

Rare earth element patterns in lake sediments as studied by neutron activation analysis

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Using instrumental neutron activation analysis, the vertical distribution of La, Ce, Nd, Sm, Eu, Tb, Yb and Lu was determined in 3 well dated sedimentary cores collected from Laguna Mar Chiquita, Argentina. Validation of the methodology was done using the Soil 7 (IAEA) reference material. The REE contents vary according to core location and lithological units, depending on the proportion of fluvial terrigenous components in the lake sediments. Lithologies with higher proportion of terrigenous components show higher REE concentrations, suggesting that the dominant REE carrier phase might be a detrital mineral. There is a consistent value of about 1.2 for $(La/Yb)_N$ and $(LREE/HREE)_N$ ratios for all sediments at the three sites, indicating a slight LREE enrichment in relation to the average shale NASC. Ce/Ce* values are close to 1.0, meaning that Ce behaves similarly to other light REE's.

Introduction

Rare earth elements have been widely used as geochemical indicators in sediments.^{1–11} These elements show small differences in their chemical properties, allowing only limited fractionation during weathering and sedimentation. Among them, only Ce and Eu present two oxidation states, being, therefore, sensitive indicators of the redox conditions in the depositional environment.

In sediments, REE contents are normalized to standard shale values, thought to represent the average composition of detrital minerals being delivered by rivers to the oceans which is similar to the average composition of the post-Archean upper continental crust.⁹ Land-derived sediments that are carried into the ocean or continental basins would thus have generally a flat shale-normalized pattern.¹² However, in certain situations, limited fractionation during weathering and diagenesis can take place.

In this paper we discuss the geochemical response of rare earth elements to water-level fluctuations during the last century of a saline lake in Central Argentina. Sediment samples of the first 60 cm of three cores were analyzed by instrumental neutron activation analysis (INAA). This is an excellent quantitative analytical technique capable of determining 8 REE's (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) and other trace elements in a wide range of concentrations.^{12–15}

Regional setting

Laguna Mar Chiquita is the largest saline lake in South America. It lies in a Quaternary tectonic depression in the Pampean plains, central Argentina, at 30°45'S and 62°30'W. The lake level has changed notably through centuries. At present, the lake has an area of ca. 6,000 km² and 12 m maximum depth.¹⁹

Based mainly on historical, stratigraphical and limnological data, many authors^{16–18} have supposed palaeoenvironmental changes that affected the lake. More recently PIOVANO et al.,¹⁹ reconstructed the lake level fluctuation based on a sedimentological model since the end of the Little Ice Age (ca. AD 1770). This was accomplished through the combination of historical and instrumental lake level data with an in-depth sedimentological and geochemical study of cores dated by the ²¹⁰Pb method. According to these authors, historical and instrumental records show that water-level fluctuations characterize the 20th century history of the lake, defining highstands during high level periods (HLP) and lowstands during low level periods (LLP). With some exceptions, low lake levels characterized the first 75 years of the century. High salinities of up to 360 g·l⁻¹ (in 1911) were reported at extreme lowstands during this period. During low lake levels lake waters were supersaturated with respect to both calcite and gypsum.²⁰ From 1976 to the present a highstand has been dominating. The lake waters show comparatively lower salinities (e.g., 29 g·l⁻¹ in 1986; 35 g·l⁻¹ in 1989),²⁰ whereas they remain supersaturated with respect to calcite but only occasionally with respect to gypsum.

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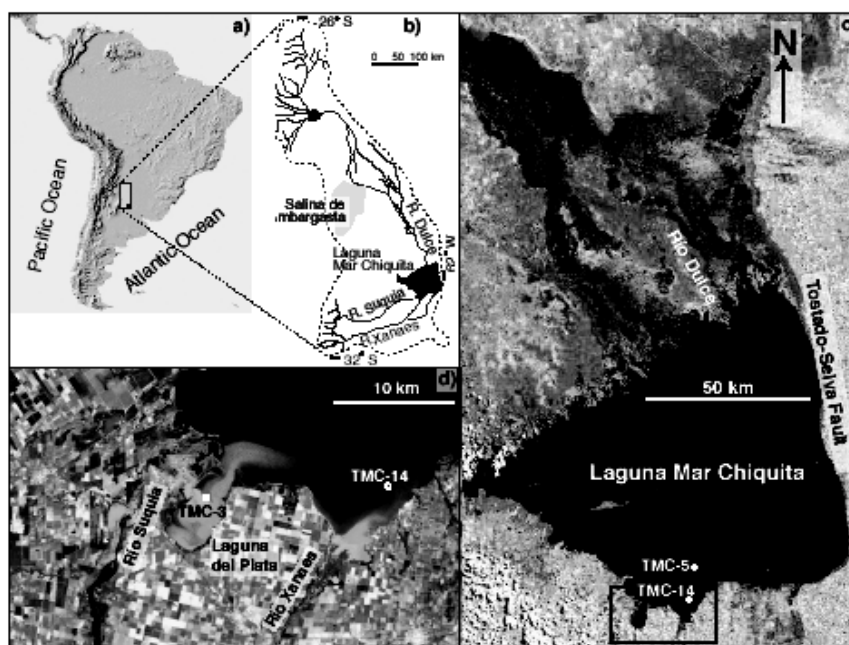


