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ORIGINAL ARTICLE

Geochemical characterization of rare earth elements in sediment profiles from the Oualida lagoon (Morocco)

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Abstract The present work assesses the temporal distribution pattern and geochemical changes of rare earth elements and Yttrium, Scandium, Thorium, and Uranium delivery into the Oualidia lagoon. Two sediment cores were retrieved from the Oualidia lagoon and analyzed using neutron activation analysis. The results indicated that heavy rare earth elements are slightly enriched the sediment cores over light rare earth elements. The highest values of REEs were recorded in the top layers of the cores and depleted with depth, suggesting a possible change in factors controlling their accumulation, including mechanical, chemical, and environmental parameters such as weathering intensity, grain size, and Fe-Mn oxides. The sediments display positive Ce anomalies, which are probably related to the submarine weathering process and detrital input. Noting also the variation of hydrodynamics conditions and confinement of the upstream part of the lagoon played a key role in changing the sediment origins. Thus, further investigation of REEs origin in the Oualidia lagoon sediment is required to identify their sources, provenances, and the factors controlling their spatial and vertical distributions. However, these results provide baseline data of occurring changes in REEs geochemical composition and constitute a typical study case to understand the link between sedimentary and geochemistry processes in a lagoonal ecosystem.

Keywords Geochemical characterization · Rare earth elements · Sediment · Oualidia lagoon

1 Introduction

The study of sediment chemistry composition is a valuable tool allowing identifying the provenance. Rare earth elements (REEs) were widely used as tracers and indicators of geochemical processes to investigate the chemical evolution of crust earth, tectonic setting, and weathering processes in watersheds (Taylor and McLennan 1985; Condie 1991; Olmez et al. 1991; Tanaka et al. 2007; Laveuf et al. 2008; Li et al. 2017). They are also used to determine anthropogenic effects, particularly unnatural liquid and solid rejects that often modify the geochemical characteristics of sediments (Guessan 2008; Mejjad et al. 2022).

The geochemistry of REEs in marine and estuarine sediment has been widely studied in the last decades (Ramesh et al. 2000; Bounouira et al. 2008; Saraee et al. 2009; Hannigan et al. 2010; Jung et al. 2012; Antonina et al. 2013; Lin et al. 2013; Och et al. 2014; Ashraf et al. 2016; Manoj et al. 2016; Elias et al. 2019). REEs composition and geochemistry have not been studied in detail in Moroccan lagoonal sediments. However, there have been few studies carried out in three Moroccan lagoons, Nador Lagoon (Bloundi 2005), Oualidia Lagoon (Mejjad et al. 2016,2022) and Sidi Moussa Lagoon (Benmhammed et al. 2021).

The Oualidia lagoon is located on the Moroccan Atlantic Coast of Abda-Doukkala between Safi and El Jadida (Hilmi et al. 2017). This region is known for the presence of upwelling throughout the year (Tamim et al. 2015). The

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upwelled water is rich in nutrients impacting marine productivity positively (Miranda et al. 2012) and consequently significantly influencing the region's socioeconomic sectors. However, the study area is exposed to substantial natural and anthropogenic pressures, including the confinement of its upstream part, coastal erosion, vulnerability to climate changes, and pollution (Zourarah et al. 2007; Maanan et al. 2014; Mejjad et al. 2018, 2020, 2022; Bouchkara et al. 2021, 2022). Currently, the Oualidia Lagoon is under pressure from human activities such as agriculture, pasturage, aquaculture, and fishing (Hassou et al. 2014; Maanan et al. 2018; Lakhlalki et al. 2020; El Aouidi et al. 2021). Besides, the lagoon viability is strongly influenced by the upstream part's water confinement and coastal erosion, where the eroded area was valued at about 1,513,800 m^2 with an estimated erosion volume of 633,383 m^3 (Bouchkara et al. 2022). Little attention was dedicated to the geochemical features of the sediments of the Oualidia lagoon in terms of geochemical composition, provenance, and processes. Zourarah et al. (2007), Maanan et al. (2014) and Mejjad et al. (2018) have investigated the Oualidia lagoon sediments in terms of heavy metals composition and their environmental effects on the lagoon environment.

This work aims at investigating the geochemical composition, behavior, provenance, and processes of REEs, Sc, Th, and U measured in dated sediments cores (see Mejjad et al. 2022; Laissaoui et al. 2018). Accordingly, the present paper represents a continued investigation of the Oualidia lagoon sediment geochemistry in light of the previously presented data.

2 Geographical setting

The Oualidia Lagoon is located on the Moroccan Atlantic coast and is known as the oyster capital of Morocco. The aquaculture activities in this lagoon started in 1950 with the creation of the first station of oyster culture. Since then, other stations have been created, and aquaculture activities have been significantly developed in the region. Other activities have been developed in the region since the 70 s, such as agriculture, pasturage, and coastal tourism. Accordingly, the study area's biodiversity richness provides the region with several socioeconomic services and goods. For this reason, the area is subjected to many projects to preserve and protect its cultural and ecological heritage (Mejjad et al. 2020). Besides, many studies were carried out on the lagoon in the framework of national and regional projects and scientific research to analyze, assess and help in the decision-making for better management of the lagoon.

3 Methods and materials

The research of geochemical characterization of rare earth elements, scandium, thorium, and uranium, was carried out on the sediment of the Oualidia lagoon (Fig. 1). The sediment cores were collected from the lagoon (see Sect. 4.1) and then analyzed for radionuclides concentrations (Pb-210, Cs-137) assessment using spectrometry alpha and gamma (in Laissaoui et al. 2018) and pollution geochronology establishment (Mejjad et al. 2018). These sediments were also analyzed for REEs contamination degree assessment (Mejjad et al. 2022) using instrumental neutron activation analysis (INAA) (See Sect. 3.2). Thus, the present study is a continued logical investigation of previous studies where we carry out a geochemical characterization of REEs, Y, Th, U, and Sc.

3.1 Sampling and physical preparation

The sediment cores were collected from the Oualidia lagoon during a sampling campaign carried out in May 2014 (Laissaoui et al. 2018) from the main channel. A 56-cm-long core was sampled from the central part of the lagoon, and a second core, 36-cm-long, was retrieved from the downstream part of the lagoon (Fig. 1). The sediment cores were identified as CO-1 (32°45′12N 9°00′52W), and CO-2 (32°46′24N 8°59′07W). The cores were sectioned into 1–2 cm slices immediately after retrieval. In the laboratory, the sediment samples were dried in an oven at a constant temperature of 80 °C for 24 h before being mechanically disaggregated to obtain a homogeneous powdered sample of approximately <2 mm. The grain size distribution of each sediment core layer of 2 cm was determined using Laser Diffraction equipment (Malvern Mastersizer 2000) using the Hydro 2000G dispersion Unit. Organic matter content was determined using a method called loss on ignition, where the weight loss was measured by weighing each sample before and after heating (Heiri et al. 2001).

