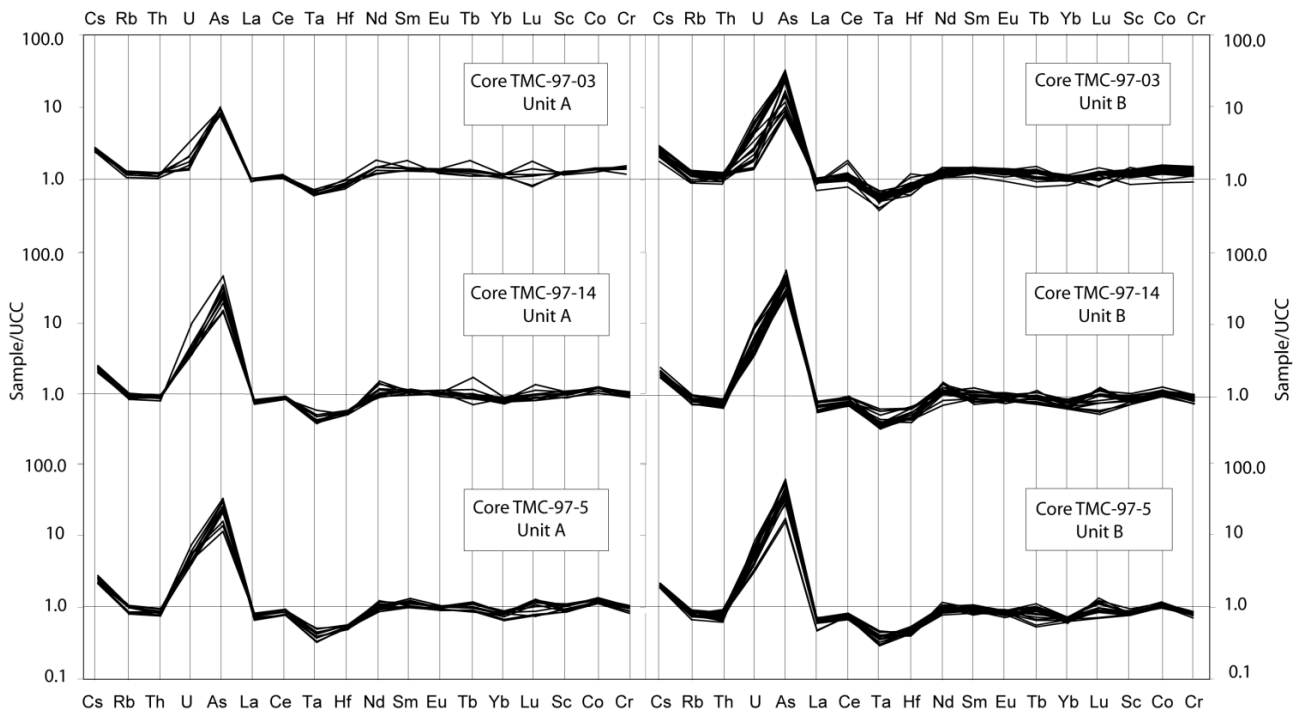
## 6. DISCUSSION

The correlation between geochemistry and lithological units indicates that major- and trace-element compositions of Laguna Mar Chiquita sediments are also sensitive to well-known hydrological fluctuations. Comparatively higher riverine sediment input occurring at high P-E ratios, and therefore during highstands, resulting in a higher proportion of allogenic minerals in Unit A. This period (i.e., from 1977) is additionally recorded by high sedimentation rates (average value  $0.94 \text{ cm y}^{-1}$ ) and bulk sediment accumulation rates in the main lake ( $0.32 \text{ g cm}^{-2} \text{ y}^{-1}$ ) as previously demonstrated by Piovano *et al.* (2002). Core TMC-97-3 retrieved in the Laguna del Plata shows the highest proportion of allogenic minerals due to the influence of the Río Suquía mouth (see sediment plume in figure 1d). The

absence of gypsum and evaporite layers in the satellite lake sediments is due to the dilution effect produced by river waters.

The correlation matrix (Tab. 3), computed with the major oxides concentration values from all individual samples, shows two main groups. Group 1 comprises  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ ; and group 2 includes  $\text{CaO}$ ,  $\text{MnO}$ ,  $\text{MgO}$  and  $\text{P}_2\text{O}_5$ . Each group of elements individually displays strong positive correlation coefficients whereas there is a negative correlation between the two groups. This contrasting relation can be ascribed to the dominance of clastic components and a common source in sediments from Unit A, leading to an enrichment in elements from group 1, meanwhile Unit B is enriched in elements from group 2 due to the abundance of authigenic minerals.

