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# Accumulation patterns of rare earths and other elements in coastal lake sediments under different land uses

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ABSTRACT

The elemental composition of sediments can provide valuable records of environmental changes, including land-use impacts. This study evaluates the role of major, trace, and rare earth elements (REE) in sediment cores from three coastal lakes in southern Brazil which have been influenced by varying land-use pressures. These differing influences range from intensive agriculture to near-pristine wetlands. Using Instrumental Neutron Activation Analysis, we quantified 25 elements in dated sediment cores and calculated enrichment factors (EF) to differentiate natural from anthropogenic contributions. The La-Sc-Th ternary diagram was employed to trace sediment provenance. Our results revealed contrasting impacts of land-use changes. Mirim Lagoon showed barium enrichment which was previously attributed to coal mining and combustion, while Mangueira Lagoon exhibited increased REE concentrations post-1950, likely linked to the use of agricultural fertiliser. Nicola Lake, by contrast, demonstrated minimal anthropogenic influence. Sediment dilution and resuspension in larger systems, such as Mirim Lagoon, mitigated observable changes despite intense land-use activities. These findings highlight the distinct responses of lake systems to land-use pressures, providing insights into their sedimentary dynamics and potential for environmental monitoring.

## 1. Introduction

The chemical composition of terrigenous sediments is controlled by the composition of the source rock (McLennan and Murray, 1998). However, the abundance of specific elements such as alkalies and alkaline earth do not reflect the composition of the source rock as they dissolve during weathering and diagenesis (McLennan et al., 1980). The geochemical composition of sediments provides crucial insights into both natural processes and anthropogenic impacts in aquatic systems (Zhang et al., 2018, 2019; Cardoso-Silva et al., 2024; Kim et al., 2024) . Elements such as rare earth elements (REE), thorium (Th), and scandium (Sc) are particularly useful tracers due to their resistance to weathering and sedimentary fractionation. These elements retain information about source rock composition, making proxies like the Th/Sc ratio valuable indicators of sediment provenance, reflecting the relative contributions of felsic and mafic rocks (McLennan and Murray, 1998; Taylor and McLennan, 2009).

REE are a group of 15 chemically similar elements (atomic numbers between 57 and 71) (Henderson, 1984). These elements are commonly normalised to the abundance in chondritic meteorites or a shale composite such as the North American Shale Composite (NASC) or the Post Achaean Australian Shale (PAAS) to interpret fractionation patterns (McLennan et al., 1980; Szefer et al., 1999; de Oliveira et al., 2007; Laveuf and Cornu, 2009). Chondrite meteorites are composed of igneous materials that have not had an extensive history of melting and recrystallisation. Thus, their REE composition presumably represents magma before any fractionation processes (Aide and Aide, 2012). Due to their limited mobility and fractionation during weathering and sedimentation

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(Rollinson, 1993), as well as the specific composition of the source rocks (McLennan et al., 1980), REE patterns in sediments can reveal historical changes in land use, particularly in regions where agricultural practices and industrial activities are important (Szefer et al., 1999; de Oliveira et al., 2007; Aide and Aide, 2012; Wang et al. 2019, 2024). REE thus may allow the differentiation of sediment sources and help to resolve anthropogenic influences (Henderson, 1984; Aide and Aide, 2012).

Rapid human population growth and the resulting increase in demand for resources have led to the conversion of land for human use, especially after 1950 (Waters et al., 2016). The 20th century saw a dramatic transformation of wetland ecosystems globally, driven by urbanisation and agricultural expansion (Ramsar, 2015). Particularly in southern Brazil's coastal plains, rice farming has replaced extensive wetland areas, altering natural hydrological and ecological dynamics (Bueno et al., 2021a, b; Menegheti, 2010). These land-use changes likely introduced new metal sources and altered sedimentation patterns. However, the extent of the impacts of land-use change remains poorly understood in many developing countries.

This study hypothesises that the sedimentary content of major, trace, and rare earth elements reflects the influence of agricultural and industrial activities across a gradient of land use. To test this hypothesis, we analysed sediment cores from three coastal lakes in southern Brazil (Mirim Lagoon, Mangueira Lagoon, and Nicola Lake) using Instrumental Neutron Activation Analysis (INAA). These sites provide a spectrum of environmental conditions, from intensive agriculture to near-pristine wetlands, offering a unique opportunity to assess the interplay between natural processes and anthropogenic impacts on sediment composition.

## 2. Materials and methods

### 2.1. Study area

Sediment cores were collected from the Mirim-Mangueira Lagoon system, located in the coastal plain of Rio Grande do Sul, southern Brazil (Fig. 1). This region covers approximately 33000 km$^2$ and contains several coastal lakes and lagoons as the result of transgressive-regressive sea-level changes during the Quaternary (Tomazelli et al., 2000; Dillenburg et al., 2017). The northern boundary of the coastal plain is characterised by basaltic rocks from the Serra Geral Formation. The southern boundary in Uruguayan territory is mainly composed of granitoids of the Santa Teresa complex (da Silva, 1979; Muzio and Artur, 1999). The sediments of the coastal plain are mostly quartz, and well-selected fine-grained terrestrial siliciclastic sediments, although the Pleistocene barriers also contain silt-clay sediments (Buchmann et al., 2009). Mirim Lagoon basin, located in the southernmost part of the coastal plain, is surrounded mainly by granitic and metamorphic rocks of the Neoproterozoic Dom Feliciano Belt (Basei et al., 2000; Oyhantçabal et al., 2010) (Fig. 1).

Mirim (3830 km$^2$) and Mangueira (746 km$^2$) lagoons are the major regional water bodies (Fig. 1). These two large freshwater lagoons are connected through the Taim Wetland, a natural reserve located north of Mangueira containing several small shallow lakes (Motta Marques et al., 2013) (Fig. 1). Since the beginning of the 20th century, natural grasslands and wetlands of the region have been replaced by rice paddies, and the water of both lagoons has been used for rice irrigation (Villanueva et al., 2000). During the 1970s, dams were constructed to meet the needs for rice irrigation and production (Borba, 2016). The major modification was the construction of a dam-lock in the São Gonçalo channel in 1977 to prevent the entry of brackish water from Patos Lagoon (indicated with a black square in Fig. 1) into Mirim Lagoon, thus converting Mirim

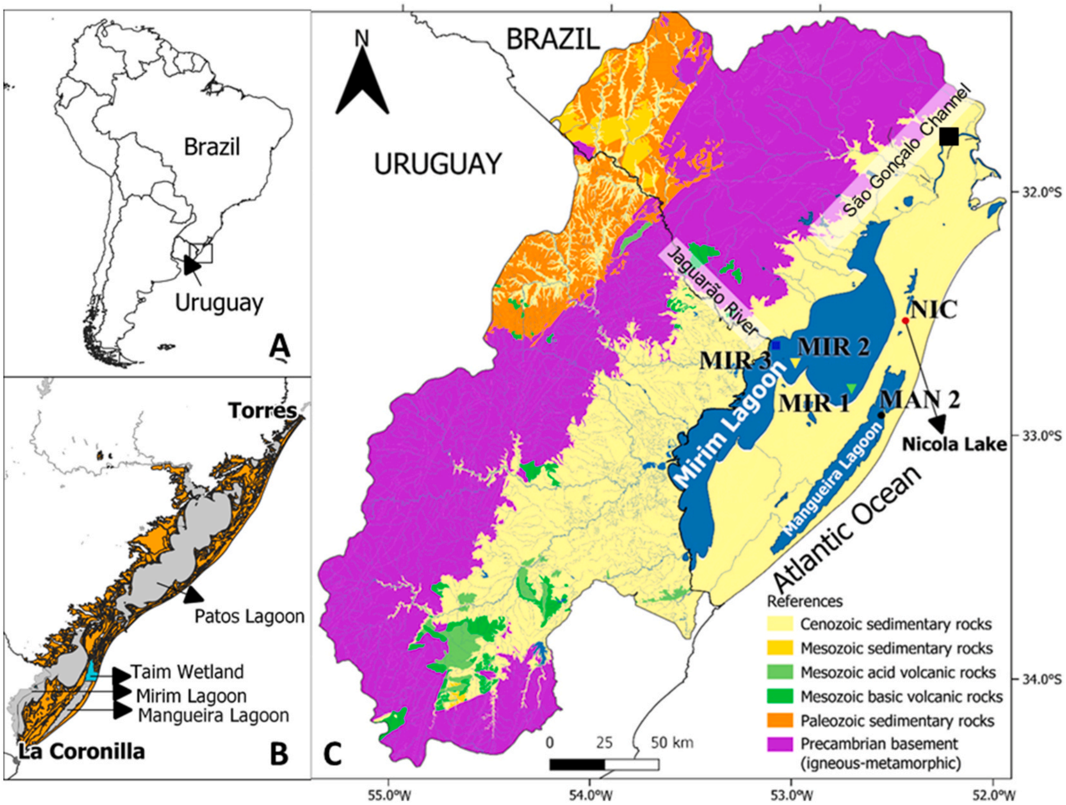

**Fig. 1.** A) Study area located in between Uruguay and Brazil, South America. B) Orange: the Rio Grande do Sul Coastal Plain, grey: main water bodies in the study area, blue: Taim Wetland. C) Rock types in the study area. The black square in the São Gonçalo channel indicates the Dam-Lock constructed in 1977 that converted Mirim Lagoon into a freshwater ecosystem. Jaguarão River is the Uruguay/Brazil boundary.