3.2 INAA analytical method

Instrumental neutron activation analysis (INAA) is a widely used method for environmental sample analysis. The technique exhibits exceptional sensitivity, allowing for the detection of trace elements at extremely low concentrations, often in the parts per billion or even parts per trillion range. Furthermore, INAA offers the advantage of being a multi-elemental analysis method, enabling the simultaneous determination of numerous elements in a single sample without the need for extensive sample preparation. In this order, INAA is the appropriate

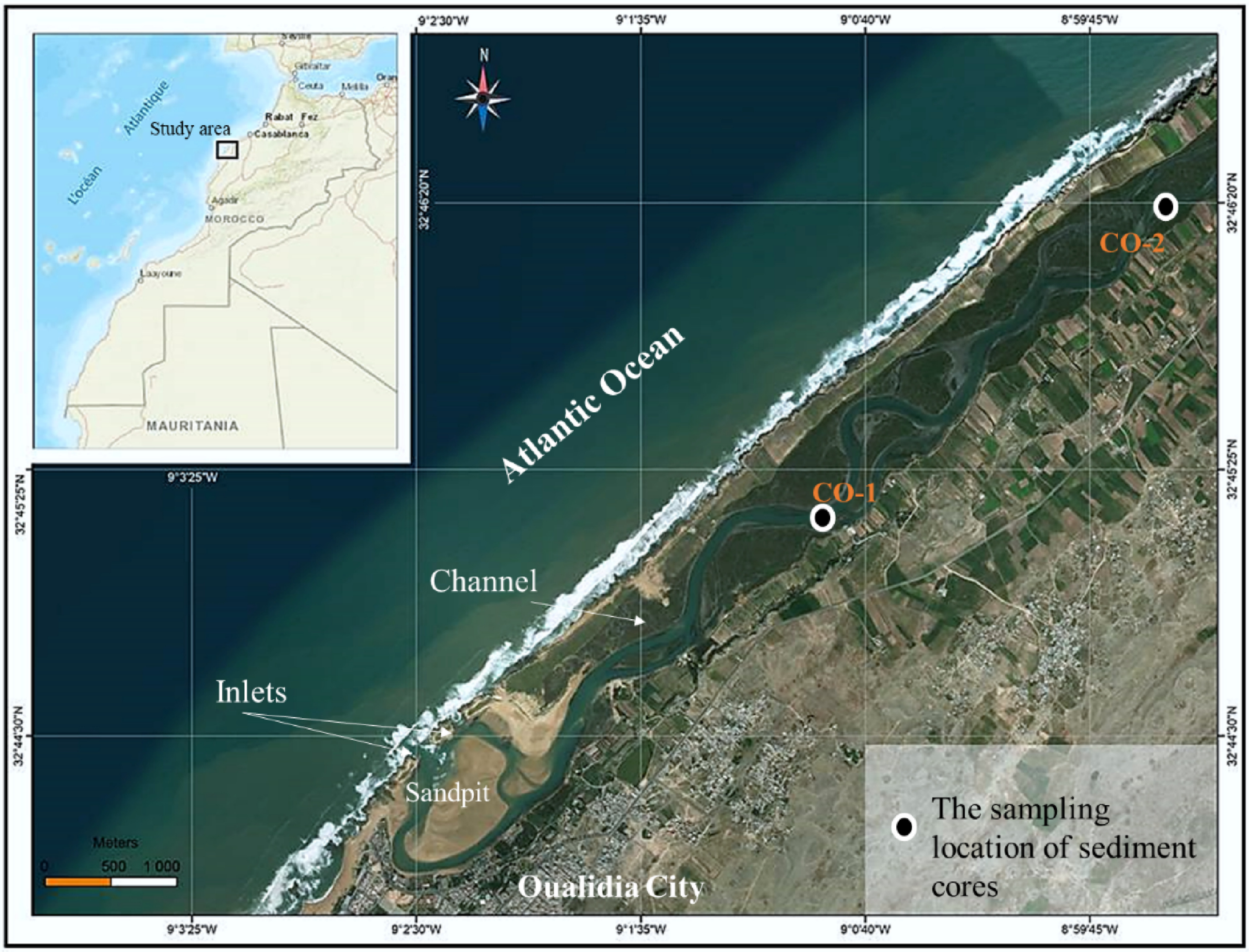


Fig. 1 Geographical location of the Oualidia lagoon and sampling zones

analytical method to measure REEs in sediment samples (Meloni et al. 1987; Minai et al. 1985).

The sediment cores samples were analyzed using Neutron Activation Analysis (NAA) technique. The irradiations of samples (Layers of 4 cm) were performed at the Neutron Activation Analysis laboratory of the National Centre for Energy, Sciences and Nuclear Techniques (CNESTEN), which hosts the first Moroccan Triga Mark II research reactor that provides mainly thermal neutrons, with a flux of 5.0 1012 n·cm^{-2}·s^{-1} at the pneumatic transfer system (PTS) and 2.0 1013 n·cm^{-2}·s^{-1} at the rotary specimen rack (Mejjad et al. 2018). In order to verify the methodology accuracy and determine the elemental concentrations, a standard reference material (NIST 2711—Montana Soil) was analyzed, where for each element, the performance for accuracy was assessed using Z-scores. All elements are generally well clustered over the reference value (|Z| 3). The obtained values were in good agreement with the certified values and the INAA reproducibility. The precision was better than 10% for nearly all elements (Table 1).

3.3 Statistical analysis

The Pearson correlation coefficient was determined by SPSS (SPSS Inc. Released in 2007. Version 16.0. Chicago, SPSS Inc.), a statistical software package. The obtained results are significant if $p<0.05$ and highly significant if $p<0.01$. Graphs were organized using the Origin 2017 software. The schematic figures were carried out using Adobe Illustrator software.

