

Estuarine Origin of the Positive La Anomaly and Super-chondritic Y/Ho Ratio of Seawater: Evidence from Mixing Experiments

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ICP-MS analyses following separation and pre-concentration of Rare Earths and Yttrium (REY) recently verified the presence of positive La and Gd anomalies and super-chondritic Y/Ho ratios in seawater. Y-Ho fractionation appears to be the most dramatic of these "unusual" REY features, but it is still uncertain where the prominent fractionation step that decouples Y from Ho (and La and Gd from the other REE) occurs. Surface-complexation of REY on marine particles with and without organic ligand contribution promotes the generation of super-chondritic Y/Ho ratios and positive La and Gd anomalies within seawater. These anomalies are nicely illustrated by the REY distribution of hydrogenetic ferromanganese crusts which show sub-chondritic Y/Ho ratios that are in marked contrast to the super-chondritic Y/Ho ratio of ambient seawater. Assuming that intra-oceanic Y-Ho fractionation ultimately controls the Y/Ho ratio of seawater, the Y/Ho ratio should increase with increasing water depth. However, close inspection of available data reveals that except for strong fractionation in the upper few hundred meters of the water column, this increase of Y/Ho ratios with water depth is not observed. Moreover, even surface seawater appears to be characterized by super-chondritic Y/Ho ratios. Hence, the most important fractionation step must occur elsewhere, either during weathering or during estuarine mixing between river and sea water. Since river water shows only slightly elevated Y/Ho ratios compared to igneous rocks and shales, terrestrial weathering apparently can be excluded. Therefore, we studied REY behaviour during estuarine mixing. To avoid the complicating effects of hydrological processes and to focus on the chemistry, we decided against sampling estuaries along transects showing variable salinities (i.e. seawater-river-water mixing ratios), but performed mixing experiments between river water and low-salinity seawater in the laboratory.

Low-salinity seawater from the Baltic Sea (Kattegatt, off Varberg, Sweden) was filtered (<0.2 micron) into 20L Nalgene bottles. River water was sampled from the rivers Nissan and Ätran in southern Sweden. Water from both "brown-water" rivers is slightly acidic (Nissan: pH 6.3, Ätran: 6.8) and rich in natural organic matter. One set of samples from each river was filtered (<0.2 micron) while the other remained unfiltered.

Filtered and unfiltered river water was mixed with seawater at various ratios in Nalgene bottles. The bottles were stored in the dark for 24h, before the mixtures were filtered again (<0.2 micron), acidified to pH 2, and spiked with Tm (the internal standard used to determine the yield of REY during the subsequent pre-concentration). After separation and pre-concentration of REY, concentrations of REY in the sample solutions were determined by ICP-MS, and the results compared to calculated concentrations assuming conservative mixing behaviour.

At salinities above 8 per mil, the REE show non-conservative mixing behavior, as indicated by measured < calculated concentrations. This discrepancy was more pronounced for the LREE than for the HREE. In experiments using non-filtered river water, non-conservative behavior was more pronounced than in experiments with filtered waters. These results are in full agreement with previously published data. The results suggest that added seawater induces aggregation and growth of colloidal particles in the river water component. The REE are bound to these organically stabilized Fe colloids and are filtered out with their carrier phase(s). In all experiments, Y showed a higher affinity for the filter-passing fraction than Ho, suggesting that the Y/Ho ratio of the dissolved REY is higher than that of the colloid-bound REY. This is compatible with the higher tendency of Ho than Y to form surface-complexes on organic and/or inorganic particles. We observed similar behavior for La relative to the other LREE, suggesting that the same process is also responsible for the positive La anomaly of seawater.

The results of our mixing experiments strongly suggest that aggregation of river colloids during mixing in the low-salinity part of estuaries produces the super-chondritic Y/Ho ratio of seawater. Future experiments will be carried out to study whether truly dissolved Y and Ho are already fractionated in river water and the admixture of seawater merely separates the colloid-bound from the truly dissolved REY fraction, or whether Y and REE are further fractionated during the estuarine mixing process.