Redox processes in estuary: Rare earth element as a proxy

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Estuary represents a transition zone at the land-sea interface, and is characterized by strong geochemical gradient due to the mixing of fresh river and saline ocean water. Riverine inputs such as nutrients, organic matter and metals have undergone significant biogeochemical alteration in the estuary before getting discharged into the ocean. Redox reactions are one of the key alteration processes which ultimately determine the fate of these species and their cycling. Seasonal changes in discharge and tidal cycle modify the supply of organic matter, dissolved O_2 and availability of electron acceptors that leads to a change in redox environment. Therefore, evaluating the redox condition becomes vital for understanding the behavior of elements in the estuary. This study aims to provide insights into the use of rare earth elements (REE) as a proxy for understanding the redox condition in part of the Mahanadi estuary, east coast of India. Among the REE, europium (Eu) is highly sensitive to redox environment, and undergo fractionation under oxidized and reduced conditions. In this study, contrasting Eu-anomaly in the bottom sediment from the upper and lower estuary has been observed. Upper estuary sediments are characterized by negative Eu-anomalies (0.75±0.26) which represent the source rock i.e., the Eastern Ghat Group of rocks. However, the lower estuary sediments show positive Eu-anomalies (1.92±0.62). Under reduced condition, Eu^{3+} is converted to insoluble Eu^{2+}, which can lead to Eu-enrichment in the sediment resulting in a positive Eu-anomaly. The reducing environment in the lower estuary has been resulted due to the presence of dense mangrove forest. To further confirm the idea of a reducing condition in the lower estuary, the relationship between Eu-anomaly and Mn, another redox sensitive element, is evaluated. Under reducing condition, insoluble Mn^{4+} reduces to Mn^{2+}, which is soluble. Thus, Mn^{2+} is released from sediment into the water column, and causes depletion in Mn content. A significant negative correlation between Eu anomaly and Mn in the estuarine sediment is observed which further supports the idea of prevailing reducing condition in the lower estuary. This unique contrast in Eu-anomaly between upper and lower

estuarine sediment in response to the redox condition has not yet been reported in any global estuary.

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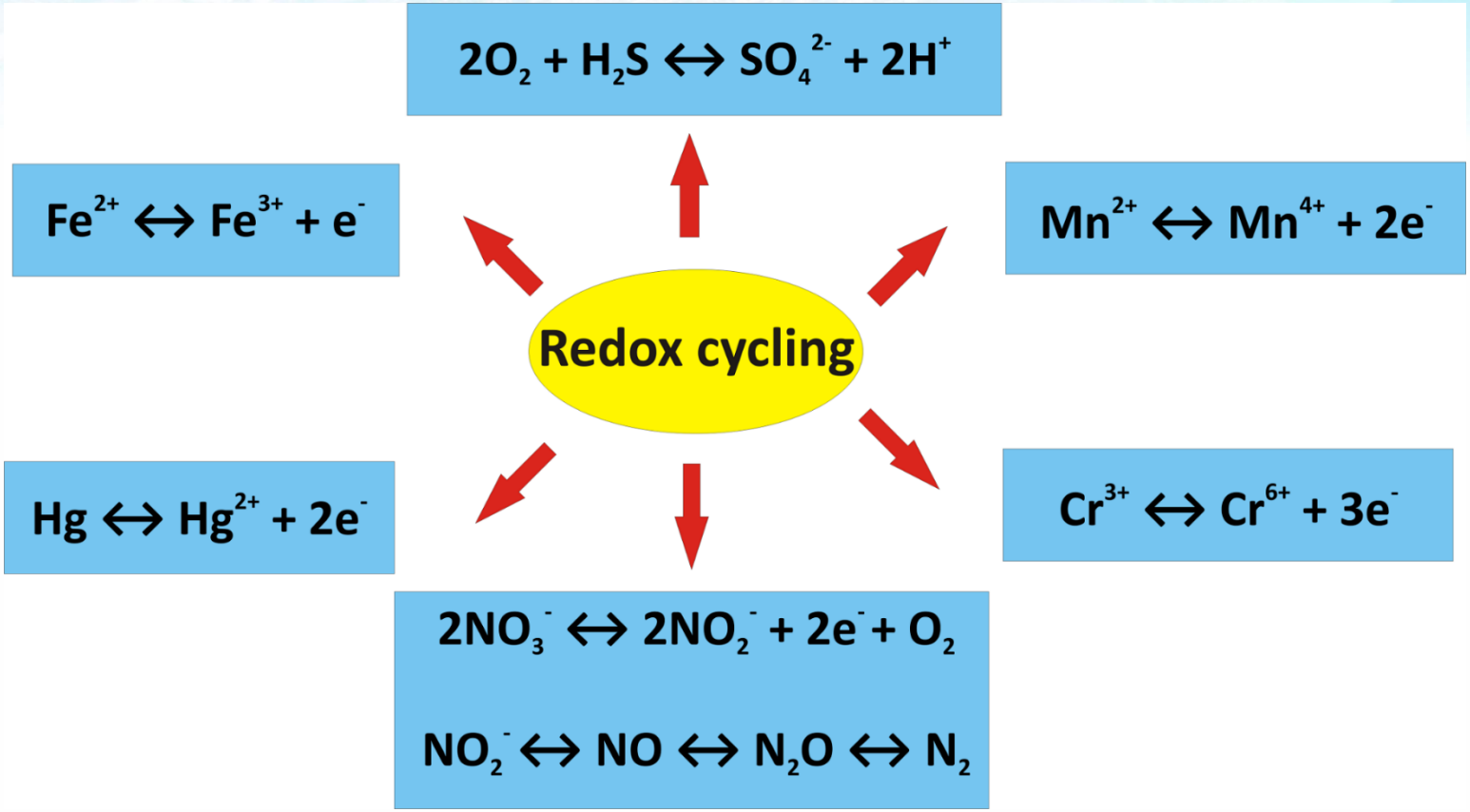
Introduction

