Multielemental determination by instrumental neutron activation analysis and recent sedimentation rates using ^{210}Pb dating method at Laguna del Plata, Cordoba, Argentina

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Laguna del Plata (Cordoba, Argentina) is a small saline lake connected to Laguna Mar Chiquita. Its level fluctuations have changed notably through the centuries with both high level (HLP) and low level (LLP) periods. The radionuclides ^{226}Ra and ^{210}Pb were analyzed in a core to determine dates and sedimentation rates. The elements As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Se, Ta, Th, U, Zn, Zr and rare earth Ce, Eu, La, Lu, Nd, Sm, Tb and Yb were determined by instrumental neutron activation analysis. Statistical analysis of elemental concentrations (cluster analysis) reflects the association of the samples along the core according to the provenance of the sediments and if they had been deposited during HLP or LLP.

Introduction

Laguna del Plata (62°51'45"–30°54'38", Cordoba, Argentina) is a small saline lake connected to Laguna Mar Chiquita. The Suquia River is the only tributary and produces a dilution in the water salinity, as compared to the main lake. The lake probably originated about 30.000 years B.P.[1]

The most striking feature of the system is its marked water level fluctuations, which define low level (LLP) and high level (HLP) periods. For example, its surface area increased from 1,960 km^2 in 1977 to 5,772 km^2 in 1982.[2] During LLP the Laguna del Plata could become isolated from the Laguna Mar Chiquita.

Neutron activation analysis (NAA) has been widely applied for soil and sediment analysis[3–6] allowing the determination of various elements such as Mn. Zn, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Sb, Se, Ta, Th, U, W, Zr, and rare earth elements.

DINESCU et al.[6] using NAA associated to X-ray diffraction, investigated the vertical distribution of 24 microelements (As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Nb, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, U, Yb and Zn) and 2 macroelements (Na and Ca), in sedimentary deposits in Matita Lake, located in Danube river delta, establishing relations among them by correlation analysis.

This paper aims to study geochemical features in a sediment core obtained in the Laguna del Plata. Multielemental analysis was performed in the sediment core samples by using instrumental neutron activation analysis (INAA) technique. The concentration of ^{226}Ra and ^{210}Pb was used to determine the dates and sedimentation rate. These results are part of a wider research project that includes the whole Mar Chiquita lacustrine system.

Experimental

An 80 cm long sediment core was extracted in November 1997, using a Beeker-type sediment sampler (Eijkelkamp), at a water-depth of 3.6 m. Bottom sediment grab samples were also collected using a Van Venn-type dredge.

Grain-size analysis of the sediments samples were performed by PIOVANO et al.[7] Grain sizes are dominantly silt and clay, indicating the prevalence of settling processes. Fine sand content is sparse in few levels of the core, and its provenance is related to Rio Suquia stream. Mean grain-size ranged from 0.044 mm to 0.00064 mm. Sediments exhibit very fine parallel lamination which is produced by variations in the grain-sizes and in the organic matter contents.

The measurement of the radionuclides ^{226}Ra and ^{210}Pb were used to determine the dates and sedimentation rate. These radionuclides were determined in each slice of the core. The samples of sediments were dried at 60 °C and sifted in sieves of 0.065 mm. The samples were then totally dissolved in mineral acids, conc. HNO$_3$, 40% HF and 30% H$_2$O$_2$, in a microwave digestor and submitted to the radiochemical procedure for the determination of Ra and Pb.

This procedure consists of an initial precipitation of Ra and Pb with 3M H$_2$SO$_4$, dissolution of the precipitate with nitrilo-tri-acetic acid at basic pH, precipitation of

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Ba(^{226}Ra)SO$_4$ with ammonium sulfate and precipitation of ^{210}PbCrO$_4$ with 30% sodium cromate. The chemical yields for both radionuclides were determined gravimetrically, by weighing Ba(^{226}Ra)SO$_4$ precipitate for ^{226}Ra and ^{210}PbCrO$_4$ precipitate for ^{210}Pb. The ^{226}Ra concentration was determined by gross alpha counting of Ba(^{226}Ra)SO$_4$ precipitate[8] and ^{210}Pb concentration through its decay product ^{210}Bi, by measuring the gross beta activity of ^{210}PbCrO$_4$ precipitate.[9] Both radionuclides were determined in a low background gas flow proportion detector. The dates were calculated by the Constant Initial Concentration (CIC) model.[10]

For the multielemental analysis of samples, approximately 200 mg of sediment (duplicate samples), about 150 mg of reference materials and synthetic standards were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multi-element synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman No. 41 filter paper.