Maximum  $\text{Al}_2\text{O}_3$  content overall Core TMC-97-3 (Fig. 3) is attributed to increasing sediment flux from Río Suquía. Intermediate values are observed in core TMC-97-14, retrieved close to the Río Xanaes mouth, but in a comparatively more distal position from the river-mouth than core TMC-97-3 (see Fig. 1c).



**Fig. 4.** Upper continental crust-normalized extended diagrams. Unit A and B individual samples from cores TMC-97-3, TMC-97-14 and TMC-97-5. The sequence of elements is determined by the order of decreasing concentration in the upper continental crust average of Taylor and McLennan (1995).

**Tab. 3.** Pearson correlation coefficients between concentrations of major elements oxides. Marked correlations are significant at  $p < 0.05$ .

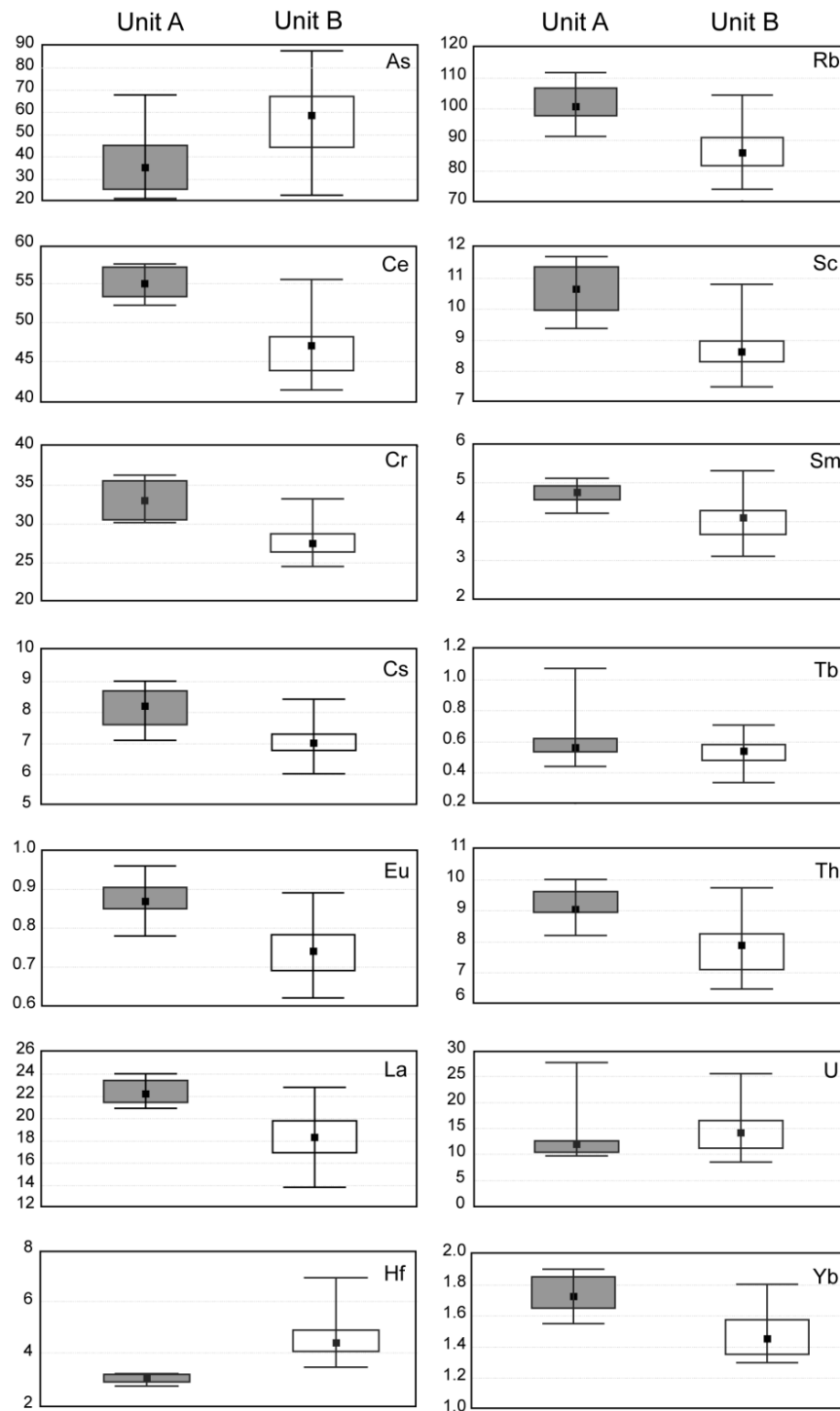
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>
SiO <sub>2</sub>	1.00	<b>0.97</b>	<b>-0.72</b>	<b>-0.78</b>	<b>-0.89</b>	<b>-0.38</b>	<b>0.93</b>	<b>0.97</b>	<b>-0.78</b>	<b>0.85</b>
Al <sub>2</sub> O <sub>3</sub>		1.00	<b>-0.72</b>	<b>-0.77</b>	<b>-0.90</b>	<b>-0.37</b>	<b>0.97</b>	<b>1.00</b>	<b>-0.71</b>	<b>0.95</b>
MnO			1.00	<b>0.77</b>	<b>0.84</b>	-0.15	<b>-0.64</b>	<b>-0.72</b>	<b>0.74</b>	<b>-0.61</b>
MgO				1.00	<b>0.72</b>	0.17	<b>-0.64</b>	<b>-0.78</b>	<b>0.57</b>	<b>-0.64</b>
CaO					1.00	-0.03	<b>-0.89</b>	<b>-0.90</b>	<b>0.72</b>	<b>-0.84</b>
Na <sub>2</sub> O						1.00	<b>-0.35</b>	<b>-0.38</b>	0.19	<b>-0.34</b>
K <sub>2</sub> O							1.00	<b>0.97</b>	<b>-0.64</b>	<b>0.96</b>
TiO <sub>2</sub>								1.00	<b>-0.71</b>	<b>0.94</b>
P <sub>2</sub> O <sub>5</sub>									1.00	<b>-0.54</b>
Fe <sub>2</sub> O <sub>3</sub>										1.00

