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Lacustrine sediments provide geochemical evidence of environmental change during the last millennium in southeastern Brazil

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Abstract

A 172 cm-long sediment core was collected from a small pristine lake situated within a centripetal drainage basin in a tropical karst environment (Ribeira River valley, southeastern Brazil) in order to investigate the paleoenvironmental record provided by the lacustrine geochemistry. Sediments derived from erosion of the surrounding cambisoils contain quartz, kaolinite, mica, chlorite and goethite. Accelerator mass spectroscopy (AMS) ^{14}C dating provided the geochronological framework. Three major sedimentary units were identified based on the structure and color of the sediments: Unit III from 170 to 140 cm (1030 ± 60–730 ± 60 yr BP), Unit II from 140 to 90 cm (730 ± 60–360 ± 60 yr BP) and Unit I from 90 to 0 cm (360 ± 60–0 yr BP). Results of major and trace element concentrations were analysed through multivariate statistical techniques. Factor analysis provided three factors accounting for 72.4% of the total variance. F1 and F2 have high positive loadings from K, Ba, Cs, Rb, Sr, Sc, Th, light rare earth element (LREE), Fe, Cr, Ti, Zr, Hf and Ta, and high negative loadings from Mg, Co, Cu, Zn, Br and loss on ignition (LOI). F3, with positive loadings from V and non-metals As and Sb, accounts for a low percentage (9.7%) of the total variance, being therefore of little interpretative use. The profile distribution of F1 scores reveals negative values in Units I and III, and positive values in Unit II, meaning that K, Ba, Cs, Rb, Sr, Sc, Th, LREE, Fe, Cr, Ti, Zr, Hf and Ta are relatively more concentrated in Unit II, and Mg, Co, Cu, Zn and Br are relatively more abundant in Units I and III. The observed fluctuations in the geochemical composition of the sediments are consistent with slight variations of the erosion intensity in the catchment area as a possible response to variations of climatic conditions during the last millennium.
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Keywords: Lake sediments; Southeastern Brazil; Late Holocene; Chemostratigraphy; Mineralogy; Climate change

1. Introduction

Lacustrine sediments contain one of the most important continental archives for the study of paleoenvironmental reconstruction. Most studies focus on paleoecological and paleoclimatic reconstructions based

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on palynological and carbon isotopic data. Elemental analyses of sediments, though less frequently used, can also provide useful information regarding provenance sources and climate change, either as an independent method (Robinson, 1994; Piovano et al., 2004; Ng and King, 2004; Yanes et al., 2006; Ruiz-Fernandez et al., 2007; Tanaka et al., 2007; Xue et al., 2007; Minyuk et al., 2007) or associated with pollen and isotopic data (Osborne et al., 1993; Goslar et al., 1999; Brauer et al., 2000; Mingram et al., 2004; Dressler et al., 2006; Parker et al., 2006; Schettler et al., 2007). The determination of mineralogical composition of sediments is another useful tool for paleoenvironmental reconstruction of lake ecosystems (Luque and Julià, 2002; Sakai et al., 2005; Fagel and Mackay, 2008; Fagel and Boës, 2008), particularly as a complement to the chemostratigraphic approach (Freitas et al., 2003; Roy and Smykatz-Kloss, 2007), as suggested earlier by Last (2001).

In Brazil, many paleoenvironmental reconstructions based on lake sediments have been conducted in recent decades (Behling, 1998; Salgado-Laboriau et al., 1998; Behling and Costa, 2001; Behling et al., 2001; Siffedine et al., 2001; Rodrigues-Filho et al., 2002; Siffedine et al., 2003; Irion et al., 2006; Ledru et al., 2006). In the southeastern Atlantic forest, a high-resolution study based on biotic and isotopic proxies was performed on the Lagoa Grande lake sediments, spanning 1039 yr (Saia, 2006; Pessenda et al., in preparation). This study indicated that a hot and humid climate prevailing in the region during the last millennium was punctuated by a short particularly warmer and wetter period between 400 and 320 yr BP.

Here we present the mineralogical and geochemical record of the Lagoa Grande sediments and compare our results with the environment reconstruction made on the same core material by Saia (2006). This is the first study in Brazil to establish a link between bulk chemistry of lake sediments and environmental changes during the last millennium, and one of the few such studies in the southern hemisphere.

2. Study area

The study area is located in the southern part of the State of São Paulo, in southeastern Brazil. Lagoa Grande (24°32′S latitude and 48°40′W longitude, ca 360 m above the sea level) is a small lake situated in a protected area of the Upper Ribeira State Park (Fig. 1). The park is a conservation unit on the left bank of the Ribeira River, approximately 350 km from the city of São Paulo, and 100 km from the Atlantic coastline. The lake developed within a centripetal drainage basin on karst topography. The catchment area is approximately 12 000 m^2 and the lake itself occupies an area of approximately 150 m^2. The present maximum water

depth is 1 m. Situated in a virtually inaccessible region, remote from direct human impacts, the lake contains largely untouched natural sediments.

Bedrock geology consists of a sequence of low-grade metasedimentary rocks of the Late Proterozoic Açungui Group (Campanha and Sadowski, 1999) formed by fine-graded limestones interbedded mainly with metasiltites and phyllites (Fig. 1). The major minerals in these rocks are calcite, quartz, mica and chlorite. This lithology gives rise to a few meters thick clayey soils classified as cambisols. The present-day climate is tropical and humid with annual mean temperatures between 14 and 27 °C. The annual rainfall averages 1600 mm, with summer maxima from December to February (40% of the annual precipitation), and winter minima (15% of the annual precipitation) from June to August (Karmann et al., 2007). The area is covered by a dense tropical rainforest.