3.4 REE normalization and elemental ratios

The measured concentrations of YREEs in 22 sediment cores layers were normalized with average concentrations of the North American Shale Composite (NASC) (Gromet et al. 1984). NASC is a reference material of 40 shales collected from the US, Antarctica, Africa, and 15

Table 1 The REEs analysis control quality

	Measured values (NIST 2711—Montana Soil)	Certified values/reference values	|Measured values-certified values|/certified values
Sc	9,05	8,50	6,47
La	41	38	7,89
Ce	68	70	2,86
Nd	26	29	10,34
Sm	5,46	5,93	7,99
Eu	1,0	1,1	8,91
Gd	4,56	5	8,80
Dy	4,67	5	4,80
Yb	3,196	3	6,53
Th	13,23	15	11,80
U	2,78	3,01	7,64

unspecified locations (Gromet et al. 1984). The fractionation between light rare earth elements (LREE) and heavy rare earth elements (HREE) was quantified by utilizing fractionation measures:

$$\left[(\mathrm{La}/\mathrm{Sm})_{\mathrm{NASC}}= (\mathrm{La}_{\mathrm{measured}}/\mathrm{La}_{\mathrm{NASC}})/(\mathrm{Sm}_{\mathrm{measured}}/\mathrm{Sm}_{\mathrm{NASC}})\right]. \quad (1)$$

$$\left[(\mathrm{La}/\mathrm{Yb})_{\mathrm{NASC}}= (\mathrm{La}_{\mathrm{measured}}/\mathrm{La}_{\mathrm{NASC}})/(\mathrm{Yb}_{\mathrm{measured}}/\mathrm{Yb}_{\mathrm{NASC}})\right]. \quad (2)$$

Anomalies of Ce and Eu anomalies were determined by applying the following Eqs. (3 and 4) (McLennan. 1989; Leleyter et al. 1999):

$$\mathrm{Ce}/\mathrm{Ce}* = 3\mathrm{Ce}_{\mathrm{N}}/(2\mathrm{La}_{\mathrm{N}} + \mathrm{Nd}_{\mathrm{N}}) \quad (3)$$

$$\mathrm{Eu}/\mathrm{Eu}* = 3\,\mathrm{EU}_{\mathrm{N}}/(2\mathrm{Sm}_{\mathrm{N}} + \mathrm{Tb}_{\mathrm{N}}) \quad (4)$$

With N=Normalized REEs, The superscript * indicates the geogenic background (NASC).

3.5 Calculation of mass transfer coefficient

The mass transfer coefficient (τ) (Liu et al. 2021) was calculated to evaluate REE mobility using the following Eq. (5):

$$\tau_{i,REE} = \frac{\left(\frac{C_{REE}}{C_i}\right)_{Sample}}{\left(\frac{C_{REE}}{C_i}\right)NASC}^{-1} \quad (5)$$

where $\mathrm{C}_{\mathrm{REE}}$ is the concentration of REEs in the sample, C_{i} is the concentration of REEs in standard materials.

The $\tau_{\mathrm{i,\ REE}}$ values are an indicator of enrichment or depletion of REEs after normalization against the element of reference (1) in standard materials (Jin et al. 2017; Liu et al. 2021), (NASC for the present study, Gromet et al. 1984). The reference element (1) comprise Fe, Al, Ti, Mn, and Ca. Fe was chosen as the reference in this study because it presents similar geochemistry to numerous trace metals, and its natural concentration is likely to be uniform (Bhuiyan et al. 2011). Positive $\tau_{\mathrm{i,\ REE}}$ values signify enrichment of REE (total or individual) in the sediment with respect to standards material; negative values designate depletion, while zero indicates that REEs are immobile.

4 Results and discussions

4.1 Sediment geochemistry and provenance

The sediments under investigation indicate changes in sediment lithology, mineralogical composition, and abundance along the cores related to the sedimentary processes and provenances (Mejjad et al. 2020). The sediments are mainly dominated by quartz and calcite (Table 2), while the other minerals present a low percentage (<8%). The abundance of quartz reflects the abundance of the sandy fraction. According to the granulometric composition analysis, the sand fraction fluctuates along with the sediment cores between 10 and 84% (Table 2); these results were reported by Mejjad et al. (2020). The decomposition of minerals, coastal erosion, or water action explained the fluctuations of quartz content. Indeed, the lagoon is under the influence of erosion; wherein a recently published study by Bouchakara et al. (2022), the eroded area in the Oualidia lagoon was found to be about 1,513,800 m^2. The highest calcite content is probably released from organisms such as foraminifera and ostracods (Bloundi 2005); indeed, the sediment samples contained an important amount of organism debris observed during the physical preparation of the samples (Fig. 2).

Organic matter shows an evolution different from finer sediment; instead, it increases with coarser sediment content in the two sediment cores. The ΣREEs show an evolution similar to finer sediments and different from OM content. It should be noted that the REE element geochemical behavior in sediment relies on the grain size distribution (Zhang et al. 2014). Indeed, Zhang and Gao (2015) highlighted that REEs were found to be more abundant in finer sediment, mainly middle REEs. The mass transfer coefficient ($\tau_{\mathrm{i,\ REE}}$) shows positive values reflecting the enrichment of REEs in the sediment and signifying that REEs are mobile. Both cores show positive values reflecting enrichment by REEs and reflecting their mobility mainly in the deepest layers (Fig. 2). The changes in the concentrations of rare earth elements could be related to their mobility along the sedimentary column. The mass

Table 2 % of Mud (Silt+Clay), Mean and its description, and Quartz and calcite composition (%)

Depths	D<0.063 mm Silt/clay (Mud %)	0.063<D<2000 mm (Sand %)	Mean (µm)	Description	Quartz %*	Calcite %*
CO-1						
0–16 cm	52<D<60	39<D<47	46.92<M<61.70	Very Coarse Silt	47<Qz<57	19<C<28
18–30 cm	20<D<47	52<D<79	68.68<M<206.8	Very fine sand & fine sand	52<Qz<64	19<C<23
32–38 cm	14<D<17	82<D<85	226.2<M<336.4	Medium Sand	55<Qz<73	14<C<16
40–52 cm	46<D<93	6<D<53	18.22<M<68.26	Coarse silt & very coarse silt	48<Qz<57	22<C<28
CO-2						
1–17 cm	44<D<54	45<D<55	62<M<87	Very Fine Sand & Very Coarse Silt	50<Qz<58	22<C<25
18–36 cm	13<D<20	79<D<86	96<M<283	Fine & medium sand	34<Qz<43	27<C<39

* Mejjad et al. (2020)

transfer coefficient values are higher in the deepest layers where the grain size of sediment became greater. Whereas, the ΣREEs values increase with the decrease in grain size, reflecting the accumulation tendency in finer sediment grain. Our results then indicate that the REEs content varies with grain size variation other than what has been reported by Li et al. (2001) and Xu et al. (2011).

4.1.1 REEs+Y, Sc, Th, and U distributions characteristics

The concentrations of rare earth elements have shown two different evolution trends over time, while the measured concentrations for the two sediment cores are almost higher in the top layers and decrease with depth. In this sense, the cores were split into two ranges in values of the REEs measured concentrations (Table 3). The local background values were determined from the bottom layers of CO-2, representing the lower values dating before the industrial era according to provided ages obtained by the applied radiometric dating, reported by Mejjad et al. (2022). The REEs values were almost higher in the top layers and depleted with depth. Except for Gd, the obtained concentrations of REEs are almost close to those found in a sediment core retrieved from Coroa do Boi Bay (Brazil), which is known as a polluted area (Costa et al. 2021). Gd shows high concentrations compared to its background value suggesting an anthropogenic origin. Indeed, Gd was reported as an emerging microcontaminant of water resources worldwide (Ebrahimi et al. 2019). The concentration ranges of uranium and thorium are higher in the top layers between the water surface and 31 cm of depth (CO-1), exceed the mean value of the upper continental crust, and then deplete, reaching lower concentrations, while CO-2 shows values almost lower than UCC (Table 3).