- Estuaries are transition zone formed by the mixing of fresh river and saline ocean water.
- Fluvial inputs (organic matter, nutrients and metals) get altered by several biogeochemical processes.
- Among them redox process plays an important role in altering these species.
- Rare earth elements (REE) consisting of 14 elements (La to Lu) typically exhibit +3 oxidation state. Among these, Eu and Ce also exist in the +2 and +4 states respectively.
- This makes Eu and Ce to act as powerful redox proxies.


$2O_2 + H_2S \leftrightarrow SO_4^{2-} + 2H^+$
$Fe^{2+} \leftrightarrow Fe^{3+} + e^-$
$Mn^{2+} \leftrightarrow Mn^{4+} + 2e^-$
Redox cycling
$Hg \leftrightarrow Hg^{2+} + 2e^-$
$Cr^{3+} \leftrightarrow Cr^{6+} + 3e^-$
$2NO_3^- \leftrightarrow 2NO_2^- + 2e^- + O_2$
$NO_2^- \leftrightarrow NO \leftrightarrow N_2O \leftrightarrow N_2$

Study Area

- The Devi river estuary, located in the east coast of India, is formed by one of the distributaries of the perennial Mahanadi river near Nuagarh, Odisha.

- This mangrove dominated micro-meso tidal estuary provides an ideal environment for evaluating the REEs as proxy of redox condition.

Methodology

- Composite surface sediment samples were collected along the salinity gradient in May 2018.
- Salinity was measured in-situ at corresponding locations using HORIBA multi-parameter instrument.
- Concentration of REE were determined using an ICP-MS after digestion of samples using a hot block digestion system

