

The Ce-Anomaly in River Suspended Matter: An Indicator of Hydrogeochemical Processes in a Boreal Catchment

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Fractionation of the REE during weathering is a key process in order to understand the river transport of the REE. The REE belong to the most depleted elements during weathering of till in northern coniferous areas. Temporal variations shown by the Ce-anomaly in the suspended particulate fraction in the Kalix River reflects these fractionation processes, and can be used to evaluate the fractionation occurring during weathering and transport of the REE in a boreal catchment. Cerium data from weekly sampling of the filter passing (<0.45 µm) and suspended particulate phase (>0.45 µm) in the Kalix River, Northern Sweden, are presented together with ultrafiltration data for colloidal particles and the solution fraction (<3 kD).

Suspended particles, colloids and the solution phase in the river generally show a negative Ce-anomaly, compared with till in the catchment. This indicate a fractionation of Ce from the other LREE during weathering and transport to the river. The Ce-anomaly in the suspended particulate phase in the river shows systematic variations. At maximum spring-flood in May no anomaly can be seen, but during the rest of the year the anomaly is negative. The anomaly is around -0.2 during summer but becomes progressively more negative during the ice-covered period, being around -0.4 shortly before ice break-up. The time series for the Ce-anomaly in the filtered phase shows an almost identical pattern compared with the particulate phase. The anomaly is though generally more negative than in the particulate phase.

Fractionation of Ce from the trivalent REE is generally caused by an enhanced uptake of Ce on particulate phases because of an oxidation of soluble Ce³⁺ to the insoluble and thermodynamically stable Ce⁴⁺ at Mn-oxyhydroxide surfaces. However, data in this study show that variations of the Ce-anomaly in the suspended particulate fraction in the river mainly reflects the amount of organic-rich colloidal particles trapped on the 0.45 µm filter. There is a linear positive correlation between increasing filtered Ce concentration and

decreasing Ce-anomaly (less negative) in the particulate fraction. Hence, the filter passing Ce fraction is an estimate of the amount of REE-enriched organic colloids in the river. Cerium is slightly depleted and shows a small negative Ce-anomaly in the upper 20 cm in the till profile. No Ce-anomaly (or slightly positive), in the dissolved phase should therefore be expected, if no significant fractionations occurred during transport from the E-horizon via near-surface-ground-water (soil water, small streams and mire water) to the river. The increasing Ce-anomaly in the suspended particles at spring-flood, and during storm events in the autumn, indicates a transfer of water from this upper till section to the river. At low discharge in winter the river water is dominated by groundwater that has formed mainly from water passing through the whole weathering profile in the till cover. Organic rich colloids enriched in LREE, including Ce, formed in the upper section of the till are precipitated (partly or totally) during transport downwards in the till profile. Furthermore, some till profiles shows an enrichment of Ce (positive Ce-anomaly) in the B-horizon, together with precipitated Fe, Al and organic matter. Hence, the REE reaching the groundwater has probably developed a negative Ce-anomaly. This is illustrated by the progressively decreasing Ce-anomaly during winter in the river, and the negative Ce-anomaly in the solution fraction.

During summer the Ce-anomaly is less negative which is a reflection of enhanced uptake of Ce due to oxidation by suspended Mn-rich particles which are formed in the river in July and August. Although Ce³⁺ can be abiotically oxidised by Mn-oxyhydroxide surfaces, the oxidation in natural systems has been suggested to be catalysed by bacteria, similar to the predominant oxidative pathway suggested for Mn²⁺. Data from several years show that the Mn-rich particles begin to form when the water temperature reaches 15°C. This indicates that bacteria may play a role for the oxidation of Mn during summer. Similarly, cerium oxidising bacteria could catalyse the enhanced uptake of Ce but this remains to be shown.