The variation of recorded values of YREEs, Sc, Th, and U is probably related to changes in deposition conditions and the proximity to the source rock or to upwelling activity characterizing the Moroccan Atlantic Coast, which could be partially attributed to the observed variation of the REEs values (Mejjad et al. 2016). Noting that in addition to the natural process, the anthropogenic factor could also contribute to the enrichment by YREEs, mainly the agriculture activities in which the use of phosphate fertilizers could enrich the sediments by the REEs (Martin and McCulloch 1999; Borrego et al. 2004; Mejjad et al. 2022). Also seeing that the top layers of sediment cores are mainly composed of fine sediment compared to the bottom layers, which may also explain the vertical distribution tendency of studied elements.

4.2 Correlation among REEs+Y, Sc, Th, and major elements/REEs

The correlation between YREEs, Sc, Th, and U major elements, fine fraction, and organic matter content display significant variations, which are probably linked to sampling location and other factors controlling the distribution, transport, and accumulation of sediments and studied elements (Table 4).

In the CO-1 core, the correlation table exhibits highly significant correlations between La–Nd, La–Y, Ce–Eu, Ce–Tb, Ce–Yb, Nd–Y, Nd–Gd, Eu–Yb, Tb–Yb, and Y–Gd ($p<0.01$) and a significant correlation recorded between Nd–Eu, Nd–Yb, Nd–Tb, and Sm–Y ($p<0.05$). The other

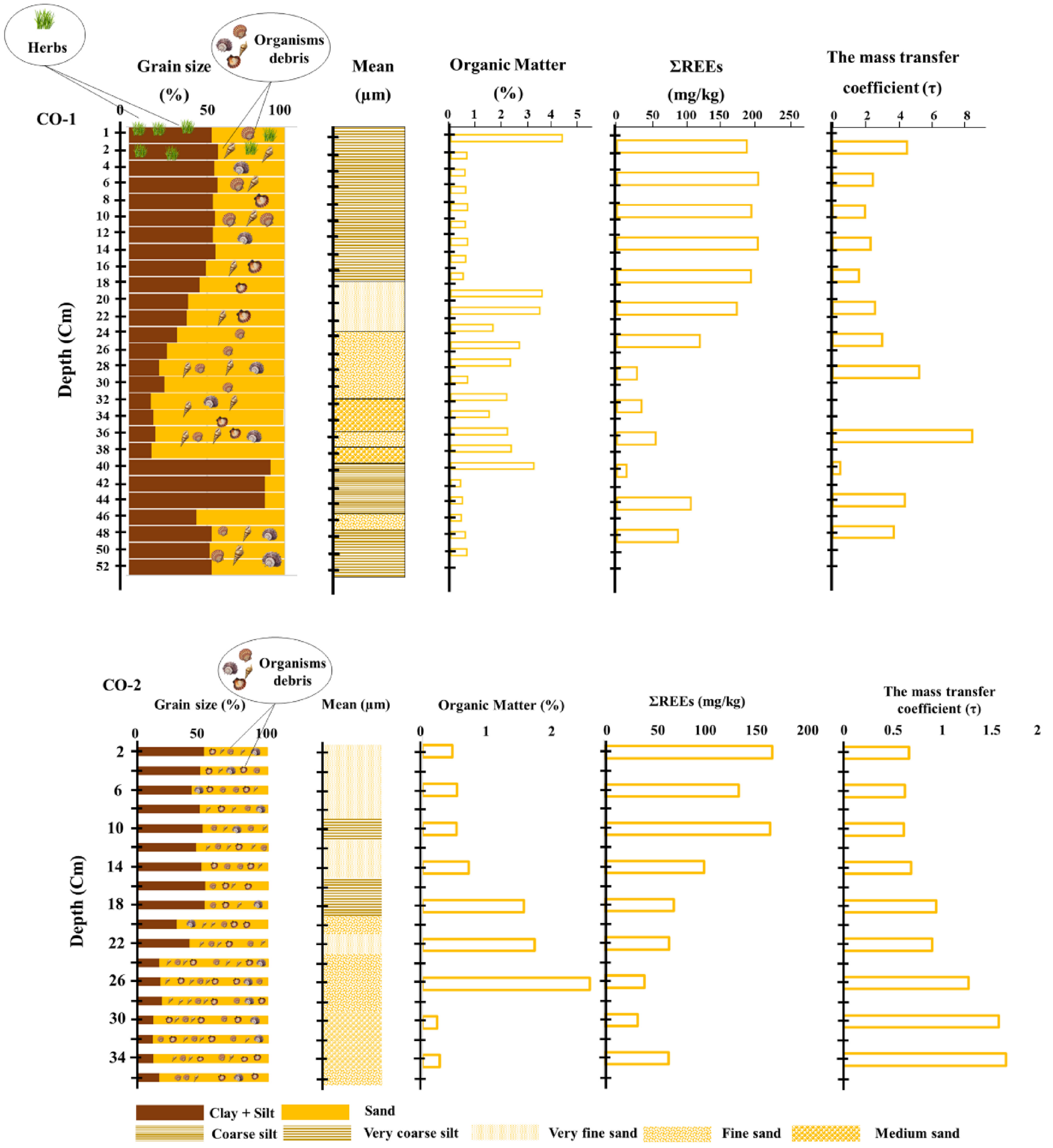


Fig. 2 Grain size distribution, mean, OM content, ΣREEs, and mass transfer coefficient (CO-1 & CO-2)

elements indicate no correlation among them ($p>0.05$). Sc, Sm, and Dy showed no significant correlations with other elements. La was significantly correlated to Nd and Tb ($p<0.01$) in CO-2. At the same time, Sm showed no correlation with all elements except Dy; also, Nd displayed no significant correlation with all elements but only with La. A highly significant correlation between Ce and Eu was noted ($p<0.01$). The similar geochemical behavior of elements during the sedimentation process is probably the cause of the significant correlation between REEs (David and Gariépy. 1987). Thorium exhibits significant correlations with REEs and Y and no correlation with Sc, Al, U, organic matter, and the sediments grain size in CO-1. In contrast, thorium shows high significant correlations ($p<0.01$) with

Table 3 Concentrations ranges of REEs, Y, Sc, Th, and U in CO-1 and CO-2 compared to the Oualidia lagoon local background[1], UCC[2], and NASC[3] values