In general, core TMC-97-5 presents the lowest Al<sub>2</sub>O<sub>3</sub> concentrations, as the influence of fluvial sediments become gradually weaker towards distal areas. Al<sub>2</sub>O<sub>3</sub> contents also show an upward increase - temporal variability - throughout the cores. Unit A, accumulated during a highstand, is more Al-rich than lowstand Unit B, as a result of comparatively higher clastic inputs from rivers (Tab. 1).

Variations in the SiO<sub>2</sub> content of these sediments have to be interpreted with caution since no biogenic-silicon was discriminated from the total concentration (Fig. 3). However, high SiO<sub>2</sub> percentages characterize both cores with relatively higher fluvial influence (cores TMC-97-14 and TMC-97-3) as well as the sediments accumulated during intervals with dominating high lake

levels (see Tab. 1). The spatial and temporal variability of K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> is also related with the amount of fluvial sediments reaching the lake and the dispersion of sediments from the river mouths. Similarities among graph patterns (e.g. K<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub> variabilities in figure 3) reinforce the notion of a common source for the elements from this group.

Although carbonate minerals are scattered throughout Unit A (TIC: 0.4 - 6.6%), Unit B shows the highest content (i.e. TIC up to 25%), which is associated with gypsum and halite. The enrichment in authigenic minerals is ruled by the evaporative phases that conduct to low lake levels and high ionic concentration. During intervals with negative P-E ratios rivers may not reach the lake diminishing the clastic input, which is indicated



**Fig. 5.** Box and whisker plots showing the percentile ranges, maximum and minimum values for trace elements and rare earth elements concentrations (ppm) in Units A (gray boxes) and B (white boxes) from cores TMC-97-14 and TMC-97-5. Central square indicates the median value (50% of the observations). The top and bottom of each box correspond to the 75<sup>th</sup> and 25<sup>th</sup> percentile values, respectively. The whiskers extending from the top and bottom of each box correspond to maximum and minimum values.

by a drop to  $0.30 \text{ cm y}^{-1}$  in the average sediment rates and, to  $0.22 \text{ g cm}^{-2} \text{ y}^{-1}$  in the bulk sediment accumulation rates (Piovano *et al.* 2002). CaO content throughout the cores is associated with the abundance of evaporitic minerals (calcite and gypsum). The low CaO contents

observed in the core retrieved in the satellite lake (TMC-97-3) indicate low carbonate precipitation rates due to the dilution effect produced by the input of river waters, meanwhile comparatively higher values for the same time interval are observed in the cores retrieved in



**Tab. 4.** Pearson correlation coefficients between concentrations of trace elements. All the correlations coefficients are significant at  $p < 0.05$ .