Fig. 1. Image of South America showing the location of Laguna Mar Chiquita (a), detail of the drainage basin (b), core location in the satellite image of the lake (c), detail of the area indicated in (c) showing the Laguna del Plata with core location (d). (Figure modified by PIOVANO et al.)¹⁹

Lake level fluctuations are distinctively recorded through variations in the characteristics of the lake sediments. 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.

Experimental

Three sediment cores were retrieved in November 1997, using a hand corer beaker sampler. Cores 05 and 14 were collected in the deepest area of the lake at 7–8 m depth, whereas core 03 was retrieved in a satellite and shallower lake, Laguna del Plata. The locations of the sample sites are shown in Fig. 1. The first 60 cm of the sediment cores were sliced 2 cm each, totaling 90 samples.

The last highstand, from 1976 to the present, corresponds to the 0–14 cm, 0–20 cm and 0–24 cm intervals in cores 03, 05 and 14, respectively.¹⁹ The remaining of the cores corresponds to the 1977–1900 lowstand interval.

All samples, previously dried at 60 °C, were passed through a 0.065 mm sieve. For the multielemental analyses approximately 200 mg of the sediment (duplicate samples) and about 150 mg of reference

material and synthetic standards were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multielement 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 material and synthetic standards were irradiated for 16 hours, under a thermal neutron flux of $10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ in the IEA-R1 nuclear reactor at IPEN - Instituto de Pesquisas Nucleares, São Paulo, Brazil. Two series of counting 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 material, and 30 minutes for the synthetic standards. 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 the VISPECT program to identify the gamma-ray peaks and by the ESPECTRO program to calculate the concentrations. Both programs were developed at the LAN/CRPQ, IPEN. The gamma-ray peaks used for rare earth elements determination were: ^{141}Ce (145.4 keV), ^{152}Eu (1408.0 keV), ^{140}La (328.8 and 1596.2 keV), ^{177}Lu (208.4 keV), ^{147}Nd (91.1 and 531.0 keV), ^{153}Sm (103.18 keV), ^{160}Tb (879.4 keV) and ^{175}Yb (396.3 keV). The validation methodology was verified by measuring the Soil 7 (IAEA) certified reference material.

Results and discussion

The sediments of the Laguna Mar Chiquita are composed of both detrital (quartz, feldspars, tourmaline, mica, clays and goethite), and authigenic evaporitic minerals (calcite, halite and gypsum). Clastic components are more abundant in HLP sediments whereas LLP sediments are enriched in evaporitic minerals. Core 03 exhibits the highest allogenic mineral contents due to the direct influxes of sediments from the Suquia river. Cores 14 and 05 are in comparatively more distal positions, and both cores display increasing quantities of evaporitic minerals during LLP. Additional information can be found in PIOVANO et al.¹⁹

Figure 2 shows the calculation of the standardized difference or Z-value that was made according to BODE.²¹ 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. All REE Z-score values were between $|Z| < 2$ indicating a good precision and accuracy of the INAA method. The detection limits (DL) for REE's in Soil 7 reference material, that show certified values for all REE except for Lu, were: 0.43 (Ce), 0.03 (Eu), 0.19 (La), 0.04 (Lu), 3.03 (Nd), 0.08 (Sm), 0.10 (Tb) and 0.08 (Yb) $\text{mg}\cdot\text{kg}^{-1}$. The DL was calculated according to the CURRIE criteria.²²

The analytical results for REE's in sediment samples taken from cores 03, 05 and 14 are summarized in Table 1. Also shown are ΣREE , $(\text{La}/\text{Sm})_{\text{N}}$, $(\text{Yb}/\text{Sm})_{\text{N}}$, $(\text{La}/\text{Yb})_{\text{N}}$, $(\text{LREE}/\text{HREE})_{\text{N}}$, and Ce/Ce^* . The normalization procedure used the REE average concentrations in the NASC – North American Shale Composite:²³ La = 32 $\text{mg}\cdot\text{kg}^{-1}$, Ce = 73 $\text{mg}\cdot\text{kg}^{-1}$, Nd = 33 $\text{mg}\cdot\text{kg}^{-1}$, Sm = 5.7 $\text{mg}\cdot\text{kg}^{-1}$, Eu = 1.24 $\text{mg}\cdot\text{kg}^{-1}$, Tb = 0.85 $\text{mg}\cdot\text{kg}^{-1}$, Yb = 3.1 $\text{mg}\cdot\text{kg}^{-1}$, Lu = 0.48 $\text{mg}\cdot\text{kg}^{-1}$. The Ce anomaly was calculated by:

$$\text{Ce}/\text{Ce}^* = 3(\text{Ce}/\text{Ce}_{\text{N}})/((2(\text{La}/\text{La}_{\text{N}}) + (\text{Sm}/\text{Sm}_{\text{N}}))$$

Figures 3, 4 and 5 display the shale-normalized REE patterns for HLP and LLP sediments in the three cores.