Sediment Cores	CO-1		CO-2		LBV Oualidia[1]	UCC[2]	NASC[3]
REEs (mg/kg)	0–31 cm	31–52 cm	0–12 cm	12–36 cm			
Modified CRS Ages	2011–1980	1980–1928	2000–1949	1949–1903			
Sc	3<Sc<17.7	1.4<Sc<10.4	3.6<Sc<13.4	4.1<Sc<18	9.21	7	–
La	12.7<La<48.2	2.3<La<5.4	9.5<La<28.7	1.7<La<8.5	4.2	30	32
Ce	51.7<Ce<101.7	22.5<Ce<60	58.6<Ce<78	15.9<Ce<35	21.32	64	73
Nd	26.3<Nd<2	0.18<Nd<5.6	5.4<Nd<15	10.5<Nd<2.7	9.15	26	33
Sm	5.9<Sm<15.5	2<Sm<2.8	3.8<Sm<6.7	1.6<Sm<3.4	1.63	4,5	5,7
Eu	1.64<Eu<5.3	0.88<Eu<1.2	2.16<Eu<3.9	0.6<Eu<1.77	0.74	0,88	1,24
Y	13.6<Y<32.3	8.4<Y<16.1	7.8<Y<30.4	11.5<Y<18.8	14	20	–
Gd	13.3<Gd<96	0.6<Gd<3.1	15.9<Gd<74.1	2.7<Gd<25.9	2.7	3,8	5,2
Tb	1.6<Tb<3.6	1.6<Tb<3.6	1.4<Tb<2.85	0.1<Tb<1.56	081	0,64	0,85
Dy	0.9<Dy<8.2	Dy<1.3	1.94<Dy<4.83	0.1<Dy<2.4	0.49	3,5	5,8
Yb	2.3<Yb<9.7	1.5<Yb<2.9	2.8<Yb<5.6	0.7<Yb<2.94	1.23	2,2	3,1
Th	12.5<Th<15.7	3.2<Th<6.6	8.9<Th<9	2.4<Th<7.8	3,5	10.4	–
U	1.02<U<7.3	2.07<U<5.92	2.3<U<3	3.6<U<4.6	3,1	2.3	–

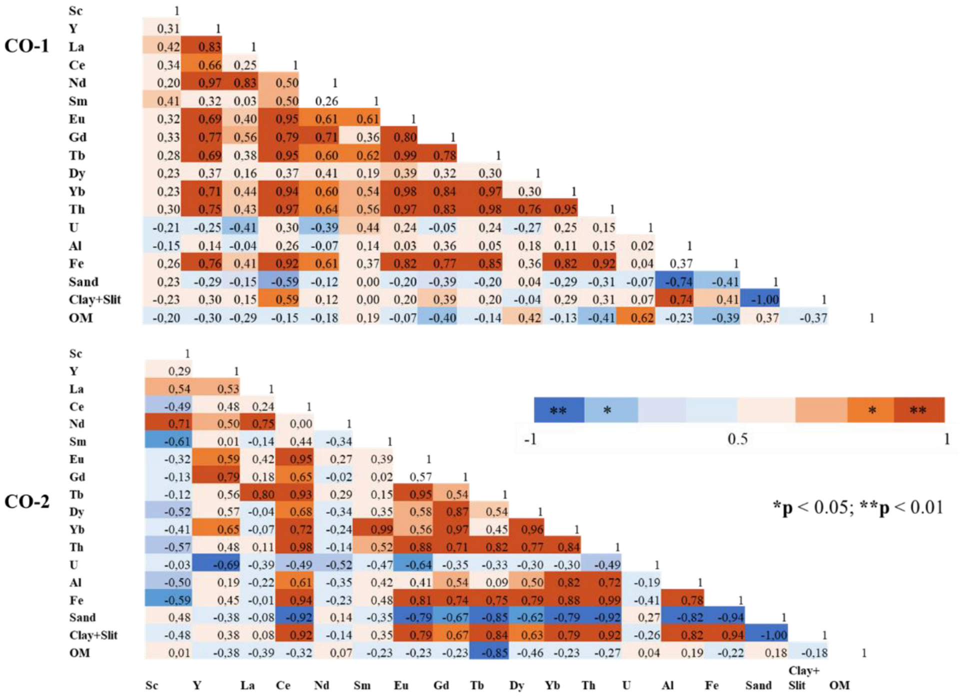
fine fraction and Al in CO-2. The significant correlation between $\sum$REEs and Th could be related to their similar behavior throughout the sedimentary processes (e.g., transport, weathering, etc.; McLennan et al. 1980). Iron and Th exhibited very high correlations in both cores. A significant correlation between Fe and REEs, mainly HREEs, indicates a preferential association of these elements with Fe (Mejjad et al. 2016). Besides, Liu et al. (2020) reported that Fe and Al-bearing oxides might be among the factors influencing the concentration of REEs in sediments. Thus, this finding suggests that Fe possibly influences the REEs distributions in our investigated samples.

Weak and no correlation between REEs and Al was observed, which is in good accordance with the mineralogical composition and granulometric distribution of sediment cores. The Oualidia lagoon sediment is mainly composed of quartz (43%<Qz<73%) (Mejjad et al. 2020), while the sand fraction along the core fluctuates between 6% and 85%, and the clay content is negligible (0.1%). Wang et al. (2014) pointed out that fine sediments with abundant clay minerals and Fe/Al/Mn comprising oxides tend to accumulate REE, while in the presence of coarse fractions, more quartz, and fewer clay minerals, this led to REEs dilution. The present results are in good line with Wang et al. (2014) finding that the change in grain size in our sediment cores is accompanied by the increase of quartz content and depletion of $\sum$REEs concentrations (Between 24 and 40 cm for CO-1 and 18–36 cm for CO-2) as shown in Fig. 3. This finding indeed implies that Al and clay minerals are not among the factors influencing the REEs concentrations, mainly in the absence of a correlation between Al and REEs and a very small amount of clay minerals.

A significant correlation was recorded between organic matter and U in CO-1, while no correlations were detected between organic matter content and other elements. Organic matter is an active geochemical agent controlling the trace elements' behavior in marine and oceanic sedimentation (Baturin 2000). Thus, the absence of correlations between OM and studied elements may indicate that organic matter does not control their distribution and geochemical behavior except uranium. It also has been reported in special investigations that during the fossilization processes of OM, this latter is converted to melanoidin-type composites capable of concentrating metals, including uranium (Manskaya and Drozdova 1964); this may explain the positive correlation between OM and U and their similar vertical distribution. No correlations were found between YREE, Sc, U, and fine fraction in CO-1; only Al shows a strong correlation with finer particles suggesting that the distribution of YREEs was not controlled by grain size or clay minerals but mainly by Fe. In CO-2, HREE, Th, Al, and Fe exhibit significant correlations with fine sediment.

