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Continental shelves as potential resource of rare earth elements

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Abstract The results of this study allow the reassessment of the rare earth elements (REE) external cycle. Indeed, the river input to the oceans has relatively flat REE patterns without cerium (Ce) anomalies, whereas oceanic REE patterns exhibit strong negative Ce anomalies and heavy REE enrichment. Indeed, the processes at the origin of seawater REE patterns are commonly thought to occur within the ocean masses themselves. However, the results from the present study illustrate that seawater-like REE patterns already occur in the truly dissolved pool of river input. This leads us to favor a partial or complete removal of the colloidal REE pool during estuarine mixing by coagulation, as previously shown for dissolved humic acids and iron. In this latter case, REE fractionation occurs because colloidal and truly dissolved pools have different REE patterns. Thus, the REE patterns of seawater could be the combination of both intra-oceanic and riverine processes. In this study, we show that the Atlantic continental shelves could be considered potential REE traps, suggesting further that shelf sediments could potentially become a resource for REE, similar to metalliferous deep sea sediments.

Introduction Rare earth elements (REE) have received considerable attention in the past ten years, in part as a result of the tightening of export quotas from the monopolistic Chinese producers which has recently sparked a wave of speculation on REE prices, as observed in 2011. Nowadays, REE are still considered critical because they are a key component of the transition towards a competitive and low-carbon energy economy¹⁻³. Thus they are essential in a wide variety of applications such as direct drive wind turbines, electric and hybrid vehicles, low-energy lighting^{4,5}. With a demand for REE thought to be growing at a rate of approximately 5 –10% per year⁶, alternative primary and secondary REE supply sources must be found. However, even if recycling of scrap consumer electronics and technical industrial components will increasingly contribute to the REE supply in the near future⁷, it will not be able to meet the increasing demand⁸. Thus mining of natural primary deposits is expected to remain as the major source of REE⁹. However, efforts must be made on the exploration of new REE enriched deposits with low environmental impact. In this respect, high concentrations of REE have been reported from deep-ocean manganese nodules^{10,11}, iron-manganese crusts^{10,12} and deep-sea muds of the Pacific Ocean floor¹³, which are being studied in detail for their economic potential. Oceans are often considered as being in a chemical steady state, thus displaying an elemental balance maintained by input/output rates. River inputs are well constrained¹⁴ and the behavior of REE during mixing of river and sea water is well studied¹⁵⁻¹⁷. However, as discussed by Rasmussen et al.¹⁸ and Lacan & Jeandel¹⁹ the amount of REE delivered to the coastal shelves and oceans must be significantly larger than previously estimated. In this context, the REE organic pool should be further considered. We report here a potential resource for REE with a focus on Atlantic continental shelves and especially actual and paleo-alluvial fan deposits.

Methods Historically, the REE have been used to trace mass transfers during geological processes occurring both in the Earth's interior and on the surface²⁰. As a matter of fact, these elements have been typically divided into light REE (LREE; La-Nd), middle REE (MREE; Sm-

Tb) and heavy REE (HREE; Dy-Lu) due to their contrasting geochemical behaviour. Their extremely low concentrations in nature imply that they can passively record mass transfers with little perturbation from thermodynamic interactions²⁰. For this reason, we consider below that the transfer of stream water to the oceans leads to estuaries where mixtures of organic and inorganic phases are separated. Thus, about 90% of REE are removed from the solution by flocculation of colloidal material (from 86% for Lu to 95% for La)²¹. Inorganic REE remaining in solution can be also fractionated when coming into contact with highly reactive particles (such as ferromanganese particles), however this proportion is minimal (only 1% of REE compared to a withdrawal of 90% by colloidal flocculation). Thus, the REE patterns of the oceans appear to reflect those of the inorganic river water fraction²². Such information is therefore unknown, and only apparent when the inorganic and colloidal organic phases are separated, for example, during estuarine mixing. The low-temperature aqueous REE behavior was investigated by focusing on available REE concentration data in selected studies on the (i) Dordogne river²³, Dordogne, Garonne rivers and Gironde estuary²⁴ (ii) Congo river²⁵ and estuary (unpublished results from Germain Bayon), (iii) Amazon river²⁶ and estuary²⁷, (iv) organic fraction from estuaries sediments²⁸ and (v) Ordovician organic rich grey monazites²⁹. The Amazon and Congo rivers were selected as they are the two majors systems flowing into the Atlantic ocean. The Dordogne river was chosen to highlight the behavior of a smaller river system.

Results and discussion For the three main rivers flowing into the Atlantic ocean (i.e., Amazon, Congo and Dordogne rivers; Figure 1), it can be observed that the REE patterns of upstream samples (Figure 1a) depict low REE concentration and a negative cerium (Ce) anomaly, whereas more organic samples downstream (Figure 1a, b, c) display higher REE concentrations (> one order of magnitude) and middle REE enriched patterns with no Ce anomaly. This corresponds to an organic sedimentary input (with for example up to 15-20 mg/L of dissolved

organic carbon in the Dordogne river²³). It can also be observed that in the Amazon estuary (Figure 1d), the REE become progressively less concentrated (up 2-3 orders of magnitude) as the salinity increases. In addition, MREE patterns evolve to more HREE enriched patterns with a gradual development of a negative Ce anomaly. Similar MREE patterns are also found in the organic fractions from sediments of the different estuaries (Figure 1e) and are further observed in organic rich grey monazites (Figure 1f), as previously observed on humic substances³⁰.

Figure 1 Upper continental crust (UCC)-normalized REE patterns in samples from (a) Dordogne River basin²³, (b) Congo River basin²⁵, (c) Amazon River basin²⁶, (d) Amazon River estuary²⁷, (e) Congo River estuary (unpublished results from Germain Bayon) and Dordogne, Garonne Rivers and Gironde estuary²⁴, (f) African continental slope and foothill sediments³¹, Amazon estuary sediments³² and Gironde estuary sediments³³, (g) organic fraction from estuaries sediments²⁸ and (h) Ordovician organic rich grey monazites²⁹. UCC values are from McLennan³⁴.

Figure 2 Sketch illustrating the REE external cycle and summarizing the processes responsible for REE fractionation from river water to organic sediments. UCC-normalized REE patterns are detailed in Figure 1, and Atlantic seawater is from Freslon et al.²⁸. UCC-normalized patterns for (a) river water, (b) river, estuarine and seawater, and (c) sedimentary organic matter and authigenic monazites.

Results highlighted in this short communication thus allow reassessing the REE external cycle (Figure 2). The river input to the oceans has relatively flat REE patterns without a Ce anomaly, whereas oceanic REE patterns exhibit strong negative Ce anomalies and HREE enrichment. Indeed, the processes at the origin of seawater REE patterns are commonly thought

to occur within the ocean masses themselves. However, the results highlighted in this short communication show that seawater-like REE patterns originate in the dissolved pool of river input (i.e., uphill watershed). Therefore, a partial or complete removal of the colloidal REE pool during estuarine mixing by coagulation is expected, as previously shown for dissolved organic matter (DOM) and iron³⁵. Indeed, Rousseau et al.²⁷ and Osborne et al.³⁶ illustrated that Amazon and Orinoco Rivers REE patterns lose their typical MREE enrichments. They associate this fractionation to colloid coagulation. These MREE patterns gradually evolves towards HREE-enriched patterns that are more similar to Atlantic Ocean water¹⁷. REE fractionation occurs because colloidal and truly dissolved pools have different REE patterns. Thus, REE patterns of seawater could be the combination of both intra-oceanic and riverine processes.

Merschel et al.³⁷ show that estuarine processes may affect the flux of DOM, Fe and REE into the ocean via salt-induced coagulation and subsequent removal of river-borne nanoparticles and colloids. In the near shore environment, DOM, Fe and REE are removed, at different rates, along the increasing salinity gradient of estuaries and shelves^{27,36,38}. The seawater REE signature could be inherited from river water³⁹. Commonly, REE signatures of ocean water are usually considered to reflect (i) the respective REE inputs from rivers, aeolian transport, hydrothermal vents and dissolution of marine carbonates and (ii) interactions with the biogeochemical cycles, involving REE-removal from surface waters by adsorption onto settling Fe-Mn particles. The strong Ce depletion and the HREE-enrichment of ocean waters are commonly attributed to the redox chemistry of Ce and to the high stability constants of HREE carbonate complexes. Nevertheless, different processes may lead to REE and/or Ce removal from solution. The most often discussed hypothesis is the occurrence of REE fractionation during estuarine mixing, enhanced by sorption on particles with extremely high surface reactivity rather than active microbial uptake, yet the exact nature of these particles (e.g., containing hydrous manganese oxide) is uncertain⁴⁰.

In this context, the Atlantic continental shelves could be considered potential REE traps and shelf sediments would, similar to metalliferous deep sea sediments¹³, represent a potential REE resource.. This latter hypothesis is illustrated by recent results from Freslon et al.²⁸ and Rousseau et al.²⁷. Indeed, by analyzing various fractions (detrital, Fe-Mn oxides, organic compounds) of sediments deposited in river estuaries, they proposed that organic matter is a major REE scavenger and possibly plays an important role in the oceanic REE budget (i.e., through direct scavenging and remineralization within the water column, up to 14% for the Congo Basin²⁸). Although high REE contents may be found in selected organic components, studies of bulk sediment in continental shelf areas reveal a high content of detrital silicate material which is known to act as a diluting agent^{13,31,41}, lowering final total REE concentrations (up to one order of magnitude for Congo margin, Figure 1f).

Eventually, based on calculation proposed by Chabaux et al.⁴², Nd flux is equal to >1 t/year in the Garonne system, which is low, compared to other major river systems, such as the Amazon main stream and its major tributaries surrounded by many floodplains that have a maximum Nd flux equal to >1000 t/year (during high-water season), constituting 30% of the river flux to the Atlantic Ocean^{39,43}. As a consequence, one can estimate a total REE input of more than 2600 t/year for the Amazon system, divided as follows: 1940 t/year of LREE, 365 t/year of MREE and 312 t/year of HREE (Table 1). The most important fluxes are the ones observed during the high water seasons (Table 1). Eastern and Western Atlantic continental shelves should thus be considered as exploration targets with a high REE potential, especially the Amazon, Orinoco and Congo estuaries. Eventually one must also consider the onshore palaeo-sedimentary-platforms in which distal clays were deposited in a reducing marine environment with organic carbon and phosphate anomalies in the same setting^{18,44}. Such a sedimentary depositional environment should be of great interest to explore for REE especially if deep diagenesis to very low grade metamorphism conditions occurred, favoring rhabdophane

(hexagonal $[\text{L-MREE}]\text{PO}_4 \cdot \text{H}_2\text{O}$) and then monazite (monoclinic $[\text{L-MREE}]\text{PO}_4$) crystallization²⁹. However, such sedimentary depositional environment could not directly be compared to Pacific deep sea muds¹³; Indeed, another possible REE source that has not previously been considered into budget is the weathering of volcanic materials⁴⁵.

	t/year Nd	t/year LREE	t/year MREE	t/year HREE
Amazon (annual ^a)	549.2	1940.4	365.4	311.9
Amazon min (low-water stage ^b)	158.1	553.1	137.6	106.9
Amazon max (high-water stage ^c)	1215.0	4457.0	716.1	602.2
Congo max (high-water stage ^c)	431.6	1733.6	177.4	153.9
Gironde & Dordogne (annual ^a)	1.2	5.3	0.6	0.3

Table 1. Assessment of Nd, LREE, MREE and HREE inputs to the Atlantic seabed sediments supported by the calculated percent removals of Sholkovitz²¹ using data from Barroux et al.⁴³, Dupré et al.²⁵, Gaillardet et al.⁴⁶, and Martin et al.²⁴. ^a corresponds to average annual REE fluxes with respect to average annual discharge. ^b corresponds to a one-year linear extrapolation considering the minimum REE input/discharge recorded during the low-water stage. ^c corresponds to a linear extrapolation for one-year considering the maximum REE input/discharge recorded during the high-water stage.

