Continental shelves as potential resource of rare earth elements

Olivier Pourret1 & Johann Tuduri2

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.

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 economy. Thus they are essential in a wide variety of applications such as direct drive wind turbines, electric and hybrid vehicles, low-energy lighting. With a demand for REE thought to be growing at a rate of approximately 5–10% per year, 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 future, it will not be able to meet the increasing demand. Thus mining of natural primary deposits is expected to remain as the major source of REE. 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, iron-manganese crusts and deep-sea muds of the Pacific Ocean floor, 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 constrained and the behavior of REE during mixing of river and sea water is well studied. However, as discussed by Rasmussen et al. and Lacan & Jeandel the amount of REE delivered to the coastal shelves and oceans must be significantly larger than previously estimated. Indeed the total burial flux of light REE (see below) is about 50 times greater than previously determined for deep-sea sediments. Recently, Freslon et al. highlight that sedimentary organic matter displays high REE concentrations and Rousseau et al. show that the dissolved REE speciation across the Amazon estuary salinity gradient is mainly controlled by coarse colloidal organic fraction which is progressively removed by coagulation as previously evidenced by Sholkovitz et al. 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.

Methods

Historically, the REE have been used to trace mass transfers during geological processes occurring both in the Earth’s interior and on the surface. 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 interactions. 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)22. Inorganic REE remaining in solution can be also sorbed and thus removed from solution when coming into contact with highly reactive particles (such as Fe-Mn oxyhydroxides)24,25. In the Amazon, 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 fraction26. 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 dissolved REE concentration data in selected studies on the (i) Dordogne27 and Garonne rivers then Gironde estuary (ii) Congo river28 and its estuary (unpublished results from Germain Bayon), (iii) Amazon river29 and estuary30, (iv) sedimentary organic matters30 and (v) Ordovician organic rich grey monazites31. 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 for which the estuarine behavior has been extensively investigated in the Gironde estuary (France)31. It must be noted that the Gironde estuary corresponds to the confluence of the Garonne and Dordogne rivers in the Atlantic Ocean.

Results and Discussion

For the three studied rivers flowing into the Atlantic Ocean (i.e., Amazon, Congo and Dordogne rivers; Fig. 1), it can be observed that the REE patterns of upstream samples (Fig. 1a) depict low REE concentration and a negative cerium (Ce) anomaly, whereas more organic samples downstream (Fig. 1a,b,c) display higher REE concentrations (one order of magnitude) and MREE 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 river)32. It can also be observed that in the Amazon and Gironde estuaries (Fig. 1d,e), 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 different estuary sediments (Fig. 1f) and in the organic fractions from sediments of these different estuaries (Fig. 1g) and are further observed in organic rich grey monazites (Fig. 1h), as previously observed on humic substances31,32.

Results highlighted in this short communication thus allow reassessing the REE external cycle (Fig. 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 iron24,25. Indeed, Rousseau et al.21 and Osborne et al.30 illustrated that both Amazon and Orinoco Rivers REE patterns lose their typical MREE enrichments. By performing ultrafiltration experiments, Rousseau et al.21 evidenced a LREE enrichment in the coarse colloidal fraction compared with the fine colloidal fraction and the truly dissolved phase. Humic substances as well as Fe-Mn oxyhydroxides (corresponding to the colloidal fraction) will favor a MREE enrichment whereas carbonate ligands (corresponding to the major anions in the truly dissolved phase) will enhance HREE enrichment. They associate this fractionation to colloid coagulation. These MREE patterns gradually evolves towards HREE-enriched patterns that are more similar to Atlantic Ocean water37.REE fractionation occurs because colloidal and truly dissolved pools have different REE patterns (i.e., MREE shape-bell pattern vs HREE enriched pattern). Thus, REE patterns of seawater could be the combination of both intra-oceanic and riverine processes.

Merschel et al.38 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 nano-particles and colloids. In the near shore environment, DOM, Fe and REE are removed, at different rates, along the increasing salinity gradient of estuaries and shelves14,21,37. The seawater REE signature could be thus 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 complexes44,45. 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 hydrus manganese oxide) is uncertain39.

In this context, the Atlantic continental shelves could be considered potential REE traps and shelf sediments would, similar to metalliferous deep sea sediments14,15, represent a potential REE resource. This latter hypothesis is illustrated by recent results from Freslon et al.20 and Rousseau et al.21. 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 Basin)30. Although high REE contents may be found in selected organic components (up to 350 mg/kg20, studies of bulk sediments in continental shelf areas reveal a high content of detrital silicate materials which are known to be depleted in REE and thus act as a diluting agent13,33,41, lowering final total bulk REE concentrations at values lower than 100 mg/kg (i.e. below concentration of UCC and thus shale composition 150 mg/kg, Fig. 1f). However, total bulk REE concentrations for Amazon estuary sediments are up to 500 mg/kg16, and could thus be considered as a potential resource of REE.
Eventually, based on calculation proposed by Chabaux et al., 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 >1200 t/year (during high-water conditions).