3. Material and methods

Samples were collected from a 172 cm core drilled in the middle part of the lake, with a vibracorer device and a 3-in diameter aluminum tube (Martin et al., 1995). The core was removed from the tube and sliced into 2 cm-thick discs. Sediment samples were collected and described in the course of a previous study that included accelerator mass spectroscopy (AMS) ^{14}C dating for 5 samples, performed at the Isotrace Laboratory, University of Toronto, Canada (Saia, 2006).

Thirty-three bulk samples were used for the present study. Samples were dried at 60 °C for 24 h, and finely ground with a tungsten mill. Bulk mineralogic composition was obtained by powder X-ray diffraction (XRD) on normal, ethylene glycol saturated and heated (at 500 °C) oriented samples. X-ray analyses were performed at the Institute of Geosciences, University of São Paulo, on a Siemens automated powder diffract-ometer equipped with a graphite monochromator. All slides were scanned over 2θ range 3–60° with a step size of 0.05°, using a CuKα radiation at 40 kV and 40 mA. The 7 Å peak, which is completely lost when samples were heated, was attributed to kaolinite. The 10 Å peak indicated the presence of sericite, and the 14 Å peak, which was not affected by chemical treatment or heating, indicated the presence of chlorite.

Chemical determination of major (Si, Al, Fe, Mg, Ca, Na, K, P, Mn and Ti) and selected trace elements (Ba, Cu, Ni, Sr, V, Y, Zn and Zr) was performed by ICP-OES at the Institute of Geosciences, University of São Paulo. Samples were taken into solution by alkaline fusion using a mixture of 0.25 g sediment powder and 0.75 g flux (lithium tetra and metaborate). 0.2 N HNO$_3$ solutions diluted to 1:1000 were analysed in an ARL-3410 sequential spectrometer. The procedures followed
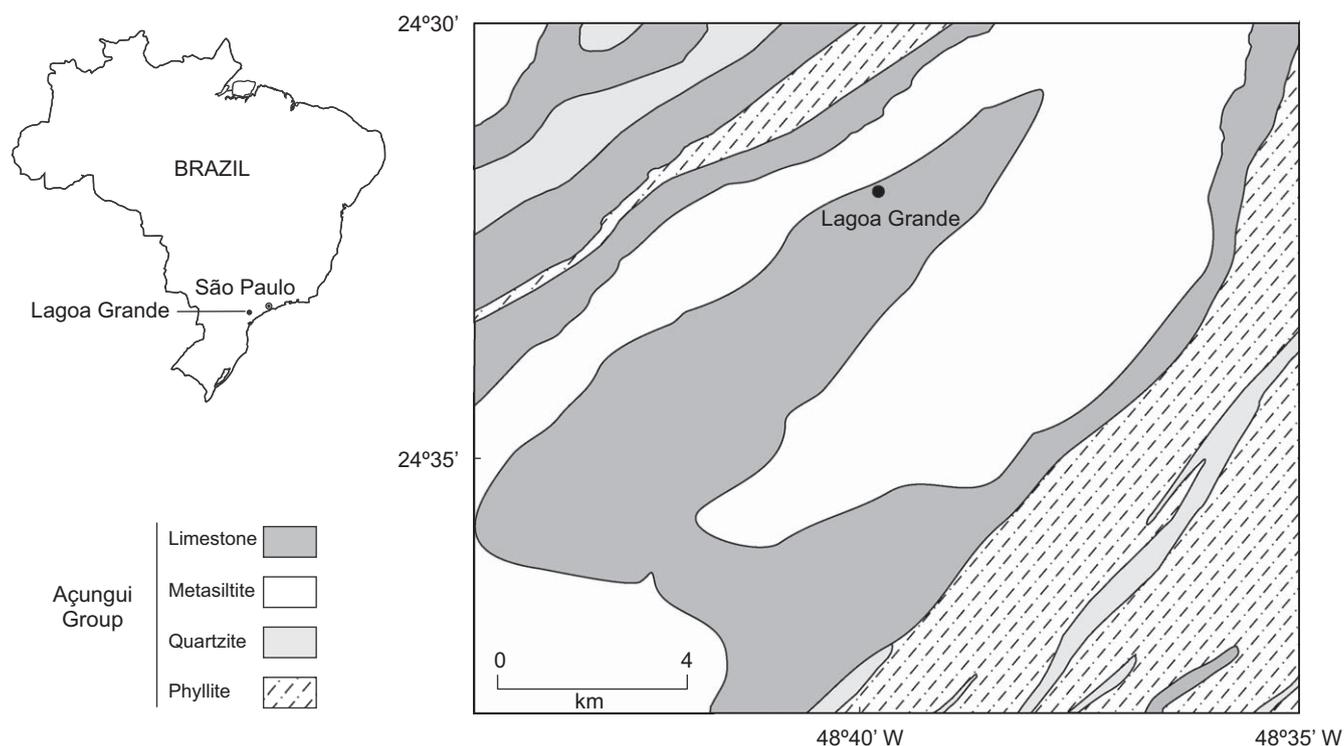
Fig. 1. Location and main geological units (modified from Campanha and Sadowski, 1999) of the Lagoa Grande area in southeastern Brazil.

were very similar to those described by Janasi et al. (1995). Total Fe was reported as Fe_2O_3. Additional trace elements (As, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Th and U), including 8 rare earth elements (REE—La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), were determined using instrument neutron activation analysis (INAA). Sample reference material and synthetic standards were irradiated for 16 h with a thermal neutron flux of 10^{12} n $cm^{-1} s^{-1}$ in the IEA-R1 nuclear reactor at the IPEN-Institute of Nuclear and Energetic Research (São Paulo). Quality control was based on the use of certified samples (NIST SRM 2704, IAEA and IWG-GIT). The lower detection limits for ICP-OES and INAA were well below the lowest measured concentrations in all samples. Precision for major and minor elements is generally better than 1%. Loss on ignition (LOI) was determined by calcination of dry samples at 1000 °C for 3 h.