$$\text{Eu anomaly} = \frac{2 \times \text{Eu}_n}{(\text{Sm}_n + \text{Gd}_n)}$$

$$\text{Ce anomaly} = \frac{2 \times \text{Ce}_n}{(\text{La}_n + \text{Pr}_n)}$$

Results and Discussion

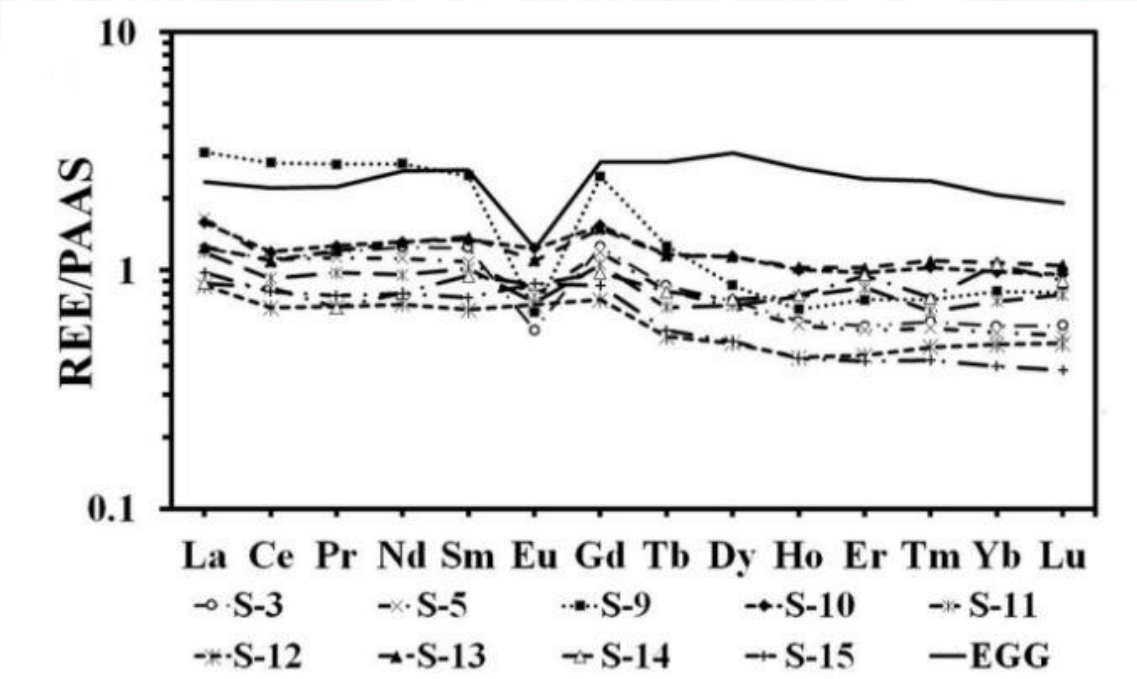
- Total REE (ΣREE) concentration: 30.37 to 497.82 mg/kg (153.8±120.3 mg/kg).

- Light REE (LREE) has higher average concentration (141.87±114.37 mg/kg) compared to the heavy REE (HREE; 11.93±7.00 mg/kg).

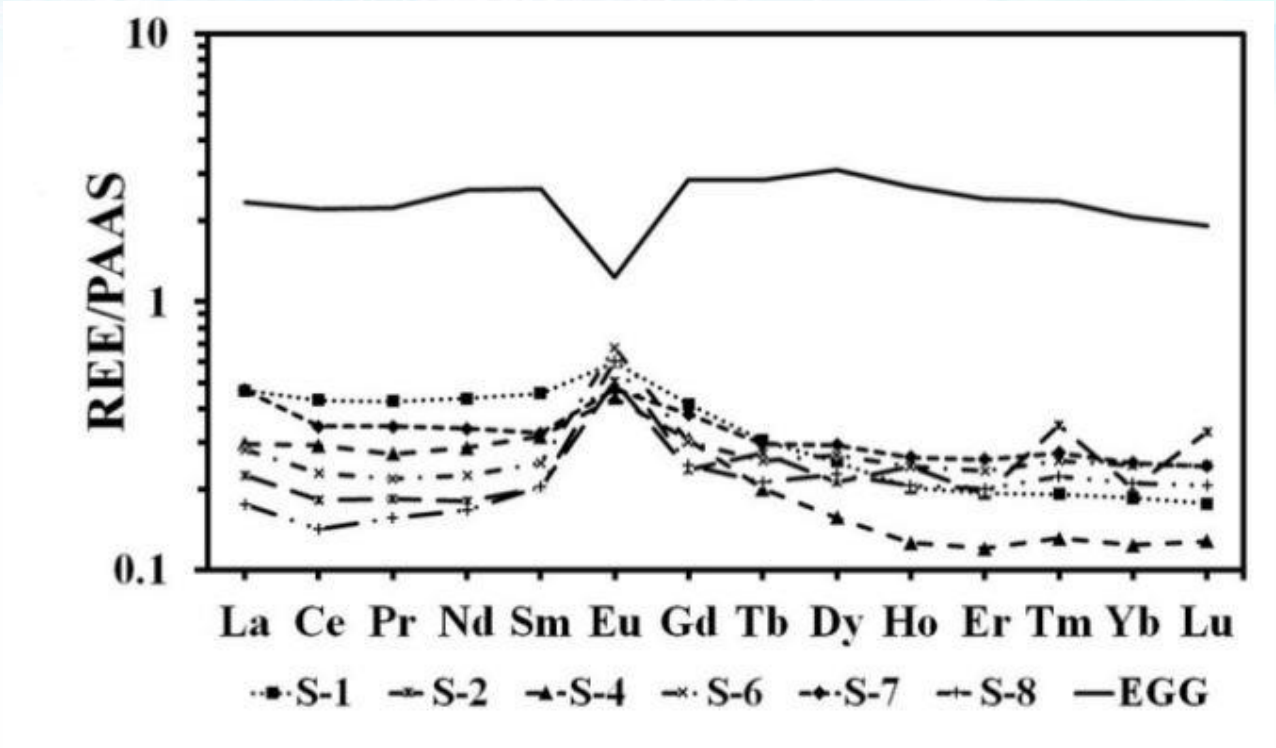
- The average LREE/HREE in the estuarine sediment is 11.16 ± 3.68. This LREE enrichment is characteristic of the Eastern Ghat Group of rocks which is the major catchment lithology of the Mahanadi river.