Sediment samples, reference materials and synthetic standards were irradiated for 16 hours, under a thermal neutron flux of 10^{12} n·cm^{-2}·s^{-1} in the IEA-R1m nuclear reactor at IPEN. Two series of counting were made: the first, after a one week decay and the second, after 15–20 days. The counting time was 2 hours for each sample and reference material and half an hour 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 ^{57}Co and ^{60}Co, respectively. The analysis of the data was made by VISPECT program to identify the gamma-ray peaks[11] and by ESPECTRO program to calculate the concentrations. Both programs were developed at the Radiochemistry Division, IPEN. The elements analyzed by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Se, Ta, Th, U, Zn, Zr and the rare earth Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. The methodology validation was verified by measuring the reference materials Buffalo River Sediment (NIST SRM 2704) and Soil 7 (IAEA).

Results and discussion

Isotopic ages are presented in Fig. 1a. The ^{210}Pb profile depicts a well-defined linear trend from level 0 cm (year 1997) to level 36 cm (year 1941). These results indicate an average accumulation rate of 0.6 cm·y^{-1}. The lower dated level (52 cm) yields a sedimentation rate of 0.7 cm·y^{-1}. Both rates are minimum theoretical rates since exposure of the lake floor due to water evaporation (subaerial exposure) was not considered during LLP.

Water level values of the lake were taken into account for years corresponding to ^{210}Pb data (Fig. 1b). Departures from the mean lake water level are expressed as positive values during HLP (levels higher than the mean) or negative values during LLP (levels lower than the mean). Water levels were obtained from a report published by Universidad Nacional de Córdoba.[12]

Although water level data are reliable for the 1967–1997 period, a LLP could have occurred during 1936–1954 (partially supported by local knowledge). Parts of these years are represented in the core below 36 cm, thus matching with the ^{210}Pb anomalous values. This fact could be attributed to lead enrichment due to long-time subaerial exposure of the lake floor during extreme dry periods.
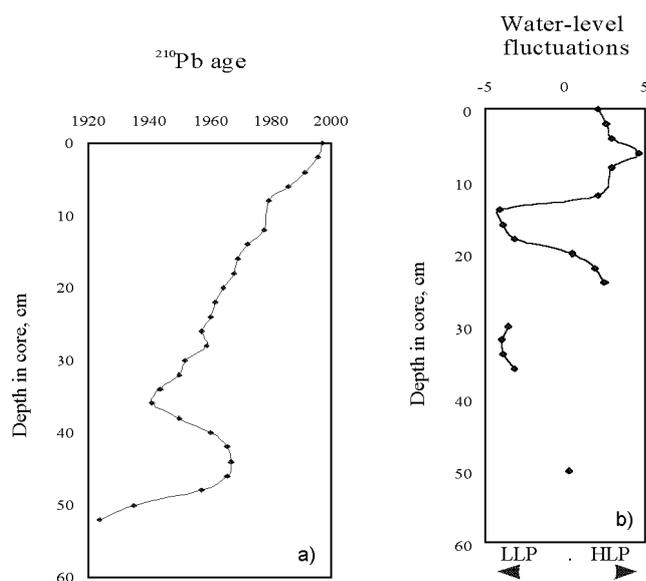

Fig. 1. Age-depth relationship for the core (a), water level fluctuations, zero value corresponds to mean lake level (b)

Two sedimentation rates can be defined when considering present-day HLP and the last LLP of the lake. The HLP is represented from 0 cm (1997) to 12 cm (1978) and has a sedimentation rate of 0.6 cm·y^{-1}. The LLP is represented from 14 cm (1972) to 20 cm (1964), and has a higher accumulation rate than the previous one, in the order of 1.0 cm·y^{-1}.