4. Results

Three major sedimentary units were identified based on the structure and color of the sediments (Fig. 2). The basal sediments (Unit III: from 170 to 140 cm) consist of faintly laminated grey and brown clays. The middle Unit II (from 140 to 90 cm) consists essentially of
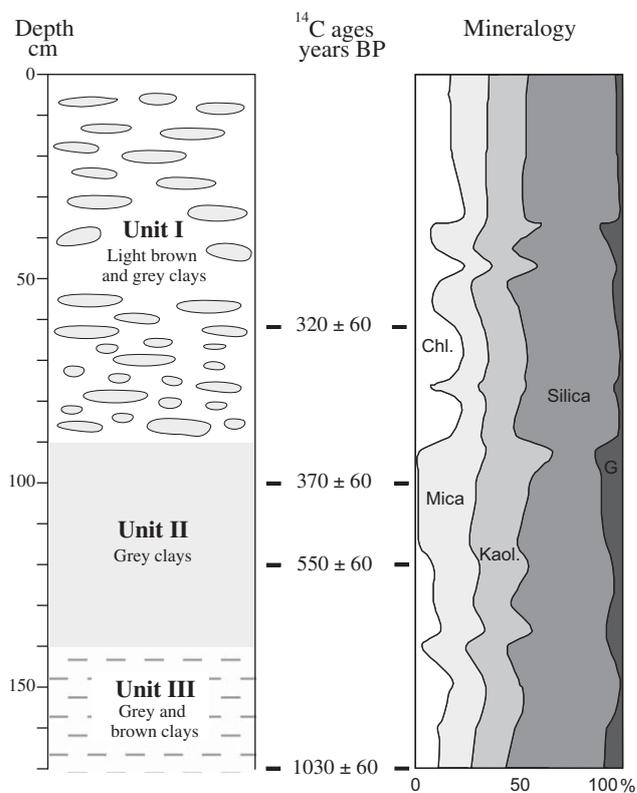
Fig. 2. Sedimentological column and mineralogical composition throughout the Lagoa Grande core profile.

massive grey clays. The uppermost layer (Unit I: from 90 cm to the surface) is composed of alternating layers of light brown and grey clays with dark nodules that are abundant mainly between 88 and 66 cm. Roots and other vegetal fragments can be found scattered throughout the core.

The chronostratigraphic data available for the core, based on five accelerator mass spectroscopy ^{14}C dates on bulk samples (Saia, 2006), are shown in Fig. 2. The extrapolated ages for Units I–III are, approximately, 0–360 ± 60, 360 ± 60–730 ± 60 and 730 ± 60–1030 ± 60 yr BP, respectively. From these results, the average sedimentation rate is estimated to be $0.17 \, \mathrm{cm \, yr^{-1}}$.

4.1. Mineral composition

The sediment samples investigated contain different proportions of the same minerals as revealed by XRD: quartz, kaolinite, mica, chlorite and minor amounts of goethite. Carbonates were not detected in the samples. The layer silicates, chlorite and mica, display sharp XRD peaks, indicating their well-ordered crystal structure.

Normative mineral concentrations (Boyle, 2004) throughout the core were calculated from XRD data and chemical composition (see Section 4.2), and are displayed in Fig. 2. Silica includes quartz and a possible amount of biogenic silica, which was not measured in this study. Unit III (170–140 cm) is defined by a stable composition with approximately the same proportions of chlorite (14.6% in average), mica (17.3% in average), and kaolinite (18.5% in average). Silica is very abundant in this unit (46.0% in average). The average concentration of goethite is 3.7%.

Unit II (140–90 cm) is marked by an upcore increasing trend of mica and kaolinite from values of approximately 20% each in the lower part of the unit (140 cm) to about 32% each in the top (90 cm). Likewise, goethite concentrations increase from 6.6% to 13.2%. This trend is more pronounced from 116 cm upward and is counterbalanced by a slight decrease of silica and a strong decrease of chlorite, which reaches its lowest abundance ($<2\%$) within this interval.

A pronounced yet irregular increase in chlorite and silica and a concomitant decrease in mica, kaolinite and goethite are observed in Unit I (90–0 cm). On average, the mineralogical composition of this unit (44.1% silica, 16.5% chlorite, 16.6% mica, 19.4% kaolinite and 3.5% goethite) is very close to that of Unit III. However, three short positive excursions of mica + kaolinite concentrations are recorded at 77, 57 and 37–43 cm.

The bulk mineralogy of the sediments is similar to that of the regional cambisoils, which represent the main source of clastic material to the lake sediments. In such soils, quartz, chlorite and mica are primary minerals inherited from the metamorphic bedrock whereas kaolinite and goethite are products of chemical weathering.

4.2. Geochemistry

Fig. 3 summarizes the geochemical stratigraphy of the core. SiO_2 (49.5–66.6%), Al_2O_3 (14.0–24.2%) and Fe_2O_3 (4.7–10.8%) are the major constituents throughout the core. All samples are strongly depleted in CaO (0.01–0.18%) and Na_2O (0.13–0.37%). LOI, which measures both water in mineral lattices and organic matter, ranges between 6.7% and 18.5%. Apart from these general observations, some differences between the units are noted.

Sediments from Unit II show higher concentrations of Al_2O_3, Fe_2O_3 TiO_2 and K_2O, and lesser concentrations of SiO_2 and MgO than those from Units I and III. The average ratio K_2O/MgO is 2.40 (0.87–9.61) in Unit II, and 0.50 (0.24–1.65) and 0.58 (0.42–0.79) in Units I and III, respectively, reflecting the dominance of mica over chlorite in Unit II, and of chlorite over mica in Units I and III. The main descriptive statistics for major elements in each unit are given in Table 1.