	As	Ce	Co	Cr	Cs	Eu	Hf	La	Lu	Nd	Rb	Sc	Sm	Ta	Tb	Th	U	Yb
As	1.00	-0.63	-0.64	-0.66	-0.70	-0.71	-0.63	-0.64	-0.29	-0.39	-0.63	-0.72	-0.63	-0.60	-0.58	-0.66	0.67	-0.72
Ce		1.00	0.66	0.77	0.71	0.79	0.85	0.80	0.35	0.50	0.76	0.90	0.77	0.67	0.68	0.79	-0.52	0.82
Co			1.00	0.77	0.95	0.85	0.54	0.85	0.42	0.49	0.89	0.88	0.82	0.70	0.70	0.86	-0.51	0.79
Cr				1.00	0.79	0.86	0.71	0.85	0.48	0.56	0.82	0.87	0.82	0.74	0.68	0.86	-0.52	0.84
Cs					1.00	0.86	0.56	0.87	0.46	0.48	0.90	0.92	0.83	0.72	0.71	0.87	-0.50	0.80
Eu						1.00	0.81	0.95	0.46	0.61	0.92	0.93	0.90	0.85	0.76	0.93	-0.56	0.95
Hf							1.00	0.80	0.37	0.52	0.72	0.79	0.76	0.72	0.65	0.74	-0.47	0.88
La								1.00	0.49	0.60	0.92	0.94	0.94	0.82	0.79	0.93	-0.47	0.94
Lu									1.00	0.39	0.43	0.45	0.54	0.42	0.45	0.46	-0.22	0.48
Nd										1.00	0.51	0.56	0.56	0.59	0.39	0.51	-0.24	0.58
Rb											1.00	0.93	0.90	0.79	0.72	0.92	-0.52	0.90
Sc												1.00	0.89	0.78	0.77	0.92	-0.56	0.91
Sm													1.00	0.75	0.72	0.90	-0.40	0.90
Ta														1.00	0.67	0.79	-0.47	0.84
Tb															1.00	0.75	-0.50	0.77
Th																1.00	-0.56	0.92
U																	1.00	-0.56
Yb																		1.00

the main water body (TMC-97-14, TMC-97-5). The upward Ca decrease in all the cores, from Unit B to A, points to the lake water evolution from more concentrated (lowstand) to more diluted stages (highstand). MnO and MgO concentrations display a similar fluctuating pattern throughout depth than CaO (i.e. diminishing from base to top along the cores), as well as increasing concentrations from the river mouths towards more distal areas (Fig. 3). The vertical fluctuations may be the consequence of fluctuating rates of Mn and, Mg co-precipitation with evaporitic minerals.