Noting that in the sediment, the REE content varies with grain size because of different factors, including mechanical, physical, and chemical and sources of material (Yiyang et al. 1990; Lee et al. 2008) and that the sampling point of CO-2 sediment core known to be affected by the confinement phenomena, which impacted the sediment

Table 4 Pearson correlation matrix for YREEs, Sc, Th, U, Al, Fe % Sand, Clay + Silt, and OM content in the sediment cores from the Oualidia lagoon



CO-1	Sc	Y	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Yb	Th	U	Al	Fe	Sand	Clay+Slit	OM
Sc	1																	
Y	0,31	1																
La	0,42	0,83	1															
Ce	0,34	0,66	0,25	1														
Nd	0,20	0,97	0,83	0,50	1													
Sm	0,41	0,32	0,03	0,50	0,26	1												
Eu	0,32	0,69	0,40	0,95	0,61	0,61	1											
Gd	0,33	0,77	0,56	0,79	0,71	0,36	0,80	1										
Tb	0,28	0,69	0,38	0,95	0,60	0,62	0,99	0,78	1									
Dy	0,23	0,37	0,16	0,37	0,41	0,19	0,39	0,32	0,30	1								
Yb	0,23	0,71	0,44	0,94	0,60	0,54	0,98	0,84	0,97	0,30	1							
Th	0,30	0,75	0,43	0,97	0,64	0,56	0,97	0,83	0,98	0,76	0,95	1						
U	-0,21	-0,25	-0,41	0,30	-0,39	0,44	0,24	-0,05	0,24	-0,27	0,25	0,15	1					
Al	-0,15	0,14	-0,04	0,26	-0,07	0,14	0,03	0,36	0,05	0,18	0,11	0,15	0,02	1				
Fe	0,26	0,76	0,41	0,92	0,61	0,37	0,82	0,77	0,85	0,36	0,82	0,92	0,04	0,37	1			
Sand	0,23	-0,29	-0,15	-0,59	-0,12	0,00	-0,20	-0,39	-0,20	0,04	-0,29	-0,31	-0,07	-0,74	-0,41	1		
Clay+Slit	-0,23	0,30	0,15	0,59	0,12	0,00	0,20	0,39	0,20	-0,04	0,29	0,31	0,07	0,74	0,41	-1,00	1	
OM	-0,20	-0,30	-0,29	-0,15	-0,18	0,19	-0,07	-0,40	-0,14	0,42	-0,13	-0,41	0,62	-0,23	-0,39	0,37	-0,37	1

CO-2	Sc	Y	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Yb	Th	U	Al	Fe	Sand	Clay+Slit	OM
Sc	1																	
Y	0,29	1																
La	0,54	0,53	1															
Ce	-0,49	0,48	0,24	1														
Nd	0,71	0,50	0,75	0,00	1													
Sm	-0,61	0,01	-0,14	0,44	-0,34	1												
Eu	-0,32	0,59	0,42	0,95	0,27	0,39	1											
Gd	-0,13	0,79	0,18	0,65	-0,02	0,02	0,57	1										
Tb	-0,12	0,56	0,80	0,93	0,29	0,15	0,95	0,54	1									
Dy	-0,52	0,57	-0,04	0,68	-0,34	0,35	0,58	0,87	0,54	1								
Yb	-0,41	0,65	-0,07	0,72	-0,24	0,99	0,56	0,97	0,45	0,96	1							
Th	-0,57	0,48	0,11	0,98	-0,14	0,52	0,88	0,71	0,82	0,77	0,84	1						
U	-0,03	-0,69	-0,39	-0,49	-0,52	-0,47	-0,64	-0,35	-0,33	-0,30	-0,30	-0,49	1					
Al	-0,50	0,19	-0,22	0,61	-0,35	0,42	0,41	0,54	0,09	0,50	0,82	0,72	-0,19	1				
Fe	-0,59	0,45	-0,01	0,94	-0,23	0,48	0,81	0,74	0,75	0,79	0,88	0,99	-0,41	0,78	1			
Sand	0,48	-0,38	-0,08	-0,92	0,14	-0,35	-0,79	-0,67	-0,85	-0,62	-0,79	-0,92	0,27	-0,82	-0,94	1		
Clay+Slit	-0,48	0,38	0,08	0,92	-0,14	0,35	0,79	0,67	0,84	0,63	0,79	0,92	-0,26	0,82	0,94	-1,00	1	
OM	0,01	-0,38	-0,39	-0,32	0,07	-0,23	-0,23	-0,23	-0,85	-0,46	-0,23	-0,27	0,04	0,19	-0,22	0,18	-0,18	1

*p < 0.05; **p < 0.01

dynamics highly (Mejjad et al. 2020) and consequently the REEs accumulation and mobility.

4.3 The shale-normalized YREE pattern

The shale-normalized REE pattern is used to assess the similarity between upper continental crusts with the measured REEs in lagoon sediments and to understand the geochemistry processes in the marine environment (Rezaee et al. 2010). The shale-normalized procedure was applied for each layer of the two sediment cores. The REEs values were normalized against the average REEs concentrations of the North American Shale Composite (NASC) (Fig. 3). The shale-normalized REE pattern exhibits some variations of HREE ratios in the topmost layers of the cores, mainly Gd. The REEs ratios of the shale-normalized indicate a strong enrichment by Gd, and a slight enrichment by Sm, Eu, Tb, and Yb in the upper layers, which deplete in the deeper layers. This observed change reveals a modification of depositional conditions or variation of elements distribution over the years. Indeed, in both cores, the ratios of the shale normalized are close to slightly higher than unity for almost all REEs indicating a significant degree of mobilization of REEs to the shale along the cores in good accordance with the mass transfer coefficient calculated values (Sect. 5.1). This indicates that the rare earth elements in the Oualidia lagoon sediments may have been issued from marine and terrigenous sources (Ashraf et al. 2016).