To compare the sediment geochemistry with that of the catchment soils (Viana Jr., 2002), the SiO_2/Al_2O_3, SiO_2/TiO_2, Al_2O_3/TiO_2, Fe_2O_3/TiO_2 and Zr/TiO_2 ratios were calculated (Table 2). Such ratios show the same range of variation in catchment soils and sediments, providing a further indication of sediment provenance from the surrounding soils.

The statistics for trace elements in each unit are displayed in Table 1. The plot of mean concentrations of selected elements in each unit normalized to the upper continental crust composition (UCC; Wedepohl, 1995) is shown in Fig. 4. All of these elements present concentrations of the same order as those of UCC, except for Cu, Sb, As and Br, which are slightly enriched in relation to UCC.

Table 3 shows the statistics for REE concentrations in each unit. Also shown are total REE concentration ($\sum$REE), light REE concentrations (LREE—La,..., Sm), heavy REE concentrations (HREE—Eu,...,Lu), LREE/HREE ratios and $(La/Yb)_{CH}$ ratios. Chondrite-normalized REE patterns for Units I–III are remarkably uniform, with steep LREE, flat HREE and a pronounced negative Eu anomaly, comparing well with the pattern of the UCC (Fig. 5). However, there are small but consistent variations in the REE characteristics between the three units. LREE concentrations, LREE/HREE ratios and $(La/Yb)_{CH}$ ratios are slightly higher in Unit II than in Units I and III while HREE concentrations are slightly lower in this unit (Table 3).

To better understand the inter-relationship between the major oxides and trace elements, an R-mode factor
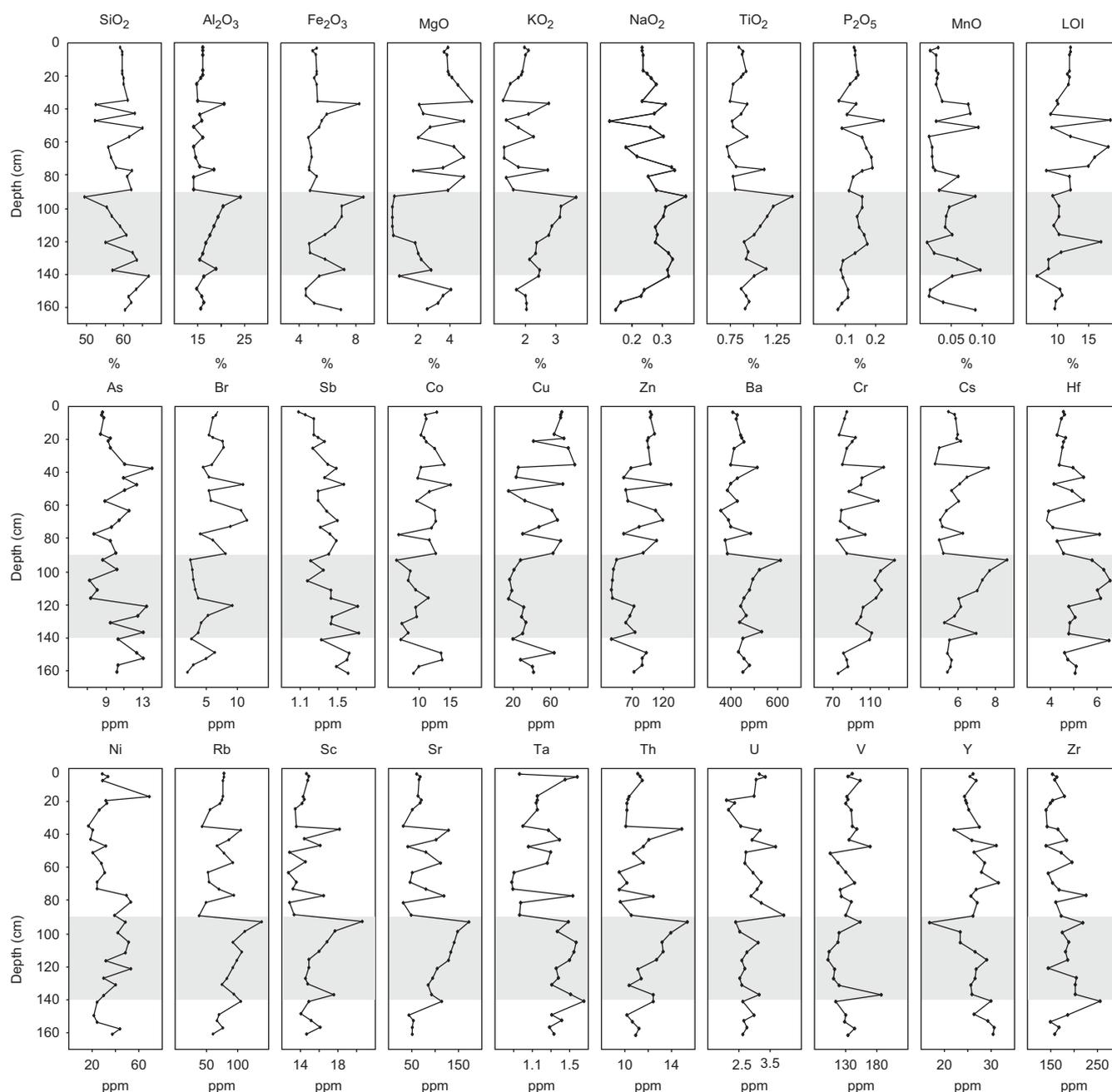
Fig. 3. Vertical concentration profiles of major and trace elements throughout the Lagoa Grande core.

analysis with varimax rotation was carried out. The data set included all trace elements analysed, and selected major elements (Fe, Mg, K, P, Ti and LOI). Three factors were extracted, accounting for 72.4% of the total variance. Factor 1 (40.5% of the total variance) has high positive loadings from K, Ba, Cs, Rb, Sr, Sc, Th, LREE, Fe, Cr, Ti, Zr, Hf and Ta, and high negative loadings from Mg, Co, Cu, Zn, Br and LOI. Factor 2 (22.2% of the total variance) also has negative loadings from Mg, Co, Cu, Zn, Br and LOI and positive loadings from K,

Ba, Cs, Rb, Sr, Sc, Th, LREE, Fe, Cr, Ti, Zr, Hf and Ta. Factor 3, with positive loadings from V and the non-metals As and Sb, accounts for a low percentage (9.7%) of the total variance, being therefore of little inter-pretative use. The loadings for F-1 and F-2 are displayed in the form of a biplot (Fig. 6).

