

Seasonal variations of the rare earth elements in a boreal river

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Weathering reactions on the continents lead to extensive fractionation between the dissolved rare earth element (*REE*) composition of river waters and that of river suspended particles and continental rocks. Both the concentration and the extent of fractionation of dissolved trivalent *REE* in river waters appear to be dependent on pH and on the presence of colloidal matter. The critical phase is most likely river colloids. River water stripped of their suspended particles and colloids by settling and coagulation, may have a solution phase with trivalent *REE* composition as fractionated as in sea water. This implies that fractionation by oceanic geochemical cycles is not the sole process behind the evolved pattern of sea water (Sholkovitz, 1995).

Large temporal variations in the dissolved *REE* concentration have been observed in river water over time scales of the order of a few days. Temporal changes in *REE* fractionation have also been observed. For example, both negative and positive Ce-anomalies have been recorded in samples from the same river (Elderfield *et al.*, 1990). The *REE* data base in river water is based on several rivers but there are only few samples in each river, and the reasons for the temporal variations have been little studied.

In this study weekly sampling of the dissolved and suspended particulate phase during 18 months in the Kalix River, Northern Sweden, is presented together with ultra filtration data (colloidal phase).

The dissolved ($<0.45 \mu\text{m}$) *REE* showed large seasonal and temporal variations. Lanthanum varied by a factor 7, between 288 and 2088 pmol l^{-1} . When water discharge increased during snow-melt in May and the dissolved *REE* concentration went up, the dissolved ($<0.45 \mu\text{m}$ and $<0.2 \mu\text{m}$) *REE* pattern changed from a relatively flat pattern to a *LREE* enrichment (compared with local till). There was a close relation between high dissolved *REE* and high DOC, which in turn was related to increased water discharge. A close relation between dissolved ($<0.45 \mu\text{m}$) Fe and Al with the dissolved *REE* in the river

suggests that weathering and transport of these elements follow similar geochemical pathways in the catchment.

Cross-flow ultra filtration was applied to investigate the role of colloids as *REE* carrier phases in the river. The 3kD regenerated cellulose Millipore Pellicon membranes used were calibrated with organic colloid standards under realistic conditions and the cut-off was determined to be $\leq 3\text{kD}$. Less than 5% losses to the filter of a humic-analogue (polyethylene glycol) colloid standard was demonstrated.

Ultra filtration of river water during spring-flood showed that colloidal particles dominated the transport of the dissolved *REE* and Fe. Less than 5% of the dissolved *REE* ($<0.2 \mu\text{m}$) were found in the fraction smaller than 3kD (3000 Dalton). For DOC on the other hand, approximately 35–45% of the dissolved fraction ($<0.2 \mu\text{m}$) passed through the 3kD filter. This is a clear indication that the colloidal *REE* are related to a specific fraction of the total DOC concentration. The colloidal fraction showed a flat to slightly *LREE* enriched pattern with a negative Ce-anomaly. However, the colloidal fraction reaching the river at spring-flood was relatively enriched, or less depleted, in Ce compared with the conditions in the dissolved phase at low DOC concentrations in the river. The solution fraction ($<3\text{kD}$) in May showed an *HREE* enrichment and supports the idea that dissolved *REE* patterns in river waters are *HREE* enriched when the colloidal fraction has been removed (Sholkovitz, 1995).

The particulate suspended phase ($>0.45 \mu\text{m}$) in the river was dominated by a Fe-rich phase, especially during winter. The amount of detrital particles in the suspended phase was relatively low except during high water discharge (Ingri and Widerlund, 1994). Approximately 10% of the particulate *REE* ($>0.45 \mu\text{m}$) were transported in detrital particles during winter. At maximum ashed suspended concentration at spring-flood, about 30% of the *LREE* and up to

60% of the *HREE* where hosted in detrital particles. However, the total amount of *REE* transported each year in particles is relatively low compared with the dissolved (<0.45µm) phase. The suspended particulate fraction (>0.45 µm) accounted for only 35% of the yearly total transport of La. These data indicate that physical erosion of detrital particles plays a minor role for the total yearly transport of *REE* in the river. Data stresses the importance of colloids in the dissolved fraction (<0.45 µm) for the transport of especially the *LREE* in this type of boreal river system.

The Ce-anomaly in the suspended particulate phase (>0.45 µm) showed systematic variations. At maximum spring-flood in May no anomaly was seen, but during the rest of the year the anomaly was negative. A systematic decrease of the Ce-anomaly was measured during the ice-covered period in winter.

Manganese rich particles are formed during summer in the river (Pontér *et al.*, 1992). The formation of these particles triggered an enhanced uptake of Ce (compared with the trivalent *REE*) from the solution fraction in the river.

High DOC and *REE* concentrations most likely originate from two compartments during snow-melt in May. Both dissolved Mn data and sulphur isotope data indicate that melt-water is flushed through the upper section of till and from peatland (Ingri *et al.*, 1997). It is likely that the most intensive weathering of the *REE* in the Kalix River catchment takes place in the upper till section and that weathering below the groundwater table is relatively small. Weathering of till in Northern Sweden produces an E-horizon that is depleted in *REE*, the *LREE* being more depleted than the *HREE* (Öhlander *et al.*, 1996). An enrichment of the *LREE* in the dissolved phase should therefore be expected in the river, if no significant fractionation's occurred during transport from the E-horizon via near-surface-ground-water (soil water, small streams

and mire water). The high concentration of *REE*, the *LREE* enriched pattern, the lack of a Ce-anomaly and the close correlation between dissolved organic carbon, Al, Fe and *REE* during spring-flood in the river, suggest a rapid transfer of soil water (upper section) to the river during snow-melt in May (and probably a transfer of mire water at heavy rains in summer and autumn) without any larger fractionation of the *REE*.

However, the relative depletion of *LREE* and the negative Ce-anomaly in the dissolved phase (<0.45 µm) during base-flow in winter indicate a fractionation of the *REE* during transport from the weathering site in the E-horizon to the river. At low discharge in winter the river water is dominated by groundwater. This groundwater has formed mainly from water passing through the weathering profile in the till cover, with only limited contact time with the bedrock. The flat to slightly *HREE* enriched pattern and the negative Ce-anomaly in the dissolved fraction in the river during winter probably reflects a water that has moved a longer distance in the soil profile, compared with the conditions during melt-water discharge. With a longer contact time a larger adsorption of the *LREE* (specifically Ce) in the soil profile can be anticipated.

References

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