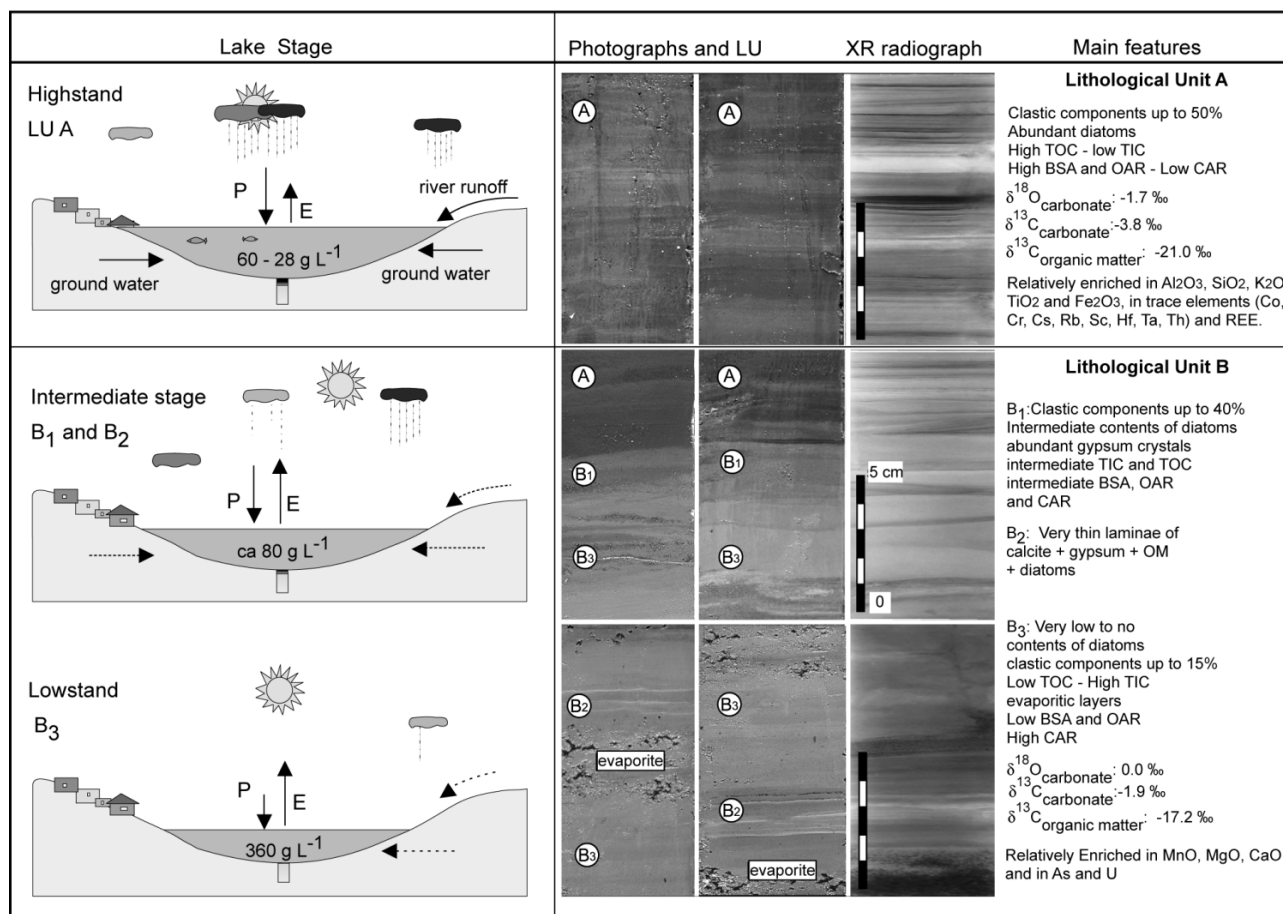
The highest sodium concentrations along the cores (Fig. 3) are matching levels with clusters of evaporite crystals dispersed in the mud (i.e., core TMC-97-14, level 18 cm) and well defined evaporitic layers (core TMC-97-14, level 44 cm). However, sodium does not exhibit a well-defined trend along the cores to clearly link its vertical variability to a specific lithological unit. Table 1, for instance, shows that average concentrations in Units A from all analyzed cores are slightly higher than average values in Unit B, while table 3 shows the lack of correlation with other elements characteristic of evaporites (group 2). The general absence of high Na contents in the sedimentary record of low lake levels (i.e., Unit B) and its variability along the core, can be explained by the high halite solubility which rules its dissolution, mobilization and later reprecipitation during early diagenetic processes (Schreiber & El Tabakh 2000). This assumption can also explain the presence of halite crystals in the record of high lake level (i.e., Unit A in Core TMC-97-14, level 18 cm). P<sub>2</sub>O<sub>5</sub> concentration does not show a marked vertical variability along the cores (i.e. from 0.2 to 0.3%; Fig. 3). In general P<sub>2</sub>O<sub>5</sub> contents are in the range of fluvial suspended sediments that reach the lake through Ríos Suquía, Xanaes and Dulce (Galván 2000). However, maximum values in Unit B and positive correlations with element from group 2 (i.e., MnO, MgO and CaO in table 2) suggest

that phosphate precipitation can additionally occur at high salinities during low lake levels.

Figure 4a shows Upper continental crust-normalized elemental concentrations for all the analyzed samples. Samples from Unit A show multi-elemental patterns that are similar to patterns from Unit B samples. The agreement between pattern shapes suggests an unvarying source for the clastic fraction during the sediment deposition, even at contrasting hydrological scenarios. However, both lithological units show different average concentrations of trace and rare earth elements (REE), as indicated in table 2. Box and whisker plots (Fig. 5) for most of trace elements and REE provide the summary statistics of the compositional range of each element in both units. Changes in the position of the box (percentiles 25 and 75), median, minimum and maximum elemental concentration values confirm the significant geochemical differences between units A and B.