In the deeper layers, the REEs patterns showed that the Ce anomaly is insignificant and displayed a similar geochemical behavior as La showed a flat pattern, revealing no Ce anomaly. This result indicates that the REEs concentrations measured in deeper layers were mainly delivered from the terrestrial materials (Minai and Tominaga 1989). Ce anomaly became slightly remarkable in the top layers of cores, suggesting a change of REEs origin into the Oualidia lagoon and in the factors controlling their accumulation and distribution and also noting that the Cerium vertical distribution is well correlated to the finer particles content, which was explained by the presence of important amounts of biogenic components that are depleted in Ce (Goldberg et al. 1963). A significant quantity of shell debris is observed in the deepest layers of sediment cores, which are also rich in sandy particles, and present a relatively high amount of calcite. This suggests that the coarser grain size is depleted in Ce, and fine grain size fractions are enriched in Ce in line with Wang et al. (2014) findings. Significant depletion of Dy was detected along with the two cores. Gd shows significant positive anomalies in the sediment cores' top layers, suggesting an anthropogenic origin of Gd in the Oualidia lagoon (Mejjad et al. 2022). This suggests that population growth and human activity development are

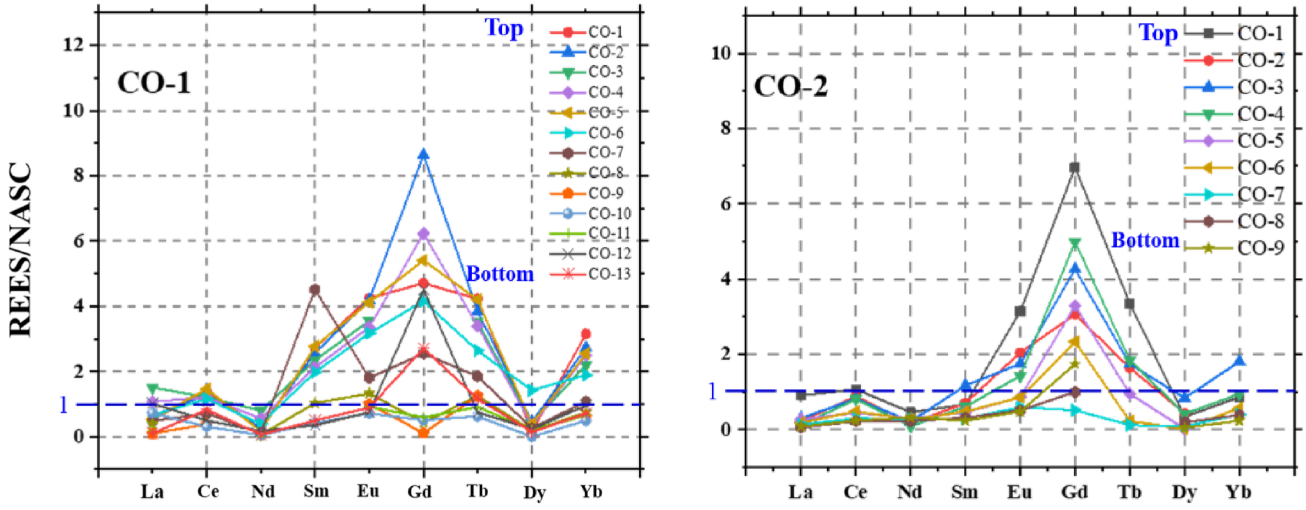


Fig. 3 Plots of NASC-normalized REE data from sediment cores (for each layer)

among the possible factors explaining the observed change in REEs concentrations during the last 60 years.

4.4 Elemental ratios, anomalies, and the total REEs

La/Yb and La/Sm ratios are used to estimate the degree of enrichment by LREEs over HREEs (Ashraf et al. 2016; Hatje et al. 2016). The values of fractionation (La/Yb) and (La/Sm) calculated for each layer of the sediment cores displayed a slight enrichment by HREEs over LREEs. The values ranged from 0.10 to 1.48 and 0.11 to 2.85 for La/Yb and La/Sm, respectively. A moderate enrichment by LREE over HREE is observed at deeper layers of cores. It has been reported by Elias et al. (2019) that in the Malaysian and Asian rivers, the higher values of La/Yb are a sign of important sedimentation rates due to terrigenous sediments delivered to the river system. The sedimentation rate (SR) in the studied lagoon is reported significant in the sampling point of CO-1 and less important in the sampling site of CO-2 (<0.2 cm year^{-1}) (Mejjad et al. 2020), explaining the lowest values of the calculated La/Yb ratios in CO-2.

The calculated La/Yb ratio along the cores is relatively low and comparable to typical values for surface waters (0.205–0.497; DeBaar et al. 1985; Zhang and Nozaki 1996) and to those found by (Elderfield and Sholkovitz 1987) in marine sediments (0.5 and 1) and less high than those calculated for the sediment of Linggi River, Malaysia (7.72–27.7; Elias et al. 2019).

Except for the top layers of CO-1, the Th/Sc ratios exhibited values close to the Shale [Post Archean Australian Shale (PAAS), 0.92], to the Upper Continental Crust (UCC, 0.75) and North American Shale Composite (NASC, 0.83), indicating a natural origin of these elements. According to Nyakairu and Koeberl (2001), the immobility of Th/Sc during the sedimentary processes (weathering, transport, and diagenesis) made it a useful tool for determining the provenance, which may point out that the Oualidia lagoon has known a change of the origin of sediment delivery into the lagoon.

The total LREEs concentrations were higher than ΣHREEs values, while the ratios of the total content of LREEs/HREEs indicate a slight enrichment by LREEs over HREEs. The ratios of ΣLREEs/ΣHREEs ranged from 1.58 to 4.05, which indicated that LREE concentrations are enriched, about two times higher over HREE. This may occur due to the high absorption of LREEs onto a finer fraction of sediments (clay and silt) (Badassan et al. 2020), mainly because LREEs present a lower ionic radius than HREEs (Kumar et al. 2014). In addition, mechanical and physical factors such as the dynamics of fluid, the coastal mixing process, and sediment transportation could cause the enrichment of LREE over HREE (Rezaee et al. 2010). Generally, LREE was the significant concentration contributing to ΣREE in the Oualidia lagoon sediment, mainly Ce with maximum and minimum values of 101.7 and 15.9, respectively, followed by Nd with a maximum value of 26.3 (n=22 sediment layers, both cores).

In both cores, the ΣHREEs evolution displayed a depletion of their values with depth, while the highest values are recorded in the top layers of the sediment cores. Generally, the highest values were slightly close to those of PAAS and higher than UCC and NASC (Haskin et al. 1968). The found values in the bottom of sediment columns were less important than UCC, NASC, and PAAS values suggesting that in the last decades, new sources have been feeding the lagoon by YREEs since the enrichment by REEs has become more significant during the period extending from 1980 to 2000.

The U/Th ratio was widely used as an indicator of redox conditions of the depositional environment of sediments (Vosoughi Moradi et al. 2016). According to Jones and Manning in 1994, ratios superior to 1.25 indicate anoxic conditions, while ratios lesser than 0.75 suggest an oxic environment. The U/Th ratios ranged from 0.07 to1.24, suggesting oxidative conditions, in good agreement with our previously calculated ratios of V/Cr and V/(V + Ni) as an indicator of redox conditions (Mejjad et al. 2018).