Lagoon into a freshwater ecosystem (Hirata et al., 2010).

The three selected lagoons represent a gradient of land use. Mirim Lagoon is surrounded by intensive agriculture, particularly rice cultivation. Mangueira Lagoon is a transition system located between agricultural areas on the west, natural wetlands mostly to the north, and pristine dunes to the east. Nicola Lake is a nearly pristine lake surrounded by wetlands within the Taim Natural Reserve.

### *2.2. Sediment collection and dating*

Sediment cores were collected between October 2006 and January 2008 using a gravity corer (50 mm diameter and 1 m long). Three cores were taken from Mirim Lagoon (MIR1, MIR2, MIR3), one from Mangueira Lagoon (MAN2), and one from Nicola Lake (NIC). Once extracted, the sediment cores were then sectioned into 1 cm intervals for the upper 10 cm and into 2 cm intervals for the remaining length. The individual samples were stored in plastic bags. In the laboratory, the sediment slices were dried in an oven at 60 °C overnight or until reaching a constant weight. $^{210}$Pb and $^{226}$Ra activities (dpm g$^{-1}$) were used to estimate sedimentation rates and chronology as described in a companion paper (Bueno et al., 2021a). To estimate sedimentation rates the Constant Flux-Constant Sedimentation (CF: CS) model was applied in all cores and the Constant Rate of Supply (CRS) model was also used in MIR1 and MAN2 cores (Appleby and Oldfield, 1983; Sanchez-Cabeza et al., 2012). All the REE and metal data reported here are original.

### *2.3. Geochemical analysis*

Twenty-five elements were analysed by Instrumental Neutron Activation Analysis (INAA) at the Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, Brazil, as described in Larizzatti et al. (2001) and Santos et al. (2007). The approach can resolve concentrations of major elements (Ca, Fe, Na), trace elements (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Th, U, Zn) and rare earth elements (REE) (Ce, Eu, La, Lu, Nd, Sm, Tb, Yb). Briefly, approximately 150 mg of dry sediment (i.e., two replicates per sample) were accurately weighed and sealed in pre-cleaned double polyethene bags. Single and multi-element synthetic standards were prepared by pipetting aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman n° 41 filter paper. All samples (sediment, reference and synthetic standards) were irradiated for 16 h 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 performed: the first after one-week decay and the second after 15–20 days. The counting time was 2 h for all samples and reference materials and 30 min for each synthetic standard. Gamma-spectrometry was conducted using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV for $^{57}$Co and 1.90 keV for $^{60}$Co. Certified reference materials ensured the precision and accuracy of the method (Buffalo River Sediment NIST SRM 2704, Soil-7 IAEA and B-EN Basalt-IWG-GIT). The analysis had a relative standard deviation ranging from 1.1 % to 8.2 %, and a relative error from 3 % to 10 %.

### *2.4. Data analysis*

The La-Sc-Th ternary diagram provides information about the provenance of the fine-grained sediments (Cullers, 1994; Yu et al., 2019; Xanthopoulou et al., 2021). This approach differentiates the contributions of low-silica parent rocks (basic) from those with high-silica source rocks (felsic) (Cullers, 1994). Here, the ternary diagram was used to distinguish potential source rocks, where the composition of basalts from the Serra Geral Formation (the northern boundary of the Coastal Plain) (GeoRoc database), the average composition of Proterozoic granites (Condie, 1993), volcanic rocks (Condie, 1993) and Andesites (Condie, 1993) were included as potential end-members of the analysed samples (Fig. 2).

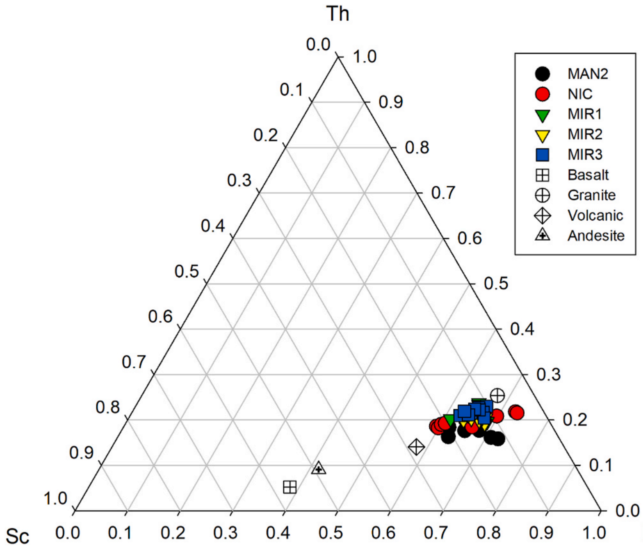

**Fig. 2.** La-Th-Sc ternary plot including data from MAN2, NIC, MIR1, MIR2 and MIR3 samples. To distinguish potential source rocks, data of basalts from the Serra Geral Formation (GeoRoc database) and the average composition of Proterozoic granites (Condie, 1993), volcanic rocks (Condie, 1993) and Andesites (Condie, 1993) were also included.

Chondrite Normalisation Curves were employed to identify REE fractionation patterns and potential anthropogenic influences. The Eu anomaly, defined as $Eu_n/Eu^*_n$ was calculated for all the analysed sediment cores. Where $Eu_n$ is the chondrite-normalised Eu concentration and $Eu^*_n$ is the predicted normalised concentration calculated from Lawrence and Kamber (2006): $Eu^*_n = (Sm_n^2 {*} Tb_n)^{1/3}$. Values of 1 indicate that there is no anomaly, a value $> 1$ (positive anomaly) indicates an overabundance and a value $< 1$ (negative anomaly) indicates an underabundance (Lawrence and Kamber, 2006). The Ce anomaly, defined as $Ce_n/Ce^*_n$ was calculated following Bau and Dulski (1996) as: $Ce^*_n = (La_n + Nd_n)/2$. Values of 1 indicate that there is no anomaly, a value $> 1$ (positive anomaly) indicates oxidising conditions and a value $< 1$ (negative anomaly) reducing conditions or Ce remobilisation (Bau and Dulski, 1996).

Finally, enrichment factors (EF) were calculated to distinguish natural from anthropogenic sources (Szefer et al., 1998). Sc was used as a normalising element since is a reliable indicator of the contribution of terrestrial materials and is structurally combined in clay minerals, making it a good indicator of grain-size variability (Loring and Rantala, 1992):

$$EF = \frac{(C_x/C_{Sc})\text{stratum}}{(C_X/C_{Sc})\text{background}}$$

where $C_X$ is the content of element X, $C_{Sc}$ is the content of Sc, here used as a normalising element. Background values were defined as the elemental concentration prior to human influence, i.e., the average concentrations of two consecutive layers older than 100 years according to the $^{210}$Pb data. To assess contamination levels using the EF, the classification proposed by Sutherland (2000) was applied, where $EF < 2$ indicates minimal enrichment, suggesting null or minimal contamination, and $2 < EF < 5$ corresponds to moderate enrichment.

## 3. Results

### *3.1. Geochemical signatures and provenance*

Results for all 25 analysed elements are presented in Table S1, but the discussion focuses on those elements commonly used to trace contamination and origin: Ba, Br, Fe, Th, U, and REE (Table 1). A La-Sc-Th ternary plot was used to assess potential source rocks, revealing a

**Table 1**
Minimum, maximum, average, standard deviation and coefficient of variation of the discussed elements (all in mg/kg except Fe) in cores MAN2, NIC, MIR1, MIR2 and MIR3. Average of the possible source rocks in the Mirim Catchment: Basalts from the Serra Geral Formation (the northern boundary of the Coastal Plain) (GeoRoc), Proterozoic granites (Condie, 1993), volcanic rocks (Condie, 1993) and Andesites (Condie, 1993). Chondrite values used for normalisation (McLennan et al., 1980) were also included.