The results obtained for Buffalo River Sediment and Soil 7 reference materials, as well as certified and information values are presented in Table 1. It can be seen that the results for the analyzed elements are, in general, in good agreement with the certified or information values. The relative standard deviations were less than 10% for most elements in both reference materials, except for Nd and Lu for Soil –7 and Buffalo river sediment materials, respectively. Figure 2 shows the calculation of the standardized difference or z-value that was made according to Bode.[13]
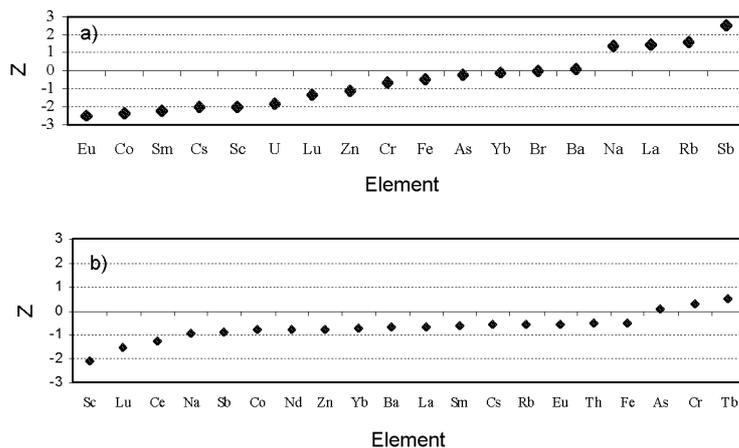

Fig. 2. Control chart (z-values) for inspection of the normalized concentrations of some elements
in the NIST SRM 2704 (a) and SOIL-7 (b) reference material samples, respectively

Table 1. Results obtained for the reference materials Soil 7 (IAEA) and Buffalo River Sediment (NIST SRM 2704) by INAA

Element	Concentration unity	SOIL-7		NIST SRM 2704	
		Found values	Literature value	Found values	Literature value
As	μg	13.5 ± 0.7	13.4 ± 0.84	23.2 ± 0.5	23.4 ± 0.8
Ba	μg	151 ± 12	(159)	417 ± 33	414 ± 12
Br	μg	8.7 ± 0.5	(7)	7.0 ± 0.7	(7)
Ce	μg	52.3 ± 0.7	61 ± 7	58.5 ± 0.7	(72)
Co	μg	8.21 ± 0.01	8.9 ± 0.9	12.4 ± 0.3	14.0 ± 0.6
Cr	μg	64 ± 1	60 ± 13	132 ± 2	135 ± 5
Cs	μg	5.0 ± 0.1	5.4 ± 0.7	5.8 ± 0.1	(6)
Eu	μg	0.89 ± 0.04	1.0 ± 0.2	1.20 ± 0.04	(1.3)
Fe	%	2.53 ± 0.08	(2.57)	4.0 ± 0.1	4.1 ± 0.1
La	μg	27.3 ± 0.4	28 ± 1	30.0 ± 0.7	(29)
Lu	μg	0.27 ± 0.02	(0.3)	0.52 ± 0.06	(0.6)
Na	μg	2303 ± 102	(2400)	5860 ± 247	5470 ± 140
Nd	μg	25 ± 3	30 ± 6		
Rb	μg	48 ± 3	51 ± 5	108 ± 5	(100)
Sb	μg	1.5 ± 0.1	1.7 ± 0.2	4.23 ± 0.09	3.79 ± 0.15
Sc	μg	8.09 ± 0.01	8.3 ± 0.1	11.8 ± 0.1	(12)
Sm	μg	4.86 ± 0.02	5.1 ± 0.4	6.3 ± 0.2	(6.7)
Tb	μg	0.70 ± 0.06	0.6 ± 0.2	8.9 ± 0.1	(9.2)
Th	μg	7.6 ± 0.3	8.2 ± 1.1		
Yb	μg	2.10 ± 0.07	2.4 ± 0.4	2.8 ± 0.1	(2.8)
Zn	μg	99 ± 3	104 ± 6	422 ± 8	438 ± 12

( ) Information values.

The calculation of the standardized difference or z-value of a result is given by:

$$Z_i = (C_i - C_{ref,i})/(\sigma^2_i + \sigma^2_{ref,i})^{1/2}$$

were C_i – concentration of element i in the reference material analysis,

$C_{ref,\,i}$ – concentration of the certified or consensus value for element i,

σ_i – uncertainty of the concentration of element i in the reference material analysis,

$\sigma_{ref,i}$ – uncertainty of the certified consensus value for element i.

If $|z|<3$, it means that the individual result of the control sample (reference material) should be in the 99% confidence interval of the target value.

Table 2 shows the results obtained for multielemental analysis in the sediment samples by INAA. The precision based in duplicate samples analysis was better than 10%.

Statistical analysis on elemental concentrations (cluster analysis, Fig. 3) reflects the association of the samples along the core according to the provenance of the sediments and if they had been deposited during HLP or LLP (Fig. 1b). For example, HLP are characterized by higher average concentrations of Co, Cr, Eu, Fe, La, Sm, Zn than during LLP. This is intimately linked to variations in the source and the nature of sediments, LLP are dominated by eolian processes and water evaporation meanwhile HLP are fluvial dominated. During LLP Laguna del Plata is isolated from the main lake (Laguna Mar Chiquita) and considered a closed-lake, explaining why sediment composition are more influenced by the wind and water evaporation. These results in combination with future mineralogical studies will provide an improved and more in-depth analyses of source identification.

