Fractionation of rare earth elements in rivers and estuaries

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Introduction

Laboratory experiments were carried out to determine how pH, colloids and salinity control the fractionation of rare earth elements (*REE*s) in river and estuarine waters. By using natural waters as the reaction media-river water from the Connecticut, Hudson and Mississippi Rivers-geochemical processes can be studied in isolation from the large temporal and spatial variability inherent in river and estuarine chemistry. Experiments confirm that *REE*s undergo extensive fractionation under low temperature conditions of natural waters. Process-oriented experiments, field studies and chemical models form a consistent picture whereby *REE* fractionation is controlled by surface/solution reactions. This research was recently submitted for publication in *Chemical Geology*.

Results, discussions and implications

The concentration and fractionation of *REE*s dissolved in river waters are highly pH dependent. Higher pH results in lower concentrations and more fractionated composition relative to the crustal abundance. With increasing pH the order of *REE* adsorption onto river particle surfaces is *LREE*s > *MREE*s > *HREE*s. With decreasing pH *REE*s are released from surfaces in the same order, *LREE*s > *MREE*s > *HREE*s.

Within the dissolved (< 0.22 um) form of river waters, Fe-organic colloids are major carriers of *REE*s. Filtration through filters and ultrafilters with progressively finer pore sizes results in filtrates which are more fractionated. The order of fractionation with respect to shale, *HREE*s > *MREE*s > *LREE*s, is most pronounced in the solution form, defined here as < 5K and < 50K ultrafiltrates. Colloidal particles have shale-like *REE* compositions which are quite distinct from those of the dissolved phase. River colloids are highly *LREE* enriched relative to the *REE* composition of the ultrafiltrates.

The addition of sea water to river water causes the coagulation of colloidal *REE*s. Fractionation accompanies coagulation with the order of salt-induced removal being *LREE*s > *MREE*s > *HREE*s. Hence, river waters, stripped of their colloidal particles by coagulation in estuaries, have highly evolved *REE* composition. That is, river water *REE*s transported in solution to the oceans are strongly *HREE* enriched and are fractionated to the same extent as that of Atlantic surface sea water. This strengthens previous conclusions that the evolved *REE* composition of sea water is coupled to chemical weathering on the continents.

While the large scale removal of dissolved river *REE*s in estuaries is well established, the release of dissolved *REE*s from river particles is a less studied process. Laboratory experiments show that there is both release and fractionation of *REE*s when river particles are leached with sea water. The order of salt-induced release of *REE*(III) (*LREE*s > *MREE*s > *HREE*s) for the Connecticut River particles is the same as that associated with lowering the pH. The release of *REE*s from river particles is potentially a large source of dissolved *REE*s to the oceans. This process could shorten the oceanic residence time of Nd (and other *REE*s) and help explain the inter-ocean variations in the Nd isotopic composition of sea water.

Using new data on dissolved and particle phases of the Amazon and Mississippi Rivers, a comparison highlights key features of *REE* fractionation in two major river systems. One intriguing feature is the well developed maximum in the middle *REE* sector of shale-normalized patterns for the dissolved (< 0.22 μm) form of Amazon River water.