| | | Ba | Br | Ce | Eu | Fe (%) | La | Lu | Nd | Sc | Sm | Tb | Th | U | Yb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MAN2 | Min | 201 | 5 | 20 | 0.5 | 0.6 | 10 | 0.1 | 9 | 2 | 1.9 | 0.2 | 2.3 | 0.5 | 0.7 |
| | Max | 360 | 63 | 57 | 1.2 | 2.5 | 27 | 0.4 | 27 | 9 | 5.4 | 0.6 | 8.1 | 2.3 | 2.3 |
| | Av. | 295 | 32 | 39 | 0.9 | 1.5 | 19 | 0.2 | 19 | 5 | 3.8 | 0.4 | 5.2 | 1.4 | 1.5 |
| | SD | 59 | 25 | 16 | 0.3 | 0.8 | 7 | 0.1 | 7 | 3 | 1.5 | 0.2 | 2.4 | 0.7 | 0.6 |
| | CV | 0.2 | 0.8 | 0.4 | 0.4 | 0.6 | 0.4 | 0.5 | 0.4 | 0.6 | 0.4 | 0.4 | 0.5 | 0.5 | 0.4 |
| NIC | Min | 302 | 9 | 46 | 1 | 2.4 | 22 | 0.2 | 25 | 5 | 4.3 | 0.5 | 6.5 | 1.9 | 1.9 |
| | Max | 492 | 35 | 52 | 1.1 | 3.4 | 25 | 0.2 | 39 | 9 | 5.1 | 0.7 | 7.9 | 3 | 2.4 |
| | Av. | 404 | 25 | 50 | 1.1 | 2.9 | 24 | 0.2 | 31 | 8 | 4.8 | 0.6 | 7.3 | 2.3 | 2 |
| | SD | 61 | 10 | 2 | 0 | 0.3 | 1 | 0 | 5 | 1 | 0.3 | 0.1 | 0.5 | 0.3 | 0.1 |
| | CV | 0.2 | 0.4 | 0 | 0 | 0.1 | 0 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| MIR1 | Min | 211 | 3 | 71 | 1 | 1.2 | 31 | 0.4 | 23 | 5 | 5.6 | 0.6 | 9.2 | 2.6 | 2.7 |
| | Max | 527 | 9 | 97 | 1.4 | 3.4 | 44 | 0.6 | 44 | 11 | 11.2 | 0.9 | 16.2 | 3.6 | 3.9 |
| | Av. | 422 | 4 | 81 | 1.2 | 1.8 | 36 | 0.5 | 33 | 7 | 7.1 | 0.8 | 11.9 | 3.1 | 3.2 |
| | SD | 146 | 2 | 9 | 0.2 | 0.8 | 5 | 0.1 | 7 | 2 | 2.1 | 0.1 | 2.5 | 0.3 | 0.4 |
| | CV | 0.4 | 0.6 | 0.1 | 0.1 | 0.4 | 0.1 | 0.2 | 0.2 | 0.3 | 0.3 | 0.1 | 0.2 | 0.1 | 0.1 |
| MIR2 | Min | 729 | 4 | 71 | 1.1 | 1.4 | 33 | 0.6 | 28 | 6 | 5.7 | 0.7 | 9.2 | 2.4 | 3.1 |
| | Max | 1354 | 7 | 88 | 1.4 | 2.7 | 40 | 0.7 | 39 | 9 | 7.1 | 1.2 | 14.3 | 3.4 | 3.8 |
| | Av. | 921 | 6 | 80 | 1.3 | 1.9 | 36 | 0.7 | 33 | 7 | 6.4 | 1 | 11.2 | 2.8 | 3.5 |
| | SD | 222 | 1 | 5 | 0.1 | 0.5 | 2 | 0.1 | 4 | 1 | 0.4 | 0.2 | 1.3 | 0.3 | 0.3 |
| | CV | 0.2 | 0.2 | 0.1 | 0.1 | 0.3 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 |
| MIR3 | Min | 475 | 4 | 59 | 0.9 | 1.2 | 27 | 0.2 | 27 | 5 | 4.9 | 0.7 | 8.9 | 2.4 | 2.2 |
| | Max | 732 | 9 | 84 | 1.2 | 2.6 | 39 | 0.4 | 60 | 9 | 6.7 | 1 | 13.5 | 3.9 | 3.3 |
| | Av. | 585 | 5 | 72 | 1.1 | 1.6 | 33 | 0.3 | 36 | 7 | 5.9 | 0.8 | 11.1 | 3 | 2.6 |
| | SD | 78 | 2 | 8 | 0.1 | 0.4 | 4 | 0 | 11 | 1 | 0.6 | 0.1 | 1.3 | 0.5 | 0.4 |
| | CV | 0.1 | 0.3 | 0.1 | 0.1 | 0.3 | 0.1 | 0.1 | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| Basalts Serra Geral | Av. | 402 | | 51 | 1.4 | | 24 | 0.4 | 26 | 35 | 5.4 | 0.9 | 6.3 | 1.5 | 2.8 |
| Proterozoic Granite | Av. | 750 | | 115 | 1 | | 48 | 0.6 | 54 | 5 | 8.7 | 1.3 | 18 | 4.5 | 3.5 |
| Felsic Volcanic Rock | Av. | 900 | | 71 | 0.8 | | 35 | 0.5 | 28 | 17 | 5.6 | 0.7 | 8.5 | 2.5 | 3.1 |
| Andesite | Av. | 560 | | 44 | 1.1 | | 17 | 0.3 | 24 | 20 | 4.5 | 0.8 | 3.7 | 2 | 2 |
| Chondrite | Av. | | | 1 | 0.1 | | 0.4 | 0 | 0.7 | | 0.2 | 0.1 | | | 0.2 |

dominant granitic composition for the analysed sediments (Fig. 2).

Thorium (Th) concentrations varied among the lagoons, with Mirim Lagoon exhibiting significantly higher levels (11.3 ± 1.6 mg/kg) compared to Nicola Lake (7.3 ± 0.5 mg/kg) and Mangueira Lagoon (5.2 ± 0.4 mg/kg) (Table S1). A strong association between Th/U and Th/Fe was observed in Mangueira Lagoon and Nicola Lake, but not in Mirim Lagoon (Fig. 3, Table 2).

The chondrite-normalised REE distribution showed enrichment in light REEs (LREEs: La to Eu) and progressive depletion in heavy REEs (HREEs: Tb to Lu) across all sites (Fig. 4). The Eu anomalies ($Eu_n/Eu^*_n$) were negative in all cores (<1), with lower values in MIR1 (0.46–0.64) and higher in MAN2 (0.74–0.88) (Fig. 5). Furthermore, cores MIR1 and MIR2 had moderate positive anomalies (1.10–1.31 and 1.08–1.22, respectively) while MIR3 showed variable values (0.86–1.20), indicating absence or slightly negative/positive anomalies depending on the sediment layer. NIC and MAN2 showed values close to 1, suggesting no marked Ce anomaly (Fig. 5).

The ΣREE vs Th plot revealed two distinct groups: Group 1 comprised cores from Mangueira Lagoon (MAN2) and Nicola Lake (NIC), with lower REE content. Group 2 included cores from Mirim Lagoon (MIR1, MIR2, MIR3), with higher REE concentrations (Fig. 6).

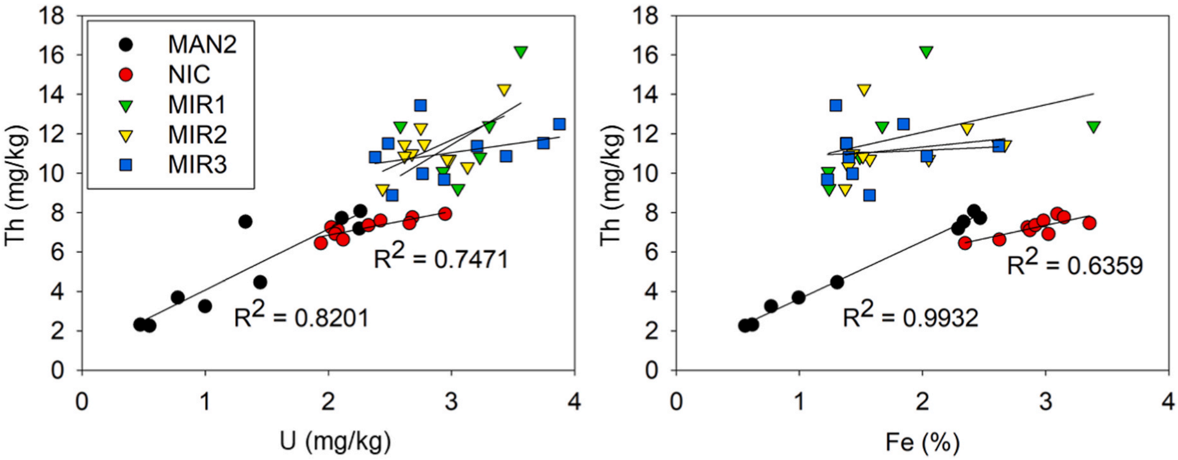

**Fig. 3.** Regression analysis Th (mg/kg) vs U (mg/kg) and Th (mg/kg) vs Fe (mg/kg) in the 5 analysed sediment cores. $R^2$ values are shown for significant regressions (p-values <0.05).

**Table 2**
Regression analysis data to infer the association between U/Th and Fe/Th in sediment cores NIC, MAN, MIR1, MIR2 and MIR3.

| | Core | Equation | R2 | p-value |
|---|---|---|---|---|
| **U/Th** | MAN | 0.9769 + 3.0916x | 0.8201 | 0.0008 |
| | NIC | 4.4342 + 1.2092x | 0.7471 | 0.0013 |
| | MIR 1 | 0.1024 + 3.781x | 0.2629 | 0.2983 |
| | MIR 2 | 3.1738 + 2.84x | 0.3765 | 0.0592 |
| | MIR 3 | 8.3625 + 0.8946x | 0.1264 | 0.3133 |
| **Fe/Th** | MAN | 0.7156 + 2.912x | 0.9932 | 7.4010E-09 |
| | NIC | 3.27 + 1.3612x | 0.6359 | 0.0057 |
| | MIR 1 | 9.2868 + 1.3979x | 0.2100 | 0.3607 |
| | MIR 2 | 10.0589 + 0.6361x | 0.0613 | 0.4905 |
| | MIR 3 | 10.5969 + 0.2832x | 0.0083 | 0.8020 |

### 3.2. *Anthropogenic influence*

Barium (Ba) showed increased enrichment factors (EF) near 2 in the uppermost layers of core MIR1 and near 3 in core MIR2 (Fig. 7). Bromine (Br) showed increased EF in cores MIR1, NIC and MAN2 since the beginning of the 1950s, while MIR 2 and MIR3 cores exhibited stable Br levels throughout the period.