Figure 1. Upper continental crust (UCC)-normalized REE patterns in samples from (a) Dordogne River basin27, (b) Congo River basin28, (c) Amazon River basin29, (d) Amazon River estuary30, (e) Congo River estuary (unpublished results from Germain Bayon) and Dordogne, Garonne Rivers and Gironde estuary31, (f) African continental slope and foothill sediments32, Amazon estuary sediments34 and Gironde estuary sediments35, (g) organic fraction from estuaries sediments36 and (h) Ordovician organic rich grey monazites (each sample corresponds to a different monazite). UCC values are from McLennan36.
season), constituting 30% of the river flux to the Atlantic Ocean. 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 season. 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. 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 [L-MREE]PO₄·H₂O) and then monazite (monoclinic [L-MREE]PO₄) crystallization. However, such sedimentary depositional environment could not directly be compared to Pacific deep sea muds.

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 Fig. 1, and Atlantic seawater is from Freslon et al. UCC-normalized patterns for (a) river water, (b) river, estuarine and seawater, and (c) sedimentary organic matter and authigenic monazites.

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

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

1. Moss, R., Tezima, E., Kara, H., Willis, P. & Kooroshy, J. The potential risks from metals bottle necks to the deployment of Strategic Energy Technologies. Energ. Policy 55, 556–564, doi:10.1016/j.enpol.2012.12.053 (2013).

2. Vidal, O., Goffe, B. & Arndt, N. Metals for a low-carbon society. Nature Geosci. 6, 894–896, doi:10.1038/ngeo1993 (2013).

3. Herrington, R. Road map to mineral supply. Nature Geosci. 6, 892–894, doi:10.1038/ngeo1947 (2013).

4. Guyonnet, D. et al. Material flow analysis applied to rare earth elements in Europe. J. Clean. Prod. 107, 215–228, doi:10.1016/j.jclepro.2015.04.123 (2015).

5. Rollat, A., Guyonnet, D., Planchnon, M. & Tuduri, J. Prospective analysis of the flows of certain rare earths in Europe at the 2020 horizon. Waste Manage. 49, 427–436, doi:10.1016/wasman.2016.01.011 (2016).

6. Massari, S. & Ruberti, M. Rare earth elements as critical raw materials: Focus on international markets and future strategies. Resour. Policy 38, 36–43, doi:10.1016/j.resourpol.2012.07.001 (2013).

7. Binnemans, K. et al. Recycling of rare earths: a critical review. J. Clean. Prod. 51, 1–22, doi:10.1016/j.jclepro.2012.12.037 (2013).

8. Du, X. & Graedel, T. E. Global In-Use Stocks of the Rare Earth Elements: A First Estimate. Environ. Sci. Technol. 45, 4096–4101, doi:10.1021/es102836e (2011).

9. Goodenough, K. M. et al. Europe’s rare earth element resource potential: An overview of REE metallogenetic provinces and their geochemical setting. Ore Geol. Rev. 72, 838–856, doi:10.1016/j.oregeorev.2015.09.019 (2016).

10. Heiri, J. R. & Koschinsky, A. 13.11 - Deep-Ocean Ferromanganese Crusts and Nodules. In Treatise on Geochemistry (Second Edition) (ed Karl K., Turekian) 273–291 (Elsevier, Oxford, 2014).

11. Bau, M. et al. Discriminating between different genetic types of marine ferro-manganese crusts and nodules based on rare earth elements and yttrium. Chem. Geol. 381, 1–9, doi:10.1016/j.chemgeo.2014.05.004 (2014).

12. Josso, P. et al. A new discrimination scheme for oceanic ferromanganese deposits using high field strength and rare earth elements. Ore Geol. Rev. 87, 3–15, doi:10.1016/j.oregeorev.2016.09.003 (2017).

13. Kato, Y. et al. Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements. Nature Geosci. 4, 535–539, doi:10.1038/ngeo1185 (2011).

14. Elderfield, H., Upstill-Goddard, R. & Sholkovitz, E. R. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. Geochim. Cosmochim. Acta 54, 971–991, doi:10.1016/0016-7037(90)90432-K (1990).

15. Elderfield, H. The oceanic chemistry of the rare earth elements in seawater. Philos. T. Roy. Soc. A 325, 105–126 (1988).

16. Hoyle, J., Elderfield, H., Gledhill, A. & Greaves, M. The behaviour of rare earth elements during mixing of river and sea waters. Geochim. Cosmochim. Acta 48, 143–149, doi:10.1016/0016-7037(84)90356-9 (1984).

17. Sholkovitz, E. R. The aquatic chemistry of rare earth elements in rivers and estuaries. Aquat. Geochem. 1, 1–34, doi:10.1007/BF01025229 (1995).

18. Rasmussen, B., Buick, R. & Taylor, W. R. Removal of oceanic REE by authigenic precipitation of phosphatic minerals. Earth Planet. Sci. Lett. 164, 135–149, doi:10.1016/S0012-821X(98)00199-X (1998).

19. Lacan, F. & Jeandel, C. Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent–ocean interface. Earth Planet. Sci. Lett. 232, 245–257, doi:10.1016/j.epsl.2004.05.004 (2014).

20. Pourret, O. et al. Rapid neodymium release to marine waters from lithogenic sediments in the Amazon River estuary. J. Geochem. Explor. 52, 1203–1219, doi:10.1016/j.geoexplor.2016.09.007 (2017).

21. Rousseau, T. C. C. et al. Formation of Monazite-(MREE) from Paleozoic Shales: Role of Host Rock Chemical Composition and Organic Matter. Mineral. Mag. 77, 2362 (2013).

22. Martin, J.-M., Hogdahl, Ø. & Philippot, J. C. Rare earth element supply to the ocean. J. Geophys. Res. 81, 3119–3124, doi:10.1029/JC081i018p03119 (1976).

23. Pourret, O., Davranche, M., Gruau, G. & Dia, A. Rare earth elements complexation with humic acid. Chem. Geol. 243, 128–141, doi:10.1016/j.chemgeo.2007.05.018 (2007).

24. Dubinin, A. V. & Rozanov, A. G. Geochemistry of Rare Earth Elements and Thorium in Sediments and Ferromanganese Nodules of the Atlantic Ocean. Lithol. Miner. Resour. 36, 268–279, doi:10.1016/S0445-5104(01)00079-3 (2001).

25. Lara, I. B. L. S., Fernandes, E. A. N., Oliveira, H., Bacchi, M. A. & Ferraz, E. S. B. Amazon estuary — assessment of trace elements in sediments. J. Radioan. Nucl. Ch. 216, 279–284, doi:10.1016/j.jnucchem.2000.09.004 (1997).

26. Chaillou, G., Anschart, P., Lavaux, G. & Blanc, G. Rare earth elements in the modern sediments of the Bay of Biscay (France). Mar. Chem. 100, 39–52, doi:10.1016/j.marchem.2009.09.007 (2006).

27. McLennan, S. M. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochim. Geophy. Geo. 2, 109, doi:10.1029/2000gc000109 (2000).

28. Osborne, A. H., Hale, B. A., Hathorne, E. C., Plancherel, Y. & Frank, M. Rare earth element distribution in Caribbean seawater: Continental inputs versus lateral transport of distinct REE compositions in subsurface water masses. Mar. Chem. 177, 172–183, doi:10.1016/j.marchem.2015.03.013 (2015).

29. Mierschel, G., Bau, M. & Dantas, E. L. Contrasting impact of organic and inorganic nanoparticles and colloids on the behavior of particle-reactive elements in tropical estuaries: An experimental study. Geochim. Cosmochim. Acta 197, 1–13, doi:10.1016/j.gca.2016.09.041 (2017).

30. Tachikawa, K., Athias, V. & Jeandel, C. Neodymium budget in the modern ocean and paleo-oceanographic implications. J. Geophys. Res.-Oceans 108, 3254, doi:10.1029/2000jc000285 (2003).

31. Schip, J., Christenson, E. A. & Byrne, R. H. YREE scavenging in seawater: A new look at an old model. Mar. Chem. 177, 460–471, doi:10.1016/j.marchem.2015.06.010 (2015).
41. Menendez, A., James, R. H., Roberts, S., Peel, K. & Connelly, D. Controls on the distribution of rare earth elements in deep-sea sediments in the North Atlantic Ocean. Ore Geol. Rev. 87, 100–113, doi:10.1016/j.oregeorev.2016.09.036 (2017).
42. Chabaux, F., Riotte, J., Clauer, N. & France-Lanord, C. Isotopic tracing of the dissolved U fluxes of Himalayan rivers: implications for present and past U budgets of the Ganges-Brahmaputra system. Geochim. Cosmochim. Acta 65, 3201–3217, doi:10.1016/S0016-7037(01)00669-X (2001).
43. Barroux, G. et al. Seasonal dissolved rare earth element dynamics of the Amazon River main stem, its tributaries, and the Curuai floodplain. Geochim. Geophys. Geosy. 7, Q12005, doi:10.1029/2006GC001244 (2006).
44. Lev, S. M., McLennan, S. M. & Hanson, G. N. Mineralogic Controls on REE Mobility During Black-Shale Diagenesis. J. Sediment. Res. 69, 1071–1082, doi:10.2110/jsr.69.1071 (1999).

Acknowledgements
This work is funded by project ANR-11-ECOT-002 ASTER “Systemic analysis of Rare Earths – Flows and Stocks”. Dr. G. Bayon is acknowledged for sharing unpublished raw data for seawater samples off Congo River. The authors thank Dr. R.E. Martinez for post-editing the English style.

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

Additional Information
Competing Interests: The authors declare that they have no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2017