Conclusions

Although long-term sedimentation rates at Laguna del Plata are estimated to range between 0.6–0.7 cm·y^{-1}, shorter-term rates differ according to the water level of the lake. During LLP sediment accumulation is faster than during HLP. This could be a consequence of direct settling to the lake of sediments transported by eolian processes. Moreover, the disconnection of the Laguna del Plata from Mar Chiquita during LLP hinders the dispersion of sediment to the main lake. An striking ^{210}Pb anomaly (38 to 50 cm) is probably produced by subaerial exposure of the lake floor. Statistical analysis on elemental concentrations (cluster analysis) reflects the association of the samples along the core according to the provenance of the sediments and if they had been deposited during HLP or LLP.
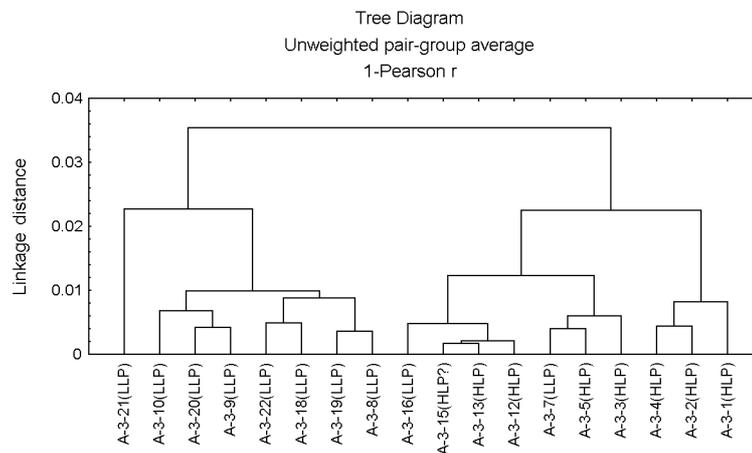

Fig. 3. Cluster for 22 samples. Samples are separated in two major groups according to the lake level during their deposition

Table 2. Concentration of the elements (in $\mu g \cdot g^{-1}$) determined by INAA in the different depths of the sediment core samples

Depht, cm	A 3-1 0–2	A 3-2 2–4	A 3-3 4–6	A 3-4 6–8	A 3-5 8–10	A 3-6 10–12	A 3-7 12–14	A 3-8 14–16	A 3-9 16–18	A 3-10 18–20	A 3-11 20–22
As	13.5	11.1	14.5	14.6	14.1	12.5	12.4	12.2	21.8	15.0	17.4
Ba	342.0	358.3	451.0	340.0	328.0	356.8	322.0	506.7	511.0	487.5	432.6
Br	26.5	25.3	28.1	13.4	12.8	18.6	15.0	21.6	22.5	31.8	26.4
Ce	67.1	69.9	72.6	75.1	73.0	75.7	76.0	69.0	106.0	115.8	67.8
Co	12.4	13.3	14.2	13.4	13.3	14.2	13.6	12.6	9.9	12.1	12.9
Cr	51.6	52.8	50.3	46.1	47.0	51.0	48.2	46.8	38.9	49.4	44.4
Cs	9.0	9.7	9.9	8.8	9.2	9.7	10.9	9.3	7.4	9.0	8.9
Eu	1.3	1.2	1.2	1.2	1.3	1.2	1.3	1.1	0.9	1.0	1.1
Fe, %	3.8	4.1	4.0	3.8	3.9	4.1	4.2	3.9	3.0	3.7	3.7
Hf	4.3	4.5	4.5	4.3	5.5	4.9	4.7	4.3	6.9	6.1	3.7
La	28.0	28.3	29.2	30.2	30.5	30.9	31.2	30.0	25.2	26.5	28.0
Lu	0.6	0.4	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.3	0.4
Na, %	3.9	3.9	4.3	3.0	2.7	3.4	2.9	3.5	4.2	4.7	2.9
Nd	30.3	37.5	28.1	47.1	31.5	39.9	30.0	31.7	28.2	32.6	34.0
Rb	172.3	127.7	217.3	128.3	177.6	140.5	180.1	126.8	104.9	123.9	101.4
Sb	0.7	0.8	0.6	0.9	0.6	0.5	0.9	0.5	0.8	0.9	0.7
Sc	12.4	13.6	13.2	13.0	12.9	13.5	13.7	13.1	13.4	16.0	12.8
Se	0.5	1.0	0.6	0.7	0.8	0.5	0.6	0.5	0.6	0.5	0.3
Sm	6.7	6.2	6.3	6.5	6.3	6.7	6.4	5.9	5.5	5.7	6.0
Ta	1.4	1.3	1.3	1.3	1.6		1.5	1.3	1.1	1.2	1.2
Tb	0.7	0.8	0.7	0.8	1.2	0.8	0.8	0.8	0.8	0.8	
Th	11.8	11.7	12.7	13.9	13.2	12.7	13.1	11.7	9.9	11.0	11.3
U	10.2	5.7	5.6	4.3	3.7	5.1	3.9	4.7	5.1	6.1	13.4
Yb	2.3	2.3	2.4	2.5	2.6	2.8	2.5	2.5	2.1	2.4	2.1
Zn	135.1	144.8	144.7	127.6	130.8	142.1	133.7	125.8	98.6	129.5	124.9
Zr	221.0	259.9	222.9	211.5	182.2	160.7	145.4	212.7	244.5	268.4	134.0

