

Rare earth elements and Sr and Nd isotopic compositions of dissolved and suspended loads from small river systems in the Vosges mountains (France), the river Rhine and groundwater

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This study provides new Sr and Nd isotope and *REE* data for both dissolved and suspended loads of groundwater and plain rivers from the Upper Rhine valley, the river Rhine and several small tributaries originating in several small drainage basins in the Vosges mountains. It therefore allows us to shed some light on the evolution of the *REE* in non-mature streams from small catchment areas downstream to the more mature plain rivers and the river Rhine. Several major conclusions can be drawn:

The dissolved load *REE* distribution patterns of the high pH samples from the plain rivers, the river Rhