

## Reassessment of the rare earth elements external cycle in french watersheds - a high potential resource for the future

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The distribution of rare earth elements (REE) was studied in streams of the Armorican Massif and the Massif Central (France). The water chemistry of both watersheds was dominated by silicate weathering. The REE distribution patterns of stream water showed, from the source to the catchment outlet, a fractionation of the upper continental crust normalized REE distribution patterns from heavy REE (HREE) enriched to more flat and middle REE (MREE) enriched patterns, together with a progressive disappearance of a negative Ce anomaly. Ultrafiltration data (at 3 or 5 kDa) showed that the ultrafiltrates had HREE-enriched patterns with negative Ce anomalies, whereas the organic colloids showed relatively flat patterns. These data thus suggest that the observed general evolution from HREE-enriched to MREE-enriched patterns with distance is related to a growing importance of organic colloids as REE carriers from upstream to downstream.

The REE patterns of the ultrafiltrates are very similar to seawater patterns. The REE pattern of seawater could thus be inherited from river water. Commonly, the REE patterns 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 cycle, 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 fractionation during estuarine mixing, enhanced by extremely high particle reactivity of the REE (e.g. with MnO<sub>2</sub>).

Results from this study thus allow to reassess the REE external cycle. Indeed, the river input to the oceans has relatively flat REE patterns without Ce anomalies, 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 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. Eventually, the Atlantic continental shelf could be considered as a potential REE trap and shelf sediments would, similar to metalliferous deep sea sediments, represent a REE potential resource and guide for exploration. This latter hypothesis will be further tested by analysing various fractions (detrital, Fe-Mn oxides, organic compounds) of sediments deposited in river estuaries at the Western Atlantic margin.

## On calculating phase equilibria for metamorphic systems

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Mike Brown has overseen a revolution in metamorphic geology, as an organiser of meetings, journal creator and editor, supporter of people and contributor to the science itself. I would like to give a personal view of an important part of that revolution—the calculation of metamorphic phase equilibria: where we are, what the challenges are, and what might be the way forward. This will be done via consideration of methodological aspects of what is needed for such calculations: 1) An extensive internally-consistent thermodynamic dataset for the end-members of minerals, fluids and melts; 2) Activity-composition relationships for these phases, extending into parts of composition space where there is little or no experimental control; 3) Methods, for example for calculating phase diagrams, that take into account the “natural” variables that are likely to be critical in metamorphic systems; 4) Software that implements these methods, using the current best thermodynamic descriptions of phases; and 5) An appropriately nuanced appreciation of reaction in metamorphic rocks, for example regarding length-scales, and the likely boundaries of application of equilibrium thermodynamics in the study of metamorphism.