The profile distribution of Factor 1 scores reveals negative values in Unit III, positive values in Unit II and negative values in Unit I with three positive spikes recorded at 77, 57 and 37–43 cm (Fig. 7). This means

Table 1. Concentration of major oxides (%) and trace elements (ppm) in three units.

	Unit I				Unit II				Unit III			
	Mean	St. dev.	Min.	Max.	Mean	St. dev.	Min.	Max.	Mean	St. dev.	Min.	Max.
SiO_2	59.33	3.25	52.35	64.96	58.57	4.91	49.53	66.62	61.69	1.29	60.32	63.36
Al_2O_3	15.72	1.60	14.03	20.70	18.34	2.59	15.41	24.15	15.63	0.61	14.79	16.21
Fe_2O_3	5.90	1.20	4.93	10.39	7.42	1.82	5.07	10.82	5.83	1.78	4.67	8.43
MgO	3.71	1.10	1.64	5.40	1.14	0.95	0.32	2.83	3.38	0.63	2.58	4.08
CaO	0.10	0.05	0.01	0.18	0.05	0.05	0.01	0.14	0.01	0.01	0.01	0.03
Na_2O	0.25	0.05	0.13	0.34	0.31	0.03	0.27	0.37	0.20	0.05	0.15	0.24
K_2O	1.84	0.43	1.29	2.76	2.73	0.47	2.15	3.65	1.95	0.16	1.71	2.05
P_2O_5	0.14	0.03	0.08	0.23	0.13	0.03	0.09	0.17	0.10	0.02	0.08	0.11
MnO	0.04	0.02	0.01	0.09	0.05	0.03	0.01	0.10	0.04	0.03	0.01	0.09
TiO_2	0.84	0.09	0.71	1.10	1.07	0.16	0.89	1.41	0.91	0.04	0.86	0.95
LOI	12.26	2.82	8.27	18.45	10.06	2.71	6.66	17.05	10.08	0.60	9.47	10.80
As	10.0	1.5	7.7	14.0	10.0	2.3	7.2	13.3	11.4	1.4	10.2	13.0
Ba	419	38	358	511	488	54	439	612	454	20	432	480
Br	7.1	2.1	4.1	11.5	4.0	2.0	2.6	9.3	4.1	2.0	2.1	6.4
Co	11.5	1.8	6.7	15.0	8.5	1.5	6.3	11.4	11.6	2.4	9.1	13.7
Cr	90.5	13.9	74.0	124.6	112.8	12.1	94.8	136.0	81.8	5.0	75.0	86.0
Cs	5.7	0.7	4.8	7.6	6.6	1.1	5.2	8.6	5.5	0.1	5.4	5.6
Cu	56.2	21.7	15.0	85.9	24.2	6.8	15.0	33.3	43.6	15.1	27.6	64.0
Hf	4.6	0.6	3.8	6.1	5.7	0.7	4.8	6.6	4.9	0.2	4.6	5.1
Ni	31.9	12.9	16.4	68.4	39.9	10.2	24.6	53.5	31.7	10.5	21.8	43.5
Rb	70.7	17.9	39.0	106.1	100.0	17.6	74.7	139.0	68.5	6.8	60.0	76.0
Sb	1.3	0.1	1.1	1.6	1.4	0.2	1.2	1.7	1.6	0.1	1.5	1.6
Sc	14.3	1.4	12.8	18.2	16.3	1.9	14.6	20.6	15.0	0.9	14.0	16.1
Sr	69.8	28.3	31.5	129.6	122.1	28.4	84.3	172.6	49.7	4.9	42.9	54.6
Ta	1.2	0.2	0.9	1.6	1.5	0.1	1.3	1.6	1.3	0.1	1.3	1.4
Th	10.9	1.3	9.5	14.9	12.6	1.5	10.3	15.4	10.7	0.4	10.2	11.2
U	3.0	0.5	2.1	3.9	2.7	0.3	2.4	3.2	2.7	0.2	2.6	3.0
V	134	14	105	168	123	26	101	185	134	8	128	144
Y	26.5	2.2	22.1	31.5	25.4	3.7	16.7	30.0	29.3	2.0	26.4	30.7
Zn	91.1	21.5	56.6	131.9	50.6	15.6	37.0	74.0	84.3	8.1	73.0	92.3
Zr	164	21	138	224	196	29	144	257	165	16	149	186

Table 2. Comparaison between the chemical composition of the catchment soils and the Lagoa Grande sediments.