- The $(La/Yb)_n$ and $(Tb/Yb)_n$ are in the range of 0.83–3.84 (1.88 ± 0.86) and 0.77–1.65 (1.25 ± 0.27), respectively. These values are similar to the Eastern Ghat Group of rocks i.e., $(La/Yb)_n$ = 2.46 and $(Tb/Yb)_n$ = 1.25 (Sarkar et al., 2015).

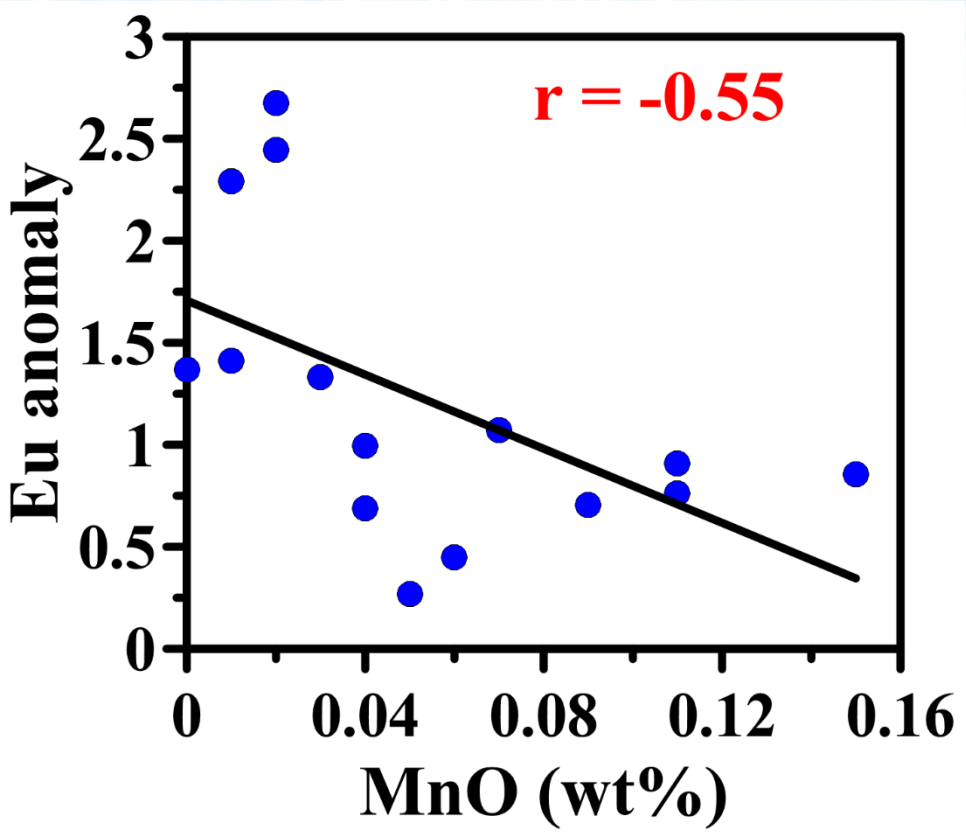
REE patterns in upper estuary sediments

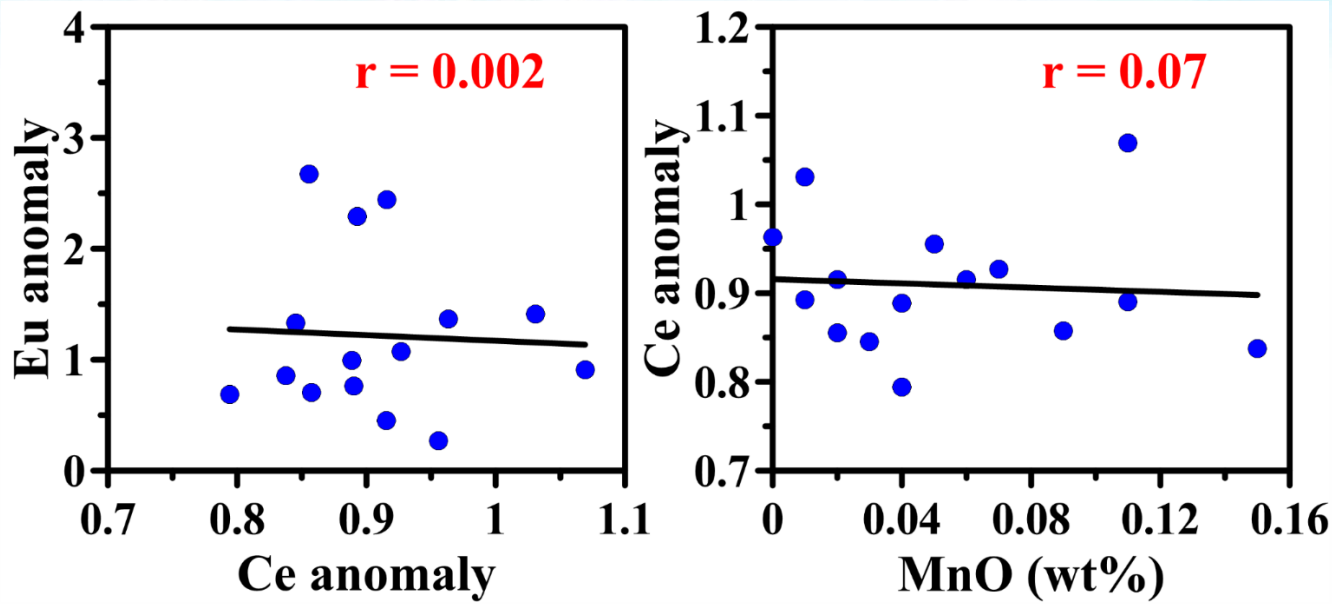


REE patterns in lower estuary sediments



Akhtar et al (2022), Chemosphere, vol. 297, 134195


r = -0.55
Eu anomaly
MnO (wt%)
0
0.5
1
1.5
2
2.5
3
0
0.04
0.08
0.12
0.16


r = 0.002
Eu anomaly
Ce anomaly
0
1
2
3
4
0.7
0.8
0.9
1
1.1
r = 0.07
Ce anomaly
MnO (wt%)
0.7
0.8
0.9
1
1.1
1.2
0
0.04
0.08
0.12
0.16

Summary

- Among REE, Eu- and Ce-anomalies are common indicator of oxidation-reduction processes.
- In this study Eu anomaly acts as an important proxy for reducing environment.
- The coupling of Eu- and Ce-anomaly cannot be generalized for understanding the redox condition.
- Source rocks play a decisive role in governing both Eu and Ce anomalies rather than redox mechanism in upper estuary.
- Contrasting Eu anomalies between upper- and lower-estuarine sediments are uncharacteristic of previously studied major global estuaries.

References

Sarkar, T., Schenk, V. and Berndt, J., 2015. Formation and evolution of a Proterozoic magmatic arc: geochemical and geochronological constraints from meta-igneous rocks of the Ongole domain, Eastern Ghats Belt, India. *Contributions to Mineralogy and Petrology*, *169*(1), pp.1-27.

Questions?

Thank You!