The ΣREE variation along the five cores (Fig. 8) confirmed the two groups identified earlier: Group 1 (MAN2, NIC) with lower REE content and Group 2 (MIR1, MIR2, MIR3) with higher REE content, further reinforcing the spatial differences in sediment composition. This grouping pattern is also supported by the PCA results (Fig. S1).

## 4. Discussion

### 4.1. *Geochemical signatures and provenance*

Rocks with granitic composition (i.e granites and acid volcanic rocks), basaltic and andesitic rock types are commonly found in the catchment of Mirim Lagoon around the Southern Brazil and Uruguay coastal plains (Bellieni et al., 1986; Muzio and Artur, 1999; Panario et al., 2014; Hueck et al., 2018). However, the La-Sc-Th ternary diagram (Fig. 2), shows a granitic nature of the lagoon's bottom sediments. The La/Th ratio between 3 and 4 for all sites also indicates an acidic composition for the sediment source (McLennan et al., 1980) consistent with the surrounding Neoproterozoic granitic rocks as the main sediment source.

Thorium (Th) is about three times more abundant than Uranium (U) (Hazen et al., 2009), a trend observed across all the sites. U and Th generally correlate in rocks and minerals (Nash, 1979), but this depends on accessory minerals (Nash, 1979; Saleh et al., 2002; Malikova et al., 2020). In the study area, fluvial inputs draining igneous and metamorphic rocks of the Neoproterozoic Sul-Riograndense Shield are primarily trapped in Mirim Lagoon (da Silva, 1979). In contrast, Mangueira Lagoon and Nicola Lake are fed primarily by rainfall and groundwater (Santos et al., 2008), and receive sediment supply from nearby Pleistocene sand barriers. The contrasting sediment sources lead to a different mineralogical composition, and thus different Th/U patterns. Similarly, the Th-Fe relationship varied across lagoons. The strong correlation observed in Mangueira Lagoon and Nicola Lake likely reflects the dominance of fine-grained sediments in transporting both Th and Fe. In contrast, the weaker Th-Fe correlation in Mirim Lagoon suggests varied sediment sources or differential transport processes, potentially influenced by the larger river inputs.

The observed enrichment of light rare earth elements (LREEs) relative to heavy rare earth elements (HREEs) in the sediment cores also reflects their origin from igneous rock sources (Aide and Aide, 2012), consistent with the geological characteristics of the region. The increase in REE content observed in Mangueira Lagoon since the 1950s likely reflects the influence of phosphate fertilisers, which are often enriched in REEs (Aubert et al., 2002; Laveuf and Cornu, 2009; Kastori et al., 2023) and coincides with the intensification of rice farming (Bueno et al. 2021b).

The slightly negative Eu anomaly (Figs. 4 and 5) is also a typical

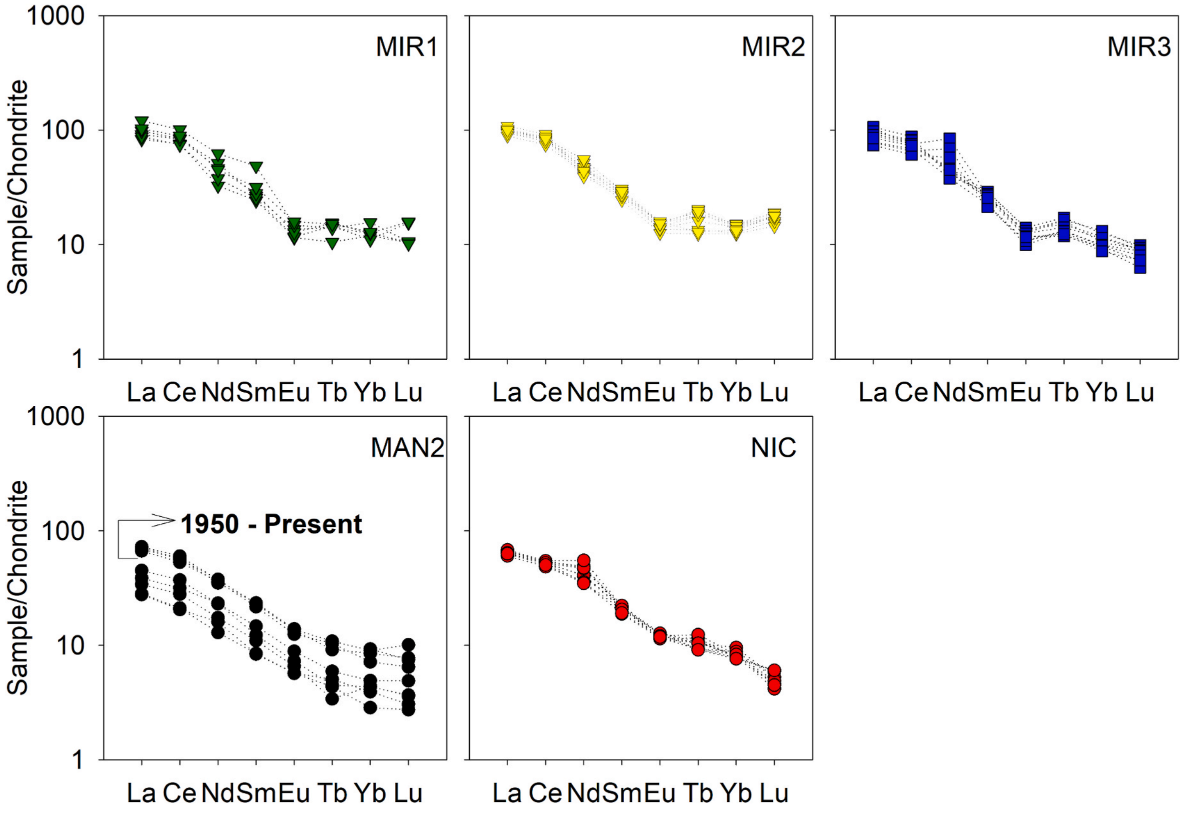

**Fig. 4.** Chondrite-normalised distribution of REE elements in Mirim, Mangueira and Nicola cores.

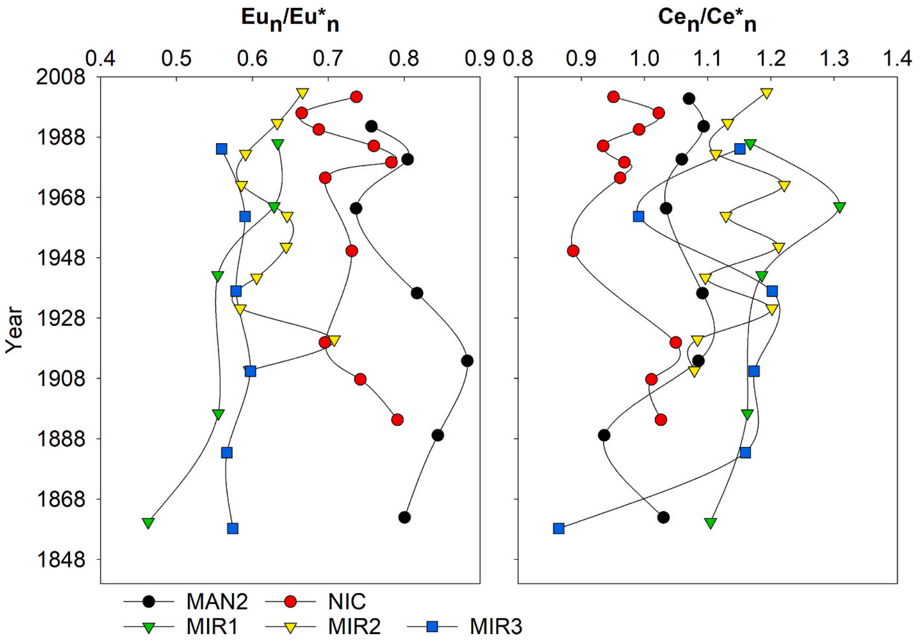

**Fig. 5.** Europium (Eu) and Cerium (Ce) anomalies calculated for cores MAN2, NIC, MIR1, MIR2 and MIR3.

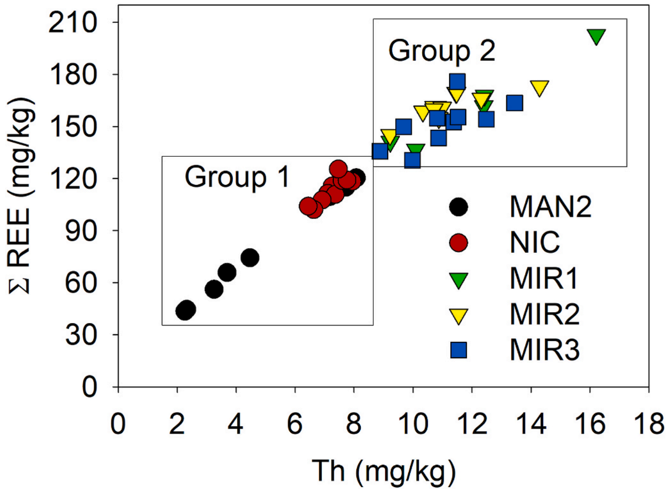

**Fig. 6.** ΣREE vs Th in Mirim, Mangueira and Nicola cores. In the scatter plot, two distinctive groups are observed: Group 1: MAN2 and NIC with lower REE content; and Group 2: MIR1, MIR2 and MIR3 with higher REE content.