The cerium anomaly (Ce_{an}) is widely used to establish the origin of sedimentary deposition (Oliveira 2003; Kumar 2014). Ce_{an} was calculated to define the origin of the Oualidia lagoon sediments. The calculated values show significant positive anomalies in the sediments column, which fluctuates between 0.61 and 9.55. The positive anomaly occurs as a consequence of a change in redox conditions in the water column (Dorval et al. 2005; Orani et al. 2019) because of the submarine weathering process and detrital input (Armstrong-Altrin et al. 2003; Madhavaraju et al. 2010), diagenesis (Armstrong-Altrin et al. 2003) and scavenging process (Masuzawa and Koyama 1989). Another study has reported that the change in the valence state of Ce(III) to Ce(IV) led to the precipitation of cerium, which could explain the higher calculated anomalies of cerium in sediment cores (Hatje et al. 2016). The increase of terrigenous influences increases Ce/Ce* values (Murray et al. 1991); the study area is currently under the terrigenous influences (Zourarah 2007; Mejjad et al. 2018), which explains the fluctuation of Ce_{an} along the sediment column.

The Ce_{an} values recorded in the bottom layers of CO-1 and CO-2 were close to those found in the Oualidia lagoon by Mejjad et al. (2016). It should be highlighted that the studied sediment core by Mejjad et al. (2016) was collected from the bed channel where the marine influences are strong, and the core was almost sandy (more than 87% of coarse sediment), which is consequently depleted in Ce. The significant correlation between Ce and Fe (Table 3) indicates that the distribution of Ce in the Oualidia lagoon sediments is mainly controlled by Fe–Mn oxyhydroxides. Besides, the occurrence of a positive anomaly of Ce is linked to the presence of Fe–Mn oxyhydroxides and enrichment of Ce over its neighbors (Piper 1974; Pattan et al. 2005), which is in good accordance with the obtained results. Accordingly, the change in Ce_{an} in the last decades reflects the change in sediment provenance resulting in an increase of detrital material input into the lagoon and a decrease in marine influences. Indeed, sediments with distinct source areas do not show substantially different Ce anomalies (Cruz et al. 2021a, b); in this sense, the fluctuations of Ce_{an} along the sediment cores may reflect mixed provenances (Table 5).

Slight and moderate positive europium anomalies (Eu_{an}) are recorded along with the sediment cores. The positive Eu_{an} occurs in the presence of detrital feldspar (Murray et al. 1991; Ramesh et al. 2000), the occurrence of strong reducing conditions (McLennan 1989), or if the study area is affected by hydrothermal or aeolian input (Elderfield 1988). Since the cores are under oxidative depositional conditions, as verified by using the U/Th ratio, and no hydrothermal influence characterized the study area, the positive Eu anomalies recorded in our sediment cores could be due to aeolian input or the presence of detrital feldspar. A significant percentage of feldspar and plagioclase was

Table 5 The elemental ratios, anomalies, and the total REEs

Depth (cm)	∑YREE	∑LREE	∑HREE	ΣLREE/ΣHREE	Ce/Ce*	Eu/Eu*	La/Yb	La/Sm	Th/Sc	U/Th	Ages
CO-1											
2	204.08	147.77	56.30	2.62	3.13	1.32	0.17	0.20	4.12	0.57	2011
9	220.50	143.58	76.91	1.86	0.95	1.30	0.68	0.64	0.98	0.07	2003
17	225.21	180.64	44.56	4.05	3.50	1.27	0.21	0.19	1.07	0.36	1995
25	232.8	157.20	75.67	2.07	1.94	0.50	0.45	0.11	0.39	0.72	1986
37	211.12	150.34	60.77	2.47	0.61	1.45	1.48	1.73	0.43	1.24	1955
45	192.20	133.71	58.48	2.28	0.68	1.54	1.06	2.85	0.48	0.43	1938
49	132.55	99.27	33.28	2.98	9.55	1.24	0.14	0.20	1.94	0.35	1932
CO-2											
2	200.52	129.42	71.1	1.82	1.47	2.17	0.8	1.14	0.68	0.26	2000
10	127.10	84.80	42.3	2.00	3.09	1.40	0.12	0.21	0.87	0.34	1959
14	114.41	70.11	44.3	1.58	7.97	1.52	0.09	0.16	1.88	0.76	1932
18	83.79	52.92	30.9	1.71	2.35	2.42	0.23	0.31	0.37	0.70	–
22	55.51	37.04	18.5	2.01	1.58	2.85	0.25	0.39	0.38	1.08	–
26	200.52	129.42	71.1	1.82	1.47	2.17	0.8	1.14	0.68	0.26	–

recorded in the deepest sediment cores, explaining the Eu enrichment in the studied sediments (Mejjad et al. 2020). However, Eu anomaly is often used as a representative of sediment weathering; a high negative Eu_{an} means extensive weathering of rocks, and a positive anomaly indicates moderate weathering (Sholkovitz 1988). The sediment core CO-2 presents significant positive anomalies (1.40–2.85) compared to CO-1 (0.50–1.54); CO-2 is retrieved from the upstream part of the lagoon where the weathering process is less important than the downstream part (Taghia et al. 2014). This suggests that the weathering process is more extensive in the downstream part compared to the upstream.

Besides, the increase in temperature could also lead to the enhancement of sediment resuspension and, consequently, to the occurrence of positive Eu_{an} (Zhu et al. 2017). The obtained ages characterized by higher Eu_{an} values are well correlated to dry seasons that occurred in Morocco in 1942, 1961, and 2000 (Ben Sari 2004).

5 Conclusion

The concentrations of rare earth elements have shown two different evolution trends over time. The granulometric composition and the distribution of YREEs revealed changes in sediment provenances where the depositional environment has become more open to terrigenous influences with a recent enrichment by detrital material.

The elementary analysis combined with mineralogical composition shows that Al and clay minerals are not among the factors influencing the REEs concentrations. The Ce_{an} in the last decades has shown variation, which reflects a change in sediment provenance resulting in an increase of detrital material input into the lagoon and a decrease in marine influences.

In this sense, the lagoon has known in the last decades an unexpected change due to a modification of factors controlling their distribution. Indeed, the granulometric and mineralogical composition associated with the distribution of YREEs and Ce_{an} revealed that the depositional environment has become more open to terrigenous influences with a recent enrichment by detrital material. The variation of depth profiles of YREEs, Sc, Th, and U concentrations was well correlated to the development of human activities in this area, suggesting that an important portion of these elements is derived from no crustal material. The discharge of wastes issued from human activities is likely to cause enrichment in REEs. Generally, the Oualidia lagoon is progressively exposed to ongoing changes with prospected sensitivity to some possible impacts.

This study provides baseline data of occurring changes in REEs geochemical composition over time and constitutes a typical study case to understand the link between sedimentary and geochemistry processes in a lagoonal ecosystem which provides an important dataset for future investigations in this region.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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