	SiO_2%	Al_2O_3%	Fe_2O_3%	TiO_2%	Zr ppm	SiO_2/Al_2O_3	SiO_2/TiO_2	Al_2O_3/TiO_2	Fe_2O_3/TiO_2	Zr/TiO_2
Soil										
AM01	68.8	15.5	3.21	1.03	228	4.4	66.8	15.0	3.1	221
AM02	54.4	22.7	10.1	1.19	256	2.4	45.7	19.1	8.5	215
AM03	73.5	12.4	4.6	0.89	200	5.9	82.6	13.9	5.2	225
AM04	48.4	24.7	12.2	1.23	244	2.0	39.3	20.1	9.9	198
AM05	61.1	16.9	7.4	0.73	186	3.6	83.7	23.2	10.1	255
Sediments										
Unit I	59.3 ± 3.3	15.7 ± 1.6	5.9 ± 1.2	0.8 ± 0.1	164 ± 21	3.8 ± 0.4	70.6 ± 7.5	18.7 ± 1.3	7.0 ± 1.4	195 ± 16
Unit II	58.6 ± 4.9	18.3 ± 2.6	7.4 ± 1.8	1.1 ± 0.2	196 ± 29	3.3 ± 0.7	56.2 ± 10.1	17.2 ± 0.7	6.9 ± 0.9	186 ± 35
Unit III	61.7 ± 1.3	15.6 ± 0.6	5.8 ± 1.8	0.9 ± 0.0	165 ± 16	3.9 ± 0.2	68.0 ± 3.8	17.2 ± 0.1	6.4 ± 1.9	182 ± 23

that the trace elements Ba, Cr, Hf, LREE, Rb, Sc, Sr, Ta, Th and Zr behave like K, Fe and Ti with relatively higher concentrations in Unit II. By contrast, the transition metals (Co, Cu and Zn) and Br follow Mg and LOI, being relatively more abundant in Units I and III.
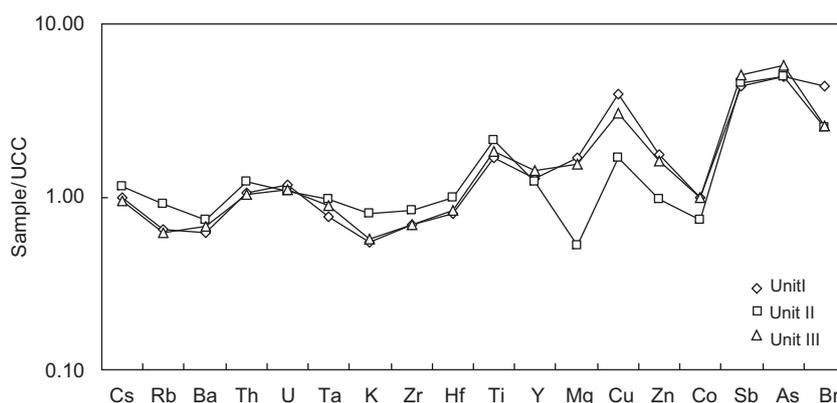
Fig. 4. Elemental patterns normalized to the composition of the upper continental crust (UCC) in each unit of the Lagoa Grande core.

Table 3. Rare earth element, total REE ($\sum$REE), light REE (La to Eu), heavy REE (Tb to Lu) concentrations (ppm), and LREE/HREE, $(La/Yb)_{CH}$, $(Eu/Eu^*)_{CH}$ ratios in three units.

	Unit I				Unit II				Unit III			
	Mean	St. dev.	Min.	Max.	Mean	St. dev.	Min.	Max.	Mean	St. dev.	Min.	Max.
La	34.8	1.7	32.6	39.7	38.4	2.3	33.0	40.6	35.5	1.3	33.5	36.5
Ce	76.6	5.4	68.5	89.3	86.2	7.1	75.6	98.3	79.8	3.6	75.0	82.9
Nd	31.7	3.1	26.2	36.3	33.5	3.0	29.1	38.0	33.1	4.4	28.7	39.1
Sm	6.0	0.3	5.5	6.7	5.9	0.3	5.5	6.4	6.7	0.4	6.3	7.1
Eu	1.2	0.1	1.1	1.4	1.2	0.1	1.1	1.3	1.4	0.0	1.3	1.4
Tb	0.9	0.2	0.6	1.4	0.7	0.1	0.5	0.9	0.8	0.1	0.7	0.9
Yb	2.9	0.2	2.5	3.2	2.5	0.3	2.2	3.0	2.9	0.2	2.7	3.2
Lu	0.5	0.0	0.4	0.6	0.5	0.1	0.3	0.6	0.5	0.1	0.5	0.6
$\sum$REE	154.6	8.2	142.4	186.8	168.7	11.7	149.9	185.8	160.6	5.5	153.4	166.6
LREE	149.1	7.9	138.0	180.5	163.8	11.4	145.6	180.5	155.1	5.3	148.0	160.8
HREE	5.5	0.3	4.4	6.4	4.9	0.3	4.4	5.3	5.6	0.2	5.4	5.9
L/H	27.1	2.1	23.5	41.0	33.6	3.2	30.4	41.0	27.9	1.5	26.4	29.7
$(La/Yb)_{CH}$	8.34	0.77	7.24	10.36	10.66	1.15	9.09	12.41	8.60	0.57	7.98	9.35
$(Eu/Eu^*)_{CH}$	0.62	0.05	0.52	0.71	0.71	0.07	0.56	0.78	0.72	0.12	0.60	0.88
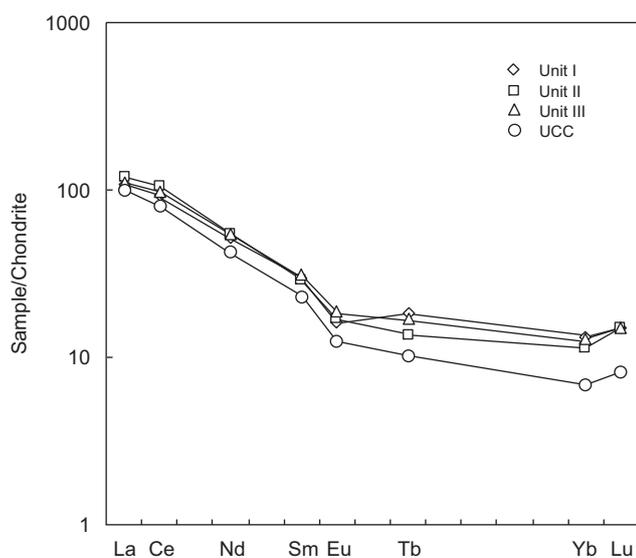
Fig. 5. Rare earth element patterns in each unit of the Lagoa Grande core and in the upper continental crust (UCC).