The correlation matrix coefficients shown in table 4, allow us to differentiate two groups of trace elements with strong reciprocal correlation: (1) Co, Cr, Cs, Rb, Sc, REE, Hf, Ta and Th; and (2) As and U. Unit A is enriched in elements from group 1, with elemental concentrations within the range showed by fluvial Quaternary sediments outcropping in the Río Suquía basin (West of the lake) as well as by Río Suquía sediments (Piovano *et al.* 1999). Thus, the trace elements enrichment in river-influenced cores (i.e., TMC-97-3 and TMC-97-14), and in the sediments deposited during highstands (Unit A) can be attributed to a higher contribution of allogenic minerals and heavy mineral suite which host this group of elements (e.g., Sholkovitz 1990).

Conversely, the As and U enrichment in Unit B could be associated to precipitated minerals. The remarkable enrichment in both elements is more likely due to evaporative concentration than to adsorption onto the mineral surfaces, as suggested by the alkaline pH and the hydrological evidence previously described.



**Fig. 6.** Modeling representing lake-level changes and the resulting sedimentary, isotopical and geochemical record (Modified from Piovano *et al.* 2002). P-E arrows indicate precipitation (P) evaporation (E) balance; the relative length of the arrows indicates de predominance of either P or E. Higher river runoff and groundwater inputs are indicated by solid arrows, whereas dotted arrows indicate comparatively low inputs. Lake water salinity is indicated. Photographs, X-ray radiographs and descriptions of lithological units. Encircled letters designate individual lithological units. TOC: total organic carbon, TIC: total inorganic carbon, BSA: bulk sediment accumulation rate, OAR: organic accumulation rate, CAR: carbonate accumulation rate, REE: rare earth elements. Isotope ratios are average values (taken from Piovano *et al.* 2004).

The previous proposed sedimentary and isotopical models for Laguna Mar Chiquita are now improved with the addition of a new proxy, such as the bulk geochemical composition of the sediments (Fig. 6). The integration of this multiproxy dataset with these models further refine existing lake level reconstructions.

## 7. CONCLUSIONS

Our results show a close correspondence between the long-term hydrological conditions and the sediment chemical composition as reflected by both major and trace element concentrations. Conversely, short-lived lake level changes (e.g. ca 1934 and 1960) had not produced noticeable effects on the bulk sediment geochemistry indicating that certain thresholds need to be overcome in order to generate a geochemical imprint in the sediments. The spatial geochemical variability observed in the sediments from litoral to pelagic areas is associated with the sediment transport from the river mouths inward the lake basin. The vertical variability at

each core site, however, represents changes in the hydrological stage of the lake.

Agricultural activities in the catchment area probably increase the fluvial clastic flux to the lake during positive hydrological balances. Although human impact cannot be ruled out as an additional factor increasing the most recent lake productivity, the higher amount of living organisms in the lake during highstands seems to be the result of comparatively lower salinities. Only the uppermost Unit A (younger than 1976) displays the highest TOC contents despite that human settlements, intensive deforestation, and agricultural activities have started as early as the end of the 19<sup>th</sup> century.

Highstand sediments accumulated during positive P/E intervals are enriched in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, and in most of the trace elements. The marked covariance among these oxides as well as among trace elements suggest an identical source. Thus, high concentrations of these elements in the sediments are indicative of a comparatively high input of fluvial detritus

during positive hydrological balances resulting in lake highstands.

Lowstand sediments accumulated during negative hydrological balances are enriched in Ca, Mn, Mg, and P as well as in As and U. High concentration of these elements are the fingerprint of high lake water salinities which promote the precipitation of evaporites.

Both groups of elements display in turn a negative correlation between them. Therefore, the geochemistry of Laguna Mar Chiquita sediments gives an additional proxy to reconstruct very recent environmental changes. These data combined with sedimentological, other geochemical and isotopic information allows the development of a robust model to reconstruct past lake level fluctuations. This model is based in a range of independently controlled proxies that go beyond instrumental and historical data. Furthermore, these results are useful to interpret similar saline lacustrine records at wider geographical and temporal scales.

The synchronous behavior of Laguna Mar Chiquita water level changes and the instrumental record of fluvial discharge variations in southeastern South America highlight the sensitivity of the lake to environmental changes at a continental scale. Thus, its sedimentary record has the potential to identify the frequency of hydrological changes at longer time scales, affording the opportunity to gain insight into paleo-circulation dynamics in subtropical South America.

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