crustal and clastic sediment signal resulting from the dominance of felsic sources or oxidative conditions during sedimentation, both of which inhibit Eu enrichment (McLennan, 2001; de Oliveira et al., 2007). This may reflect the input of materials with a granitic continental origin to coastal lagoon sediments since Eu fractionation is common in magmatic differentiation processes (Lee and Tanaka, 2021). Thus, the consistent negative Eu anomaly across all sediment samples reflects the input of granitic material and clastic sediments from the continent.

Ce tends to show positive anomalies in oxidised environments due to oxidation to $Ce^{4+}$ and precipitation as $CeO_2$ (Bau and Dulski, 1996; Zhang and Shields, 2022; Junqueira et al., 2024). The positive anomalies observed in MIR1 and MIR2 suggest that the depositional conditions in these cores were more oxidising than the other wetland-dominated lagoons. The absence of a clear Ce anomaly in NIC and MAN2 could indicate that the system was not oxidising enough to cause significant $Ce^{4+}$ enrichment. Mangueira Lagoon and Nicola Lake are shallow systems supporting large macrophyte communities and connected to extensive wetlands (Finkler Ferreira et al., 2018; Bueno et al., 2021a). The presence of dense vegetation enhances organic matter content that promotes anoxic conditions in sediments (Finkler Ferreira et al., 2018).

Thorium is also a reliable proxy for terrestrial input due to its limited reactivity in sedimentary environments (McLennan, 2001), and showed a strong linear relationship with ΣREE (Fig. 6). This suggests that terrigenous rather than autochthonous materials are the dominant source of REE and Th in these systems. Mirim sediment cores are enriched in Th compared with Mangueira and Nicola cores also indicating a different sediment composition and source as previously observed. Overall, these findings show how both natural geological processes and human activities influence sediment geochemistry. Despite a common granitic composition, the differences in Th and Fe/U patterns, and REE, suggest variations in sediment sources or transport pathways across the three lagoons offering clues about how land use affects them.

### *4.2. Sediment composition and anthropogenic influence*

Barium (Ba) did not present significant and positive correlations with other elements in Mirim Lagoon, suggesting a unique anthropogenic source. Barium enrichment in sediments in the Mirim Lagoon basin was previously linked to coal mining and combustion from the nearby Candiota coal mine (Pires and Querol, 2004; Ilha, 2019; Bueno et al., 2021b) since Ba is found in coal in large concentrations (Choudhury and Cary, 2001; Nalbandian, 2012; Hao et al., 2022). The Candiota coal mine is Brazil's largest coal mine and has been active since 1863, while the Candiota thermoelectric complex has been active since 1961. Both are located near a tributary of the Jaguarão River draining to Mirim Lagoon, representing a likely source to cores MIR1 and MIR2.

Bromine (Br) correlated with organic carbon (carbon data from Bueno et al., 2021a) in Mirim Lagoon and Nicola Lake, but not in Mangueira Lagoon (Table S2). This suggests that Br in Mangueira Lagoon may have an additional source, or it may be influenced by changes in sediment grain size (Mayer et al., 1981; Kandasamy et al., 2018). The principal component analyses (Fig. S1) revealed that Br explains most of the variance between the previously observed groups, especially in core MAN2 after 1950. Active transgressive dune fields in the area suggest that aeolian transport is important near Mangueira Lagoon (Dillenburg et al., 2017). Modern coastal dune formations that

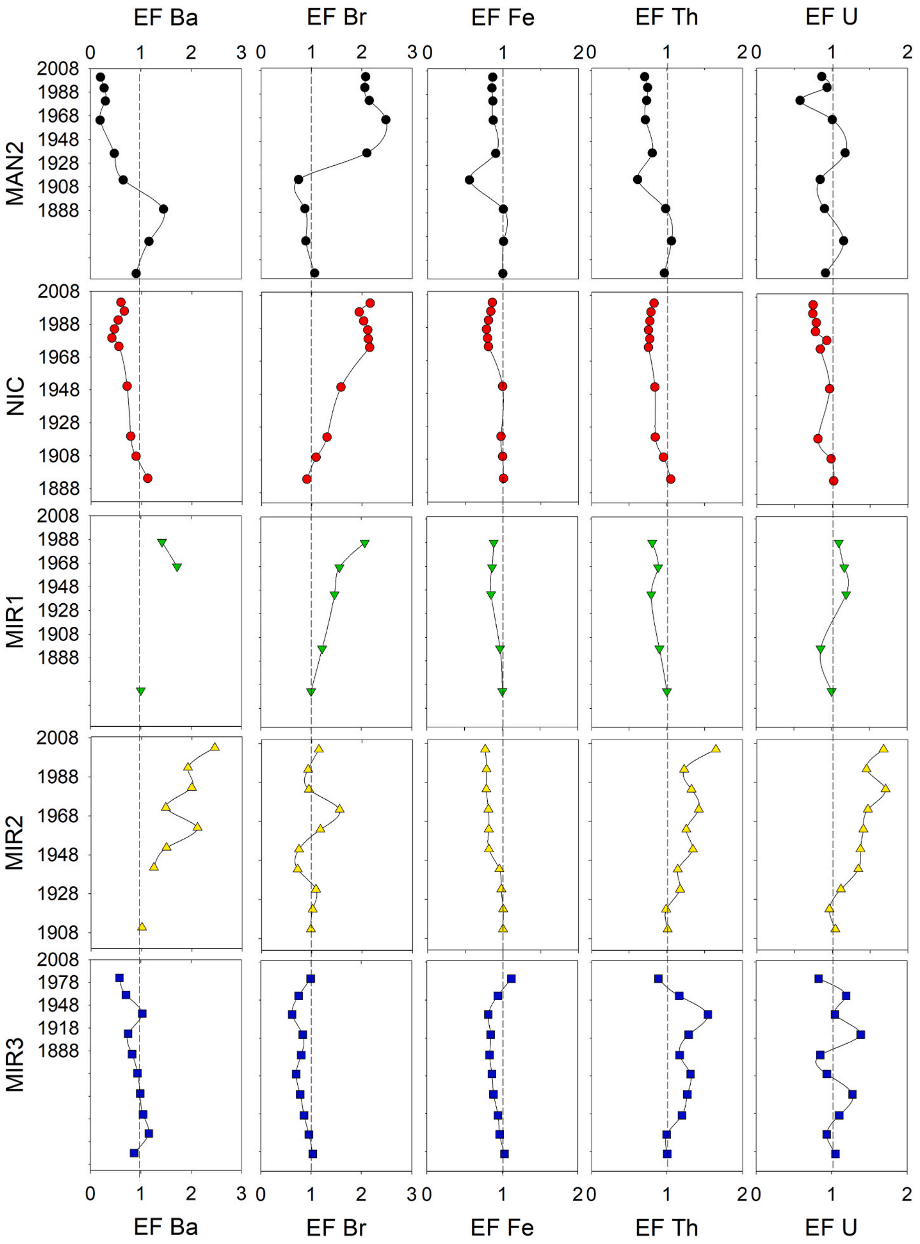

**Fig. 7.** Enrichment factor for Ba, Br, Fe, Th, and U in the 5 analysed sediment cores.

were active in 1947 are currently fully vegetated due to the regional stabilisation of dunes which is the result of increased precipitation and a decrease in wind drift over the last 50 years (Dillenburg et al., 2017; Perez et al., 2021). This transition to an increased vegetation cover may also have influenced the greater accumulation of Br in Mangueira Lagoon. Br is also used in agriculture as a soil fumigant and as a component of K-fertilisers (Kabata-Pendias and Pendias, 2001). Its enrichment in Mangueira Lagoon became particularly notable after 1950, coinciding with significant wetland transformations into agricultural land in the area (Bueno et al., 2021b; Avila et al., 2024). This suggests that agricultural practices could represent an additional source of Br.

Th and Fe are mainly associated with fine-grained sediments (Loring and Rantala, 1992; Titayeva, 1994). Their relationship varied across lagoons. In Mangueira Lagoon and Nicola Lake, a strong correlation was observed between Fe and Th, and decreasing EF since the 1950s represents a decrease in the finer sediment fraction towards recent sediments as previously observed by Bueno et al. (2021a).