Our set of geochemical data allows for some linear correlation analyses between the REE's. The results are given in Table 2 and include the total suite of samples (90). There are very strong positive correlations ($r > 0.9$) between Eu/Sm, Eu/Yb, La/Sm, La/Yb, La/Eu and Sm/Yb, and strong correlations ($r > 0.7$) between Ce/Eu, Ce/La, Ce/Sm, Ce/Yb, Eu/Tb, La/Tb, and Tb/Yb. Less well correlated with regard to the whole data set are Nd and Lu.

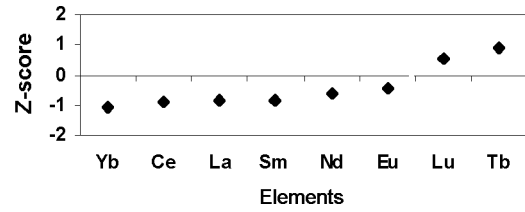


Fig. 2. Z-score values for REE elements in the reference material Soil 7 (IAEA)

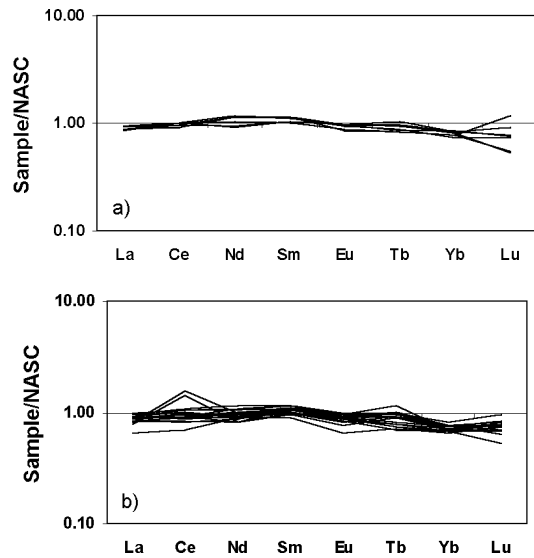


Fig. 3. Shale-normalized REE patterns for HLP (a) and LLP (b) sediments in the core 03

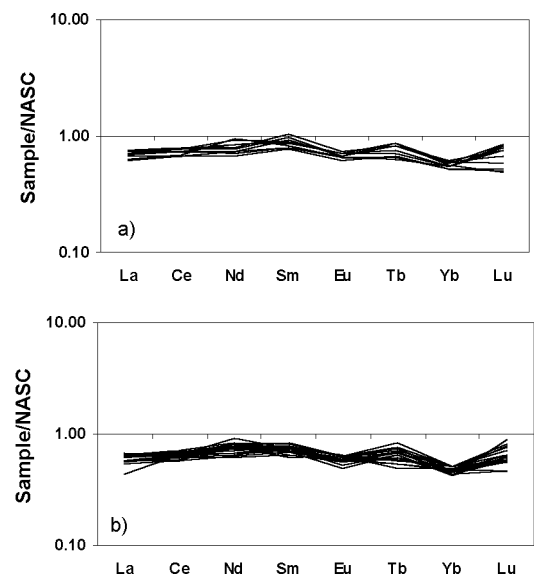


Fig. 4. Shale-normalized REE patterns for HLP (a) and LLP (b) sediments in the core 05

Table 1. Average concentrations (in $\text{mg}\cdot\text{kg}^{-1}$) of REE in sediments and normalized ratios from LLP and HLP

Sample	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Σ REE	$(\text{La}/\text{Yb})_{\text{N}}$	$(\text{La}/\text{Sm})_{\text{N}}$	$(\text{Yb}/\text{Sm})_{\text{N}}$	Ce/Ce*
Core 03													
High level	29.25	70.15	36.50	6.38	1.16	0.83	2.47	0.37	147.10	1.15	0.82	0.71	0.98
Low level	27.83	71.49	31.28	6.01	1.09	0.76	2.21	0.36	141.01	1.25	0.85	0.68	1.03
Core 05													
High level	22.27	53.48	26.23	4.96	0.84	0.65	1.71	0.32	110.46	1.26	0.80	0.63	0.97
Low level	18.58	46.77	24.70	4.11	0.74	0.53	1.47	0.31	97.20	1.23	0.81	0.66	1.02
Core 14													
High level	22.41	55.06	28.11	4.69	0.88	0.61	1.74	0.30	113.80	1.25	0.85	0.68	1.01
Low level	18.61	46.93	27.79	3.94	0.75	0.54	1.48	0.29	100.34	1.22	0.84	0.69	1.04

