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Boron isotopes behaviour during weathering of silicate rocks

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Among the large number of studies dedicated to boron isotopes in waters, few concern waters in silicate geological environments (e.g. mainly basalts and granites). In this study, we report data from waters draining various silicate environments from the literature (Alps, French Guiana, Pyrenean and Massif Central mineral springs, Canada) and a new set of B isotopic data determined on waters collected over granitoid dominated bedrock (Alps, Massif Central, western France, Black Forest, Finland).

Grounded on detailed studies from the French Guiana [1] and the Vienne district [2], available data of groundwaters in crystalline host rocks highlight the potential of boron isotopes used as a geochemical tool to help constrain solute sources and water-rock interaction processes. Detailed studies of these waters systematically indicate positive correlation between B/HCO₃ ratios and pH, considered as a proxy of weathering intensity. When plotted on a $\delta^{11}\text{B}$ vs. B diagram, the data clearly define distinct fields. The trend defined by these fields indicates a preferential ¹⁰B enrichment with increasing boron content. Reported in a $\delta^{11}\text{B}$ vs. pH, a progressive ¹⁰B enrichment with increasing pH is observed in waters. We assume this relationship to be related to dissolution of silicates and most of the water samples plot on the trend between the potential rain water end-member and the end-member evolved by dissolution of silicates. The field of Massif Central mineral spring waters plot outside this trend by their pH values. The lower pH values observed in this area compared to the Pyrenean and Alpine Foreland waters are due to the dissolved CO₂ enrichment that led to a decrease of pH.

The investigated case histories strongly suggest an inverse correlation between the groundwater pH and their $\delta^{11}\text{B}$. This relation, previously demonstrated experimentally, is best defined in the French Guyana coastal aquifer and in the Vienne because of the wide pH range naturally present in waters. The different correlations observed between the groundwater geochemistry, the pH and the $\delta^{11}\text{B}$ signatures are related mainly with the weathering of the silicate host rocks.

References

- [1] Négrel, Ph., Petelet-Giraud, E., Casanova, J. and Kloppmann, W. (2002) *Water Resour. Res.*, **38** (11), 1262.
[2] Casanova, J., Négrel, Ph., Kloppmann, W. and Aranyossy, J.F. (2001) *Geofluids*, **1** (2), 91-102.

4.5.85

Variations in colloidal carrier phases and size fractions associated with the rare earth elements in a boreal river

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Size fractions and association to colloidal carrier phases for the rare earth elements (REE) were investigated before, during and after a spring flood in boreal Kalix River, northern Sweden. Prefiltered (100 μm) water samples were compared with ultrafiltration fractions (0.22 μm , 10kDa and 1kDa), results from Field-Flow Fractionation (FFF) experiments, and deployments using Diffusive Gradients in Thin films (DGT).

During maximum spring flood the discharge in the river increases from $\sim 70 \text{ m}^3 \text{ s}^{-1}$ to $\sim 1600 \text{ m}^3 \text{ s}^{-1}$. Concentrations of REE, Fe and total organic carbon increases during this event while major elements like Na, Ca, Cl and SO₄ are diluted. Results from ultrafiltrations show that the REE mainly are transported with particulate and colloidal material. Concentrations of diffusible REE determined with DGT are broadly comparable with concentrations in 10kDa permeates.

Two colloidal carrier phases with distinctly different chemical composition and size could be detected with FFF; one phase rich in carbon, and another in Fe. The Fe-rich phase is important during winter (before the spring flood), and the carbon-rich phase dominate during maximum flow and summer. FFF experiments also show association of REE to the Fe-rich material during winter but not during spring and summer.

Concentrations of REE in water and ultrafiltration samples, and from DGT deployments were normalized to concentrations determined in unweathered local soil. The REE patterns are flat during winter and summer, but LREE enriched at peak spring flood. It has previously been shown that REE released by weathering in the E-horizon are enriched in the lighter elements. Adsorption of LREE in the B-horizon causes the soil solution which finally reaches the ground water to have a flat REE pattern.

It is suggested here that the LREE enriched pattern which is observed in the river during peak discharge derives from mobilization of organic colloids from the upper part of the soil. These organic colloids, which have not been affected by adsorption in the B-horizon, can enter the river more or less directly due to rising water levels and overland flow.