The ΣREE vertical variation along the five cores (Fig. 8) also provided evidence for the two previously observed groups: Group 1, MAN2 and NIC with lower REE content; and Group 2, MIR1, MIR2 and MIR3 with higher REE content, where an increase in REE content is notable in core MAN2, especially after 1950. Considering that Mirim and Mangueira were formed at different geological times (Tomazelli et al., 2000), and have different sediment sources, it is likely that they have different mineralogy and sediment composition.

Although the studied enrichment factor values did not indicate significant contamination in Mangueira Lagoon, there was a notable change in the sediment composition after the 1950s (Table 1, Fig. 7), which seems to be related to rice farming. Although Mirim Lagoon also sustains intensive rice farming, the larger lagoon area (five times larger than Mangueira Lagoon) and larger river inputs likely contributed to sediment dilution and resuspension. Hence, changes in vertical profiles were less evident in Mirim Lagoon.

Overall, our geochemical data indicate that sediment sources differ among the studied lagoons. Mirim Lagoon, for example, receives

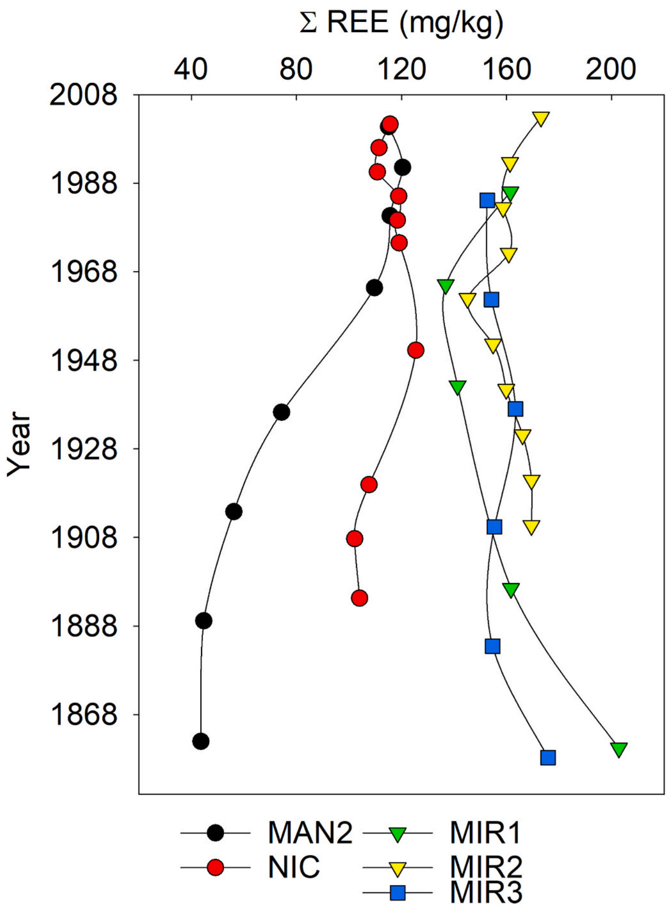

**Fig. 8.** Vertical distribution of the summation of analysed REE in all analysed sediment cores.

significant fluvial input, whereas Mangueira Lagoon and Nicola Lake are primarily influenced by local sedimentary inputs from the Pleistocene sand barriers, rainfall, organic matter from nearby wetlands, and aeolian transport. The La-Sc-Th ternary diagram confirms a dominant granitic composition, but the differences in ΣREE vs Th trends suggest two distinct sedimentary groups: Mirim Lagoon, with higher REE content and stronger fluvial influence, and Mangueira/Nicola, with lower REE concentrations and greater local inputs. Temporal shifts, such as the observed REE enrichment in Mangueira Lagoon after 1950, reveals the increasing impact of land-use changes mostly related to rice farming.

## 5. Conclusions

Major, trace and rare earth elements (REE) were valuable tracers of environmental change in coastal lagoon systems subjected to varying land-use pressures. Two depositional environments are distinguished, one with a larger drainage area influenced by large river inputs (Mirim Lagoon), and the other more isolated and subject to wind deposition and wetland organic matter (i.e. Mangueira Lagoon and Nicola Lake). Our results show that the sedimentary composition of the coastal lagoons is influenced by both natural geological processes and anthropogenic activities.

The impact of anthropogenic activities in Mirim and Mangueira Lagoon was implied from (1) Ba enrichment in Mirim Lagoon associated with the coal mining and burning, (2) a recent decrease in the EF of Th and Fe implying less fine-grained sediments potentially due to rice irrigation, and (3) the observed REE enrichment in Mangueira Lagoon after ca. 1950 likely related to increased fertiliser usage. This study also demonstrates the value of using REE and other elemental proxies to assess long-term environmental changes, particularly in regions undergoing rapid agricultural and industrial development. Our findings emphasise the importance of monitoring sediment composition in coastal ecosystems, as this provides insights into the effects of land-use change on sediment dynamics.

## CRediT authorship contribution statement

**Carolina Bueno:** Writing – original draft, Conceptualization. **Christian J. Sanders:** Validation. **Deborah I.T. Favaro:** Validation. **Santiago Guerrero:** Writing – review & editing, Formal analysis. **Felipe Hax Niencheski:** Validation. **Carlos Andrade:** Writing – review & editing. **William Burnett:** Writing – review & editing. **Isaac R. Santos:** Writing – review & editing, Visualization, Investigation.

## Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the author used ChatGPT/OpenAI to improve language and readability. After using this tool/service, the author reviewed and edited the content as needed and takes full responsibility for the content of the publication.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jsames.2025.105576.

## Data availability

Data will be made available on request.

## References

Aide, M., Aide, C., 2012. Rare earth elements: their importance in understanding soil genesis. ISRN Soil Science 2012, 783876. https://doi.org/10.5402/2012/783876, 11.

Appleby, P.G., Oldfield, F., 1983. The assessment of 210Pb data from sites with varying sediment accumulation rates. Hydrobiologia 103, 29–35.

Aubert, D., Stille, P., Probst, A., Gauthier-Lafaye, F., Pourcelot, L., del Nero, M., 2002. Characterization and migration of atmospheric REE in soils and surface waters. Geochim. Cosmochim. Acta 66, 3339–3350. https://doi.org/10.1016/S0016-7037(02)00913-4.

Avila, A.S.P., Bottezini, S.R., Diniz, D., Bueno, C., Perez, L., Martínez de la Escalera, G., Piccini, C., Leonhardt, A., García Rodríguez, F., Weschenfelder, J., 2024. The effect of fluvial avulsion on the Holocene chronostratigraphic record and the agricultural signal of the world's largest coastal lagoonal system. Sci. Total Environ. 942, 173757. https://doi.org/10.1016/j.scitotenv.2024.173757.

Basei, M.A.S., Siga Jr., O., Masquelin, H., Harara, O.M., Reis Neto, J.M., Preciozzi, F., 2000. In: Cordani, U., Milani, E., Thomaz Filho, A., Campos, D. (Eds.), The Dom Feliciano Belt (Brazil-Uruguay) and its Foreland (Rio de la Plata Craton): framework, tectonic evolution and correlations with similar terranes of southwestern Africa. Tectonic evolution of South America. 31 IGC, Rio de Janeiro, pp. 311–334.

Bau, M., Dulski, P., 1996. Distribution of yttrium and rare-earth elements in the penge and kuruman iron-formations, transvaal supergroup, South Africa. Precambr. Res. 79, 37–55. https://doi.org/10.1016/0301-9268(95)00087-9.

Bellieni, G., Comin-Chiaramonti, P., Marques, L., Melfi, A., Nardy, A., Papatrechas, C., Piccirillo, E., Roisemberg, A., Stolfa, D., 1986. Petrogenetic aspects of acid and basaltic lavas from the paraná plateau (Brazil): geological, mineralogical and petrochemical relationships. J. Petrol. 27, 915–944. https://doi.org/10.1093/petrology/27.4.915.

Borba, V., 2016. Bacia da Lagoa Mirim e o Programa Regional 35 – FAO/ONU: projeto internacional em espaço binacional. Centro de Literaturas e Culturas Lusófonas e Europeias, Faculdade de Letras da Universidade de Lisboa Instituto Europeu de Ciências da Cultura Padre Manuel Antunes Biblioteca Rio-Grandense Lisboa, Rio Grande. ISBN – 978-989-8814-39-5.

Buchmann, F.S.C., Caron, F., Lopes, R.P., Ugri, A., Lima, L.G., 2009. Panorama Geológico da Planície Costeira do Rio Grande do Sul. In: Ana Maria Ribeiro; Soraia Girardi Bauermann; Carolina Saldanha Scherer. Quaternário do Rio Grande do Sul: Integrando Conhecimentos. Porto Alegre: Sociedade Brasileira de Paleontologia, pp. 35–56.

Bueno, C., Sanders, C.J., Niencheski, F.H., Andrade, C., Burnett, W., Santos, I.R., 2021a. Organic carbon accumulation in oligotrophic coastal lakes in southern Brazil during the last century. J. Paleolimnol. 66, 71–82. https://doi.org/10.1007/s10933-021-00187-9.