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Author Contributions

O.P. and J.T. co-wrote the paper.

Competing financial interests

The authors declare no competing financial interests.

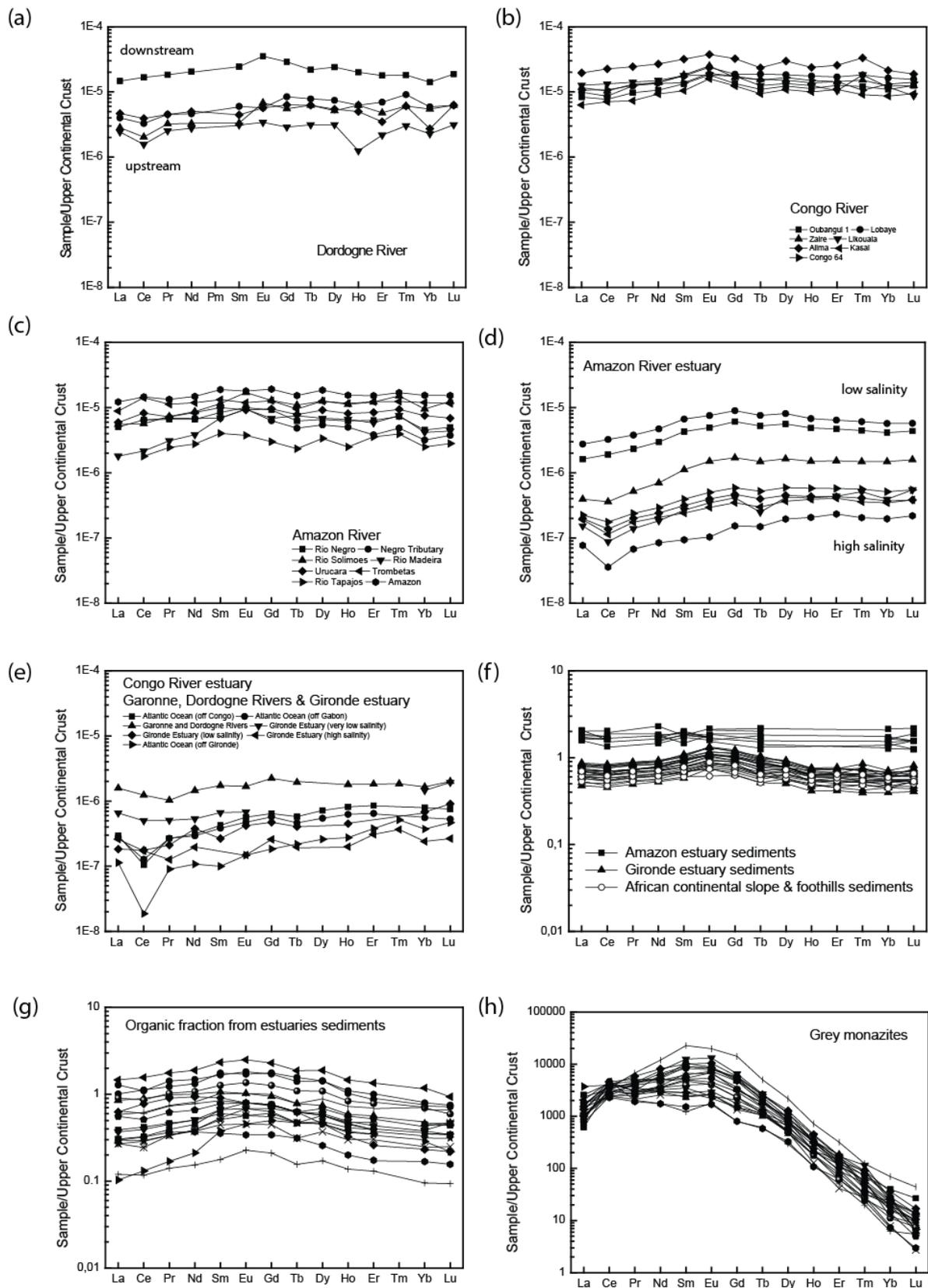


Figure 1

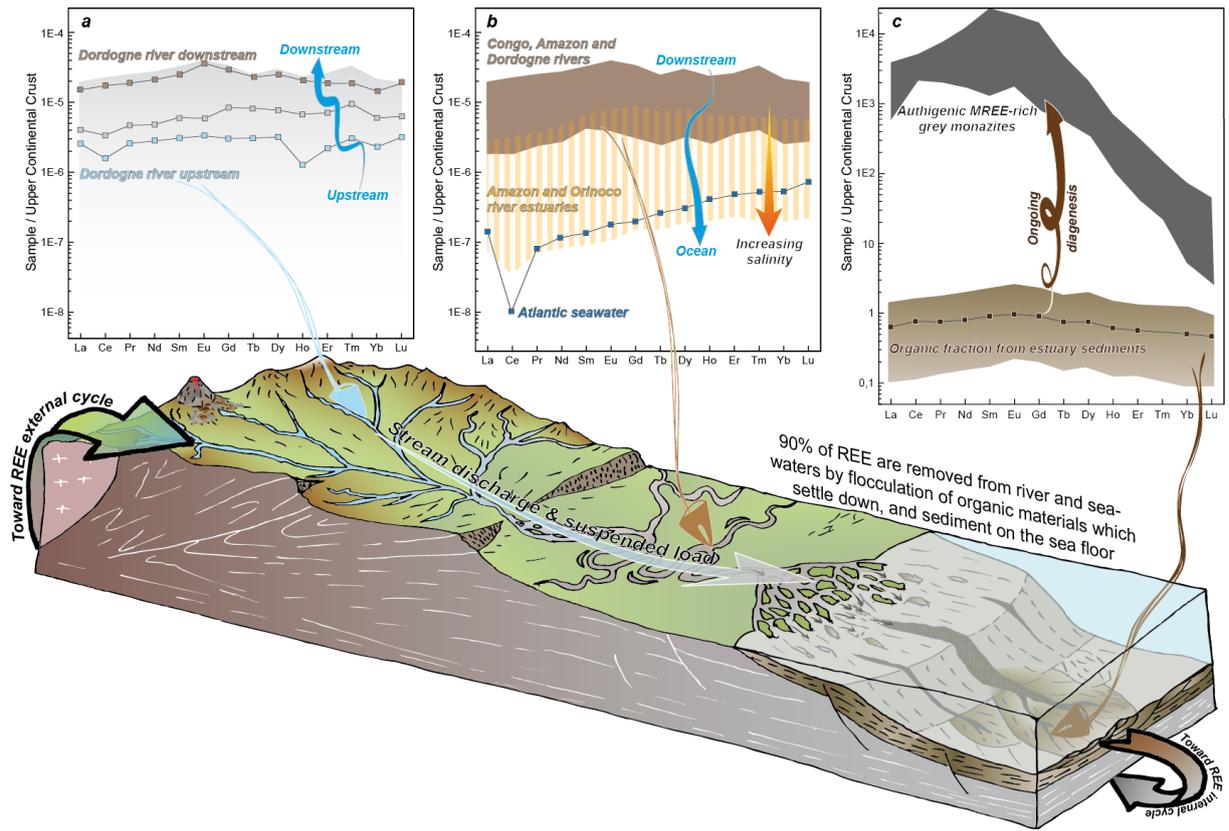


Figure 2

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