Depht, cm	A 3-12 22–24	A 3-13 24–26	A 3-14 26–28	A 3-15 28–30	A 3-16 30–32	A 3-17 32–34	A 3-18 34–36	A 3-19 36–38	A 3-20 38–40	A 3-21 40–42	A 3-22 42–44
As	21.9	13.5	14.5	11.2	24.9	20.8	35.4	34.1	41.1	37.0	44.0
Ba	390	336	353	327	358	311	435	446	512	693	521
Br	18.1	22.1	21.8	23.5	22.5		13.4	9.9	12.5	10.0	12.5
Ce	78.6	71.1	74.7	77.2	76.8	72.0	63.0	61.9	67.7	58.0	72.0
Co	15.7	14.1	14.3	15.4	14.6	13.6	14.4	11.9	11.7	11.0	15.0
Cr	52.6	48.4	49.7	50.2	48.5	45.5	45.9	39.2	38.2	40.0	49.0
Cs	10.5	9.4	10.5	10.6	10.7	10.4	9.9	7.9	8.3	8.0	10.4
Eu	1.2	1.1	1.2	1.1	1.2	1.1	1.2	1.1	1.1	1.0	1.3
Fe, %	4.5	4.1	4.2	4.4	4.6	4.3	4.1	3.4	3.3	3.6	4.3
Hf	4.0	4.1	3.9	3.4	3.5	4.1	4.4	4.9	4.7	5.0	6.0
La	30.2	28.2	29.4	29.4	31.1	30.5	29.5	27.0	28.7	25.0	32.0
Lu	0.4	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3
Na, %	2.7	3.1	3.3	3.1	3.2	3.8	3.0	2.9	2.8	2.6	3.2
Nd	37.7	30.1	29.8	35.6	35.0	31.8	30.8	27.1	35.7	32.1	37.6
Rb	143.6	127.0	141.7	139.4	147.9	141.5	146.6	110.3	110.3	116.0	161.0
Sb	0.7	0.2		0.6	0.4	0.7	0.7	0.7	0.8	0.6	0.8
Sc	15.0	13.6	14.2	14.9	14.9	14.8	13.9	11.7	11.6	11.0	15.2
Se	0.5	0.5	0.5	0.4	0.5	0.6	0.6	0.6	0.5	0.6	0.7
Sm	6.5	6.1	6.4	6.6	6.6	6.3	6.0	5.6	6.0	6.2	6.7
Ta	1.2	1.1	1.1	1.1	1.5	1.2	1.4	1.4	1.1	1.1	1.3
Tb	0.9	0.8	1.0	0.8	0.9	0.8	0.8	0.8	0.7	0.6	0.8
Th	13.2	12.1	12.4	12.3	13.3	11.9	11.6	10.8	10.9	10.0	12.0
U	6.9	7.2	9.3	3.8	4.1	7.5	5.3	4.9	19.6	18.6	18.8
Yb	2.1	2.1	2.2	2.1	2.2	2.2	2.4	2.3	2.2	2.1	2.6
Zn	168.7	129.7	135.8	142.6	139.4	123.8	115.0	92.8	94.9	91.0	124.0
Zr	156.4	147.5	133.6	144.8	119.5	160.6	198.0	160.2	261.2	205.0	290.0

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