Table 2. Pearson correlation coefficients between REE's

	Ce	Eu	La	Lu	Nd	Sm	Tb	Yb
Ce	+1.00							
Eu	+0.79	+1.00						
La	+0.80	+0.95	+1.00					
Lu	+0.35	+0.46	+0.49	+1.00				
Nd	+0.50	+0.61	+0.60	+0.39	+1.00			
Sm	+0.77	+0.90	+0.94	+0.54	+0.56	+1.00		
Tb	+0.68	+0.76	+0.79	+0.45	+0.39	+0.70	+1.00	
Yb	+0.82	+0.95	+0.94	+0.48	+0.58	+0.90	+0.77	+1.00

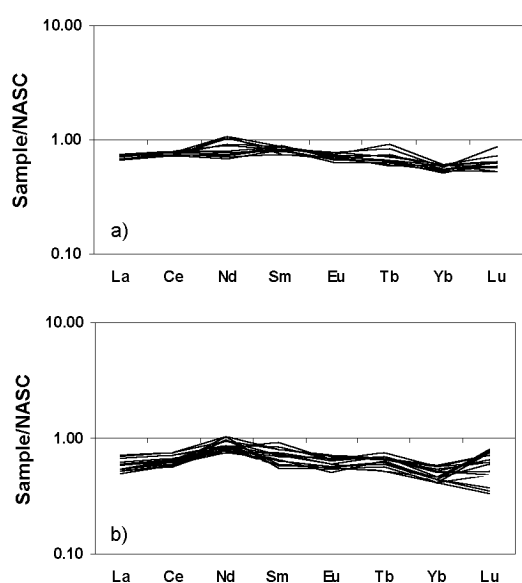


Fig. 5. Shale-normalized REE patterns for HLP (a) and LLP (b) sediments in the core 14

Conclusions

REE contents vary according to both core location and lake level fluctuations. Σ REE concentrations increase from the most distal core 05 (averages: LLP = $97 \text{ mg}\cdot\text{kg}^{-1}$; HLP = $110 \text{ mg}\cdot\text{kg}^{-1}$) and core 14 (averages: LLP = $100 \text{ mg}\cdot\text{kg}^{-1}$; HLP = $114 \text{ mg}\cdot\text{kg}^{-1}$) to core 03 (averages: LLP = $141 \text{ mg}\cdot\text{kg}^{-1}$;

HLP = $147 \text{ mg}\cdot\text{kg}^{-1}$). In each core, the Σ REE is systematically higher in sediments corresponding to the high level period (HLP) than in those corresponding to the low level period (LLP). Although there are significant differences in the total REE contents in core 03 in comparison to cores 05 and 14, and in HLP in comparison to LLP sediments, they all display similar nearly flat shale-normalized patterns (Figs 3, 4 and 5). Shale-normalized values of REE are around 1.0 for core 03 sediments, and slightly less than 1.0 for core 05 and core 14 sediments. Core 03 sediments are, therefore, similar to the average shale in REE contents. Cores 05 and 14 sediments, with a greater amount of autigenic minerals, are depleted in REE's in relation to the average shale. These data indicate that the variation in REE's concentration depends on the proportion of the terrigenous components of the sediments. Sediments with higher proportion of clastic components (core 03 samples compared to cores 05 and 14 samples, and HLP compared to LLP sediments in each core) have higher REE concentrations, suggesting that detrital mineral are the dominant phase hosting REE. Published data regarding global REE averages also show higher REE contents in clastic than in chemical sediments.¹

There is a consistent value of about 1.2 for $(\text{La}/\text{Yb})_{\text{N}}$ and $(\text{LREE}/\text{HREE})_{\text{N}}$ ratios for all sediment levels at the three sites, indicating a slight LREE's enrichment. This value is in the range commonly found in river suspended loads.²⁴ $(\text{La}/\text{Sm})_{\text{N}}$ and $(\text{Yb}/\text{Sm})_{\text{N}}$ ratios are around 0.8 and 0.7, respectively, showing little variations. In general, Ce/Ce* values are close to 1.0, meaning that Ce

behaves similarly to other light REE. Only two samples taken at site 03 (3–9 and 3–10) present slightly positive Ce anomalies, probably reflecting local conditions of higher redox potential. This remarkable stability in the calculated parameters for all samples regardless of the ratio of terrigenous to autigenic minerals is another evidence that REE's are probably associated with clastic phases, that additionally reflect changing environmental conditions of the lake.

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