5. Discussion

Elements with negative loadings on F-1 and F-2 reflect the association of chlorite with the transition metals (Co, Zn and Cu), LOI and Br. This probably represents the input into the lake of material eroded from the uppermost organic horizons of the catchment soils. In the O-horizon of soils, many metals are found forming stable organo-metallic compounds. This is particularly the case for Zn and Cu, which are among the most essential elements for plant growth, being strongly recycled within the root zone and accumulated in the humus layer (Blaser et al., 2000). In addition to natural processes such as nutrient cycling, the accumulation of metals in topsoils can also be attributed to atmospheric deposition caused by anthropogenic activities (Rasmussen, 1998; Baizer and Sterckerman, 2001; Hernandez et al., 2003; Reimann et al., 2007). Bromine, on the other hand, was probably supplied to the sediments by precipitation. Its origin is generally
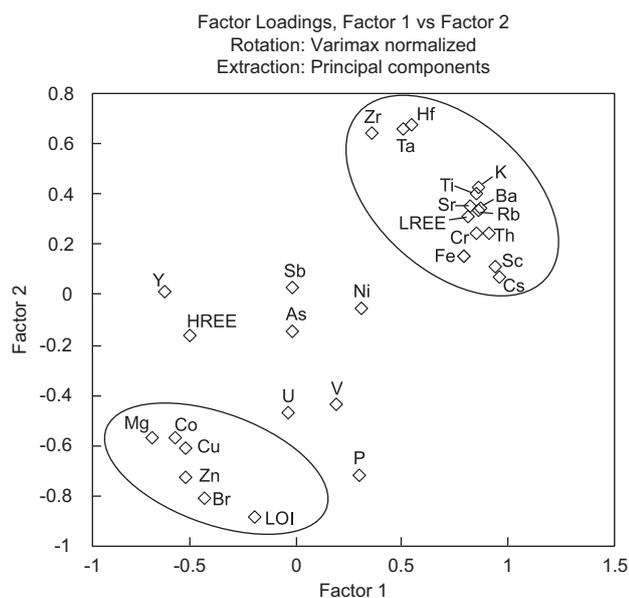
Fig. 6. Biplot of the results of factor analysis: F1 versus F2.
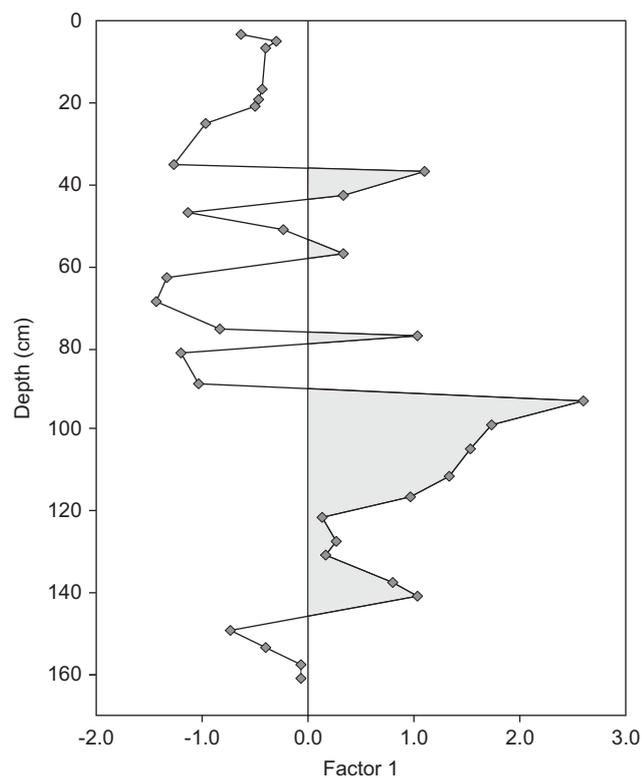
Fig. 7. Variation of Factor 1 scores throughout the Lagoa Grande core profile.

assumed to be oceanic (aerosols), but there are also terrestrial sources of Br derived from decay of organic matter (Roos-Barraclough et al., 2002). Similar to the transition metals, Br has a high binding affinity for organic matter (Ng and King, 2004; Rasmussen et al.,

1998). Whatever the source of Br and the transition elements, their association with the sediment organic fraction in the Lagoa Grande seems to have been at least partially controlled by geochemical processes within the catchment area prior to the transport of the sediments into the lake.

Elements with positive loadings on F1 and F2 reflect the association of mica, kaolinite and goethite with large ion lithophile elements of low mobility during weathering (Ba, Cs, Rb, Sr and LREE), and with elements commonly assumed to be immobile (Ti, Cr, Sc, Zr, Hf and Ta). This geogenic association may have been brought about by erosion and removal of deeper soil layers in the catchment area, where these elements are found at the highest abundance.

REE patterns in sediments seem to have been inherited from their metamorphic precursors, where part of Eu is present as Eu^{2+}. However, some fractionation may have taken place within the soil profiles in the source area, leading to a selective loss of LREE during weathering, as suggested by the significant correlation between $\sum$REE and the ratio $(La/Yb)_{CH}$ ($r^2 = 0.7$, $p = 0.001$).