Bueno, C., Alves, F.L., Pinheiro, L.M., Perez, L., Agostini, V.O., Fernandes, E.H.L., Möller, O.O., Weschenfelder, J., Pinho, G.L.L., Wallner-Kersanach, M., Moura, R.R., Durán, J.M., Etchevers, I., Costa, L.D.F., Werlang, C.C., Bortolin, E., Machado, E., Figueira, R.C.L., Ferreira, P.A.L., Andrade, C., Fornaro, L., García-Rodríguez, F., 2021b. The effect of agricultural intensification and water-locking on the world's largest coastal lagoonal system. Sci. Total Environ. 801, 149664. https://doi.org/10.1016/j.scitotenv.2021.149664, 2021.

Cardoso-Silva, S., Kim, B.S.M., de Lima Ferreira, P.A., Benedetti, B., Goyenola, G., Iglesias, C., Figueira, R.C.L., López-Rodríguez, A., Moschini-Carlos, V., Texeira de Mello, F., Meerhoff, M., Pompêo, M., 2024. Reconstructing 90 years of anthropogenic activities in a subtropical reservoir: a chemometric and paleolimnological perspective. Environ. Sci. Pollut. Res. 31, 55756–55773. https://doi.org/10.1007/s11356-024-34718-4.

Choudhury, H., Cary, R., 2001. Barium and barium compounds. In: Concise International Chemical Assessment Document 33. World Health Organization, Geneva. ISSN 1020-6167.

Condie, K.C., 1993. Chemical composition and evolution of the upper continental crust: contrasting results from surface samples and shales. Chem. Geol. 104, 1–37. https://doi.org/10.1016/0009-2541(93)90140-E.

Cullers, R.L., 1994. The chemical signature of source rocks in size fractions of Holocene stream sediment derived from metamorphic rocks in the Wet Mountains region, Colorado, U.S.A. Chem. Geol. 113, 327–343. https://doi.org/10.1016/0009-2541(94)90074-4.

da Silva, M.A.M., 1979. Provenance of heavy minerals in beach sands, southeastern Brazil: from Rio Grande to Chui (Rio Grande do Sul state). Sediment. Geol. 24, 133–148.

de Oliveira, S.M.B., da Silva, P.S.C., Mazzilli, B.P., Favaro, D.I.T., Saueia, C.H., 2007. Rare earth elements as tracers of sediment contamination by phosphogypsum in the Santos estuary, southern Brazil. Appl. Geochem. 22, 837–850. https://doi.org/10.1016/j.apgeochem.2006.12.017.

Dillenburg, S.R., Barboza, E.G., Rosa, M.L.C.C., Caron, F., Sawakuchi, A.O., 2017. The complex prograded Cassino barrier in southern Brazil: Geological and morphological evolution and records of climatic, oceanographic and sea-level changes in the last 7–6 ka. Mar. Geol. 390, 106–119. https://doi.org/10.1016/j.margeo.2017.06.007.

Finkler Ferreira, T., Crossetti, L.O., Motta Marques, D.M.L., Cardoso, L., Fragoso, Jr CR., van Nes, E.H., 2018. The structuring role of submerged macrophytes in a large subtropical shallow lake: Clear effects on water chemistry and phytoplankton structure community along a vegetated-pelagic gradient. Limnologica 69, 142–154. https://doi.org/10.1016/j.limno.2017.12.003.

GeoRoc. Geochemistry of Rocks of the Oceans and Continents. http://georoc.mpch-mainz.gwdg.de/georoc/ Accessed December 2024.

Hao, H., Zhang, M., Wang, J., Fu, Z., Balaji, P., Jiang, S., 2022. Barium in coal and coal combustion products: Distribution, enrichment and migration. Energ. Explor. Exploit. 1–19. https://doi.org/10.1177/01445987221086981.

Hazen, R.M., Ewing, R.C., Sverjensky, D.A., 2009. Evolution of uranium and thorium minerals. Am. Min. 94, 1293–1311. https://doi.org/10.2138/am.2009.3208.

Henderson, P., 1984. General geochemical properties and abundances of the rare earth elements. In: Henderson, P. (Ed.), Rare Earth Element Geochemistry. Elsevier, Amsterdam.

Hirata, F.E., Moller, J., Mata, M.M., 2010. Regime shifts, trends and interannual variations of water level in Mirim Lagoon, southern Brazil. PANAMJAS 5, 82–94.

Hueck, M., Oyhantçabal, P., Philipp, R.P., Stipp Basei, M.A., Siegesmund, S., 2018. The Dom Feliciano Belt in Southern Brazil and Uruguay. In: Basei, Stipp (Ed.), Geology of Southwest Gondwana. https://doi.org/10.1007/978-3-319-68920-3_11.

Ilha, J.G., 2019. Avaliação do Impacto Ambiental em Duas Drenagens na Região de Candiota. RS. Trabalho de conclusão de curso (Graduação) - Universidade Federal do Rio Grande do Sul, Instituto de Geociências, Curso de Geologia. Porto Alegre, p. 155. BR-RS. http://hdl.handle.net/10183/204986.

Junqueira, T.P., Harrison, A.L., Leybourne, M.I., Vriens, B., 2024. Rare earth element patterns in sediments from the Great Lakes basin. Appl. Geochem. 176, 106218. https://doi.org/10.1016/j.apgeochem.2024.106218.

Kabata-Pendias, A., Pendias, H., 2001. Trace Elements in Soils and Plants, third ed. CRC Press, Boca Raton, p. 403.

Kandasamy, S., Lin, B., Lou, J.-Y., Kao, S.-J., Chen, C.-T.A., Mayer, L.M., 2018. Estimation of marine versus terrigenous organic carbon in sediments off southwestern Taiwan using the bromine to total organic carbon ratio as a proxy. J. Geophys. Res. Biogeosci. 123, 3387–3402. https://doi.org/10.1029/2018JG004674.

Kastori, R.R., Putnik-Delić, M.I., Maksimović, I.V., 2023. Rare earth elements application in agriculture. Acta Agric. Serb. 28, 87–95. https://doi.org/10.5937/AASer2356087K.

Kim, B.S.M., Amorim, E.P., Cardoso Silva, P.S., Figueira, R.C.L., Braga, E.S., Fávaro, D.I.T., 2024. Vintage analysis on superficial sediments to predict future trends in metal contamination of Santos and São Vicente Estuarine System. J. Trace Elem. Miner. 3, 10004. https://doi.org/10.1016/j.jtemin.2023.100049.

Larizzatti, F.E., Fávaro, D.I.T., Moreira, S.R.D., Mazzilli, B.P., Piovano, E.L., 2001. Multielemental determination by Instrumental Neutron Activation Analysis and recent sedimentation rates using 210Pb dating method at Laguna del Plata, Cordoba, Argentina. J. Radioanal. Nucl. Chem. 249, 263–268. https://doi.org/10.1023/A:1013271316393.

Laveur, C., Cornu, S., 2009. A review on the potentiality of Rare Earth Elements to trace pedogenetic processes. Geoderma 154, 1–12. https://doi.org/10.1016/j.geoderma.2009.10.002.

Lawrence, M.G., Kamber, B.S., 2006. The behaviour of the rare earth elements during estuarine mixing—revisited. Mar. Chem. 100, 147–161. https://doi.org/10.1016/j.marchem.2005.11.007.

Lee, S.-G., Tanaka, T., 2021. Europium isotope fractionation in highly fractionated igneous rocks with large Eu negative anomaly. Geochem. J. 55, e9–e17. https://doi.org/10.2343/geochemj.2.0631.

Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci. Rev. 32, 235–283. https://doi.org/10.1016/0012-8252(92)90001-A.

Malikova, I.N., Strakhovenko, V.D., Ustinov, M.T., 2020. Uranium and thorium contents in soils and bottom sediments of lake Bolshoye Yarovoye, western Siberia. J. Environ. Radioact. 211, 106048. https://doi.org/10.1016/j.jenvrad.2019.106048.

Mayer, L.M., Macko, S.A., Mook, W.H., Murray, S.M., 1981. The distribution of bromine in coastal sediments and its use as a source indicator for organic matter. Org. Geochem. 3, 37–42. https://doi.org/10.1016/0146-6380(81)90011-5.

McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochem. Geophys. 2, 1021. https://doi.org/10.1029/2000GC000109.

McLennan, S.M., Murray, R.W., 1998. Geochemistry of sediments. In: Geochemistry. Encyclopedia of Earth Science. Springer, Dordrecht. https://doi.org/10.1007/1-4020-4496-8_143.

McLennan, S.M., Nance, W.B., Taylor, S.R., 1980. Rare earth element-thorium correlations in sedimentary rocks, and the composition of the continental crust. Geochim. Cosmochim. Acta 44, 1833–1839. https://doi.org/10.1016/0016-7037(80)90232-X.

