

Highly contrasted Rare Earth Element patterns in shallow groundwaters from very small catchments

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Concentrations of Rare Earth Elements (*REE*) in large rivers (Amazon, Mississippi, Indus...) are often used as key constraints to determine chemical and physical erosion rates and fluxes on the global scale (Goldstein and Jacobsen, 1987; Sholkovitz, 1995; Elderfield *et al.*, 1990; Gaillardet *et al.*, 1997).

Few works, however, have been dedicated to study fundamental processes which control *REE* hydrochemistry upstream, at the water-rock interface. Using data from groundwaters, Smedley (1991) suggested that *REE* in deep waters closely reflect the lithology of their host rocks. More recently, Johannesson *et al.* (1997) proposed that complexation processes play dominant role on the distribution pattern of *REE* in waters. Both authors acknowledged the usefulness of *REE* to investigate water-rock interactions.

The present study concerns the spatial and temporal variability of *REE* concentrations in shallow groundwaters associated with three very small catchments located in western France (Brittany and Normandy). All the catchments benefit from the same temperate oceanic climatic conditions, and have low permeability soils. Basement rocks have granitic or shaly compositions. The data are used to further elucidate the nature of fractionation processes that control the *REE* chemistry of shallow, continental waters.

Data

REE concentrations were determined on 0.2 μm -filtered water samples by ICP-MS. In all three catchments, *REE* patterns turn out to be very different from those found in large rivers. Major differences include: (a) the presence of strong positive Eu-anomaly ($\text{Eu}/\text{Eu}^* = 1.1$ to 8) in some of the analysed waters; (b) the existence of marked enrichments of the *LREE* and *MREE* over the *HREE*;

and (c) the fact that overall *REE* concentrations are often much higher (by a factor of 10 to 100) than those observed in large rivers. Moreover, variations in local hydrologic conditions within the three investigated small catchments appear to play a major role on the hydrochemistry of *REE*. For example, water from well-drained zones often yields a strongly negative Ce-anomalies ($\text{Ce}/\text{Ce}^* = 0.06$ to 0.5) whereas no such anomalies are found in waters from waterlogged domains than those from well-drained domains (see Fig. 1).

Discussion

Thus it appears that the hydrochemistry of *REE* is much more complex in small catchment and small rivers than it is in large rivers. Three different mechanisms may explain the variability of the *REE* patterns obtained in this work:

(1) *redox conditions* may control the behaviour of Ce in the studied waters, since Ce can occur as Ce^{3+} (reducing conditions) as well as Ce^{4+} (oxidizing conditions). When Ce^{3+} is oxidized into Ce^{4+} , it can precipitate from solution to insoluble Ce-oxide and be adsorbed onto particles leading to a Ce depletion in the solution. It is worth noting that it has been previously shown that redox conditions are themselves strongly influenced by the hydrology of the studied catchments.

(2) the presence of *organic colloidal material* in surface waters may play an important role on the transport of *REE*. Indeed we observed a marked positive correlation between *REE* concentrations in these waters and Dissolved Organic Carbon (DOC). Furthermore, a pronounced decrease of *LREE* concentrations arises when the waters are filtered using 0.02 μm , or lower pore size filters.

(3) *lithology* variations (i.e. the granitic or shaly nature of the bedrocks) appear to have some

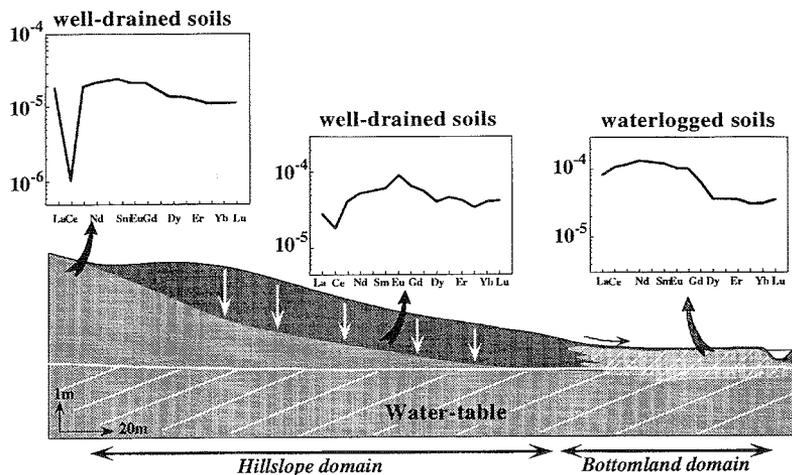


FIG. 1. Shale normalized *REE* concentrations of surface waters from the Naizin catchment (France).

influence on the hydrochemistry of *REE* since concentrations in water from shaly catchments are generally higher than in waters flowing over granitic substrates. However, variations in bedrock lithologies seem to have no role on the shape of the *REE* patterns. Indeed, identical patterns with marked Eu anomalies were found both in granitic and shaly catchments.

Conclusion

The major result which stems from this study is that whatever the studied catchment is, the waters from the well-drained hillslope and these recovered from the bottomland zone exhibit contrasted *REE* patterns which may record contrasting redox conditions and colloidal phase occurrence.

Thus it appears that the presence of well-drained against waterlogged domains and the consequences this has on redox processes and the distribution of organic matter strongly control the hydrochemistry of

the *REE* in such small catchments. However, it should not be ignored that the three investigated catchments are all located in areas of intensive agriculture. The exact role of human activities onto the hydrochemistry and *REE* patterns of these waters is not clear at present.

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