The composition of the Lagoa Grande sediments can be therefore described in terms of a dominant geogenic component largely derived from the B-horizon of the surrounding soil profiles, and a minor component related to the O-horizon of these soils. This component is relatively more concentrated in the uppermost (Unit I) and the lowermost zones (Unit III) of the sedimentary column as compared with the intermediate zone (Unit II). A possible cause for this is the variation in the erosion regime in the catchment area. At the onset of the sedimentation (Unit III: 1030–730 yr BP), the incision of deeper layers of soil was reduced as a result of the relative stability of the catchment. Under such conditions, a greater proportion of biogenic elements was accumulated in the sediments. Probably as a response to an increase in the erosion intensity, during the period corresponding to the Unit II deposition (730–360 yr BP), deeper layers of the soil profile were increasingly incised, and the inflow of those materials into the lake led to a relative depletion of the biogenic component of the sediments. This trend was enhanced during the latter part of the period (490–360 yr BP). From 360 yr BP onward the concentration of the biogenic component in the sediments has been again increased, suggesting the resumption of more stable conditions in the catchment area, except for brief episodes of enhanced erosion around 340, 280 and 170–200 yr BP.

The changes in the erosion regime can be assumed to be controlled by climate fluctuations. Thus, a shift toward increased rainfall, particularly if it occurs in the summer months increasing the seasonality, enhances erosion in the catchment area. This would increase the

supply of geogenic material into the lake, diluting the material from the more organic topsoil.

A link can thus be established between the geochemical signature of the sediments and the climatic conditions at the time of their deposition. During the last millennium, in the Lagoa Grande region, the wetter period inferred from the geochemical data (from 730 to 360 yr BP, with the wettest conditions between 490 and 360 yr BP) overlaps approximately that suggested by palynological and isotopic data (400 to 320 yr BP) as a particularly warm and wet period (Pessanada et al., in preparation). Indeed, there is additional evidence for a very humid climate in the Ribeira River valley during the same period, deduced from the oxygen isotope composition of speleothems from the Cristais cave, which belongs to the same karst system (Burns and Cruz, in preparation).

Slight climatic fluctuations during the last millennium have been recorded in other regions of the southern hemisphere, and have been related to the "Little Ice Age" (LIA). This period, spanning from the 14th to the 19th century, was characterized in high latitudes of the northern hemisphere by colder temperatures and expanded glaciers (Luque and Julià, 2002; Pederson et al., 2005). In the southern hemisphere, LIA was characterized in the tropical Andes by a maximum glacier advance between the end of 16th century to the 18th century (Rabatel et al., 2005; Solomina et al., 2007), and a generally wetter climate. Thus, a high rainfall period corresponding to the LIA has been recorded in the Quelccaya ice cap in Peru (Thompson et al., 1986), and in the sediments of Lago Puyehue in Chile (Bertrand et al., 2005). Estimates for the Lake Titicaca level are also consistent with these results (Abbot et al., 1997). Such a wetter climate during LIA in the southern hemisphere contrasts with a decrease in rainfall from AD 1600 to 1900 recorded in the sediments of the Cariaco basin (10°N) in Venezuela (Haug et al., 2001). This out-of-phase pattern in precipitation north and south of equator was interpreted in terms of a southward displacement of the Intertropical Convergence Zone (ITCZ) over the South America continent during this period (Haug et al., 2001; Peterson and Haug, 2006).

6. Summary and conclusions

(1) In the Vale do Ribeira region, a sequence of limestones interbedded with metasiltites and phyllites has been deeply weathered, producing an extensive dissolution of carbonates. This gave rise to a typical karstic landscape where a lake – Lagoa Grande – developed within a polygonal depression. The main detrital source for the Lagoa Grande sediments is the insoluble residue from the dissolution of carbonates.

(2) A 1030-yr sediment core retrieved from the lake was divided into three units, based on visual inspection and confirmed by chemical and mineralogical composition. The upper (Unit I: 0–90 cm depth) and the lower units (Unit III: 140–170 cm depth) contain higher amounts of chlorite, Co, Cu, Zn, As, Br and Sb than the intermediate unit (Unit II: 90–140 cm depth). On the other hand, this unit is richer in mica, kaolinite and lithophile elements such as Ba, Cs, Rb and LREE than Units I and III.

(3) The variations in geochemical and mineralogical composition throughout the core are attributed to environmental changes in the catchment area during the last millennium. In this interpretation, we hypothesized that during the early stage of the lake formation, from 1030 yr BP (bottom of the core) to 730 yr BP, under a warm and humid climate similar to the present, the landscape was covered by a fully developed rainforest that protected soils from erosion. As a result of a moderate incision of the soil profiles, the elements preferentially bound to the organic matter, abundant in the O-horizon, have been relatively concentrated in the sediments. A slight fluctuation of climatic conditions toward increasing rainfall and seasonality from 730 to 360 yr BP led to a deeper erosion of soil profiles, which attained horizons with composition significantly different from that of the surface. This event is signaled in the sediments by dilution of the organic bound elements by the geogenic elements, which are more abundant in the deeper horizons of the catchment soils. The wettest condition of this period, as inferred from the geochemical data, occurred between 490 and 360 yr BP. From this time onward, with decreasing precipitation, erosion was reduced, the geogenic elements declined in abundance, and their decreased diluting effect led to the recovery of the signature characteristic of the sediments deposited during the early stage of the lake formation.

(4) In the Ribeira River valley in southeastern Brazil, as well as in other regions of South America, a period of enhanced humidity corresponds roughly to the time of the "Little Ice Age", and is anticorrelated with drier climatic conditions recorded by the Cariaco sediments in northern South America (Venezuela, 10°N) during the same period. This apparent synchronization of hydrologic regimes in north and south tropical zones is attributed to a southward shift in the latitudinal position of the ITCZ during LIA (Haug et al., 2001; Peterson and Haug, 2006).

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