Menegheti, J.O., 2010. O cultivo de arroz irrigado e a conservação da biodiversidade da Lagoa Mirim e entorno. Oportunidade para sensibilização e tomada de consciência de possíveis ações condutoras à minimização dos efeitos ambientais. In: Alba, Filippini (Ed.), Sustentabilidade Socioambiental da Bacia da Lagoa Mirim. Embrapa Clima Temperado Pelotas, RS. ISBN: 978-85-85941-51-2.

Motta Marques, D.M.L., Rodrigues, L.H.R., Fragoso Júnior, C.R., Crossetti, L.O., Cardoso, L.S., Collischonn, W., Tassi, R., They, N.H., Bemvenuti, M.A., Garcia, A., Vieira, J.P., Canterle, E.R.B., Cardoso, M.A.G., Becker, V., Paulo, V.G., Bravo, J.M., Souza, R., Ribeiro, C.V., Callegaro, V.L.M., Silva, S.A., Werner, V.R., Rosa, Z.M., Villanueva, A.O.N., Moresco, A., Condini, M.V.L., Burns, M.D.M., Würdig, N.L., 2013. O Sistema Hidrológico do Taim. In: PELD - CNPq: dez anos do Programa de Pesquisas Ecológicas de Longa Duração do Brasil: achados, lições e perspectivas, pp. 200–224.

Muzio, R., Artur, A.C., 1999. Petrological features of the Santa Teresa Granitic Complex Southeastern Uruguay. J. S. Am. Earth Sci. 12, 501–510. https://doi.org/10.1016/S0895-9811(99)00033-4.

Nalbandian, H., 2012. Trace Element Emissions from Coal. IEA Clean Coal Centre, 978-92-9029-523-5.

Nash, J.T., 1979. Uranium and Thorium in Granitic Rocks of Northeastern Washington and Northern Idaho, with Comments on Uranium Resource Potential. United States Department of the Interior Geological Survey. Open File Report 79-233.

Oyhantçabal, P., Siegesmund, S., Wemmer, K., Layer, P., 2010. The Sierra Ballena Shear Zone in the southernmost Dom Feliciano Belt (Uruguay): Evolution, kinematics, and deformation conditions. Int. J. Earth Sci. 99, 1227–1246. https://doi.org/10.1007/s00531-009-0453-1.

Panario, D., Gutiérrez, O., Sánchez Bettucci, L., Peel, E., Oyhantçabal, P., Rabassa, J., 2014. Ancient landscapes of Uruguay. In: Rabassa, Jorge, Ollier, Clifford (Eds.), Gondwana Landscapes of Southern South America. Springer Earth System Sciences, Serie, pp. 161–199.

Perez, L., Crisci, C., Lüning, S., de Mahiques, M.M., García-Rodríguez, F., 2021. Last millennium intensification of decadal and interannual river discharge cycles into the Southwestern Atlantic Ocean increases shelf productivity. Glob. Planet. Change 196, 103367. https://doi.org/10.1016/j.gloplacha.2020.103367.

Pires, M., Querol, X., 2004. Characterization of Candiota (South Brazil) coal and combustion by-product. Int. J. Coal Geol. 60, 57–72. https://doi.org/10.1016/j.coal.2004.04.003.

Ramsar, 2015. State of the World's Wetlands and their Services to People: A compilation of recent analyses. Ramsar Briefing Note 7. March 2015.

Rollinson, H.R., 1993. Using Geochemical Data: Evaluation, Presentation, Interpretation. Longman Geochemistry Series 384.

Saleh, G.M., Dawood, Y.H., Abd El-Naby, H.H., 2002. Petrological and geochemical constraints on the origin of the granitoid suite of the Homret Mikpid area, south Eastern Desert, Egypt. J. Mineral. Petrol. Sci. 97, 47–58. https://doi.org/10.2465/jmps.97.47.

Sanchez-Cabeza, J.A., Díaz-Asencio, M., Ruiz-Fernández, A.C., 2012. Radiocronología de sedimentos costeros utilizando 210Pb: modelos, validación y aplicaciones. IAEA. Organismo Internacional de Energía Atómica. Viena. STI/PUB/1538. ISBN: 978–92–0–325210–2.

Santos, I.R., Fávaro, D.I.T., Schaefer, C.E.G.R., Silva-Filho, E.V., 2007. Sediment geochemistry in coastal maritime Antarctica (Admiralty Bay, King George Island): Evidence from rare earths and other elements. Mar. Chem. 107, 464–474. https://doi.org/10.1016/j.marchem.2007.09.006.

Santos, I.R., Machado, M.I., Niencheski, L.F., Burnett, W., Milani, I.B., Andrade, C.F.F., Peterson, R.N., Chanton, J., Baisch, P., 2008. Major Ion Chemistry in a Freshwater Coastal Lagoon from Southern Brazil (Mangueira Lagoon): Influence of Groundwater Inputs. Aquat. Geochem. 14, 133–146. https://doi.org/10.1007/s10498-008-9029-0.

Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. 39, 611–627. https://doi.org/10.1007/s002540050473.

Szefer, P., Kusak, A., Szefer, K., Glasby, G.P., Jankowska, H., Wolowicz, M., Ali, A.A., 1998. Evaluation of the anthropogenic influx of metallic pollutants into Puck Bay, southern Baltic. Appl. Geochem. 13, 293–304. https://doi.org/10.1016/S0883-2927(97)00098-X.

Szefer, P., Glasby, G.P., Stüben, D., Kusak, A., Geldon, J., Berner, Z., Neumann, T., Warzocha, J., 1999. Distribution of selected heavy metals and rare earth elements in surficial sediments from the polish sector of the Vistula Lagoon. Chemosphere 39, 2785–2798. https://doi.org/10.1016/S0045-6535(99)00208-8.

Taylor, S., McLennan, S., 2009. Planetary Crusts: Their Composition, Origin and Evolution (Cambridge Planetary Science). Cambridge University Press, Cambridge. https://doi.org/10.1017/CBO9780511575358.

Titayeva, N.A., 1994. Geochemistry of Uranium and Thorium. In: Nuclear Geochemistry. CRC Press, p. 296.

Tomazelli, L.J., Dillenburg, S.R., Villwock, J.A., 2000. Late quaternary geological history of Rio Grande do Sul coastal plain, Southern Brazil. Rev. Bras. Geociênc. 30, 474–476.

Villanueva, A.O.N., Motta-Marques, D., Tucci, C.E.M., 2000. The Taim wetland conflict: a compromise between environment conservation and irrigation. Water Int. 25 (4), 610–616.

Wang, L., Han, X., Liang, T., Guo, Q., Li, J., Dai, L., Ding, S., 2019. Discrimination of rare earth element geochemistry and co-occurrence in sediment from Poyang Lake, the largest freshwater lake in China. Chemosphere 217, 851–857. https://doi.org/10.1016/j.chemosphere.2018.11.060.

Wang, S., Wang, Z., Gao, S., Zhang, X., Zeng, J., Wu, Q., 2024. Rare earth elements in lake sediments record historic environmental influences from anthropogenic activities. Ecol. Indic. 159, 111680. https://doi.org/10.1016/j.ecolind.2024.111680.

Waters, C.N., Zalasiewicz, J., Summerhayes, C., Barnosky, A.D., Poirier, C., Gałuszka, A., Cearreta, A., Edgeworth, M., Ellis, E.C., Ellis, M., Jeandel, C., Reinhold, L., McNeill, J.R., deB Richter, D., Steffen, W., Syvitski, J., Vidas, D., Wagreich, M., Williams, M., Zhisheng, A., Grinevald, J., Odada, E., Oreskes, N., Wolfe, A.P., 2016. The Anthropocene is functionally and stratigraphically distinct from the Holocene. Science 351, aad2622. https://doi.org/10.1126/science.aad2622.

Xanthopoulou, V., Iliopoulos, I., Avramidis, P., 2021. Assessment of clayey raw material suitability for ceramic production, in the Northern Peloponnese, Greece. Archaeol. Anthropol. Sci. 13, 50. https://doi.org/10.1007/s12520-021-01297-1.

Yu, R., Lin, C., Yan, Y., Hul, G., Huang, H., Wang, X., 2019. Distribution and provenance implication of rare earth elements and Sr-Nd isotopes in surface sediments of Jiulong River, Southeast China. J. Soils Sediments 19, 1499–1510. https://doi.org/10.1007/s11368-018-2135-8.

Zhang, K., Shields, G.A., 2022. Sedimentary Ce anomalies: Secular change and implications for paleoenvironmental evolution. Earth Sci. Rev. 229, 104015. https://doi.org/10.1016/j.earscirev.2022.104015.

Zhang, Y., Su, Y., Liu, Z., Sun, K., Kong, L., Yu, J., Jin, M., 2018. Sedimentary lipid biomarker record of human-induced environmental change during the past century in Lake Changdang, Lake Taihu basin, Eastern China. Sci. Total Environ. 613–614, 907–918. https://doi.org/10.1016/j.scitotenv.2017.09.185.

Zhang, Y., Yu, J., Su, Y., Du, Y., Liu, Z., 2019. Long-term changes of water quality in aquaculture-dominated lakes as revealed by sediment geochemical records in Lake Taibai (Eastern China). Chemosphere 235, 297–307. https://doi.org/10.1016/j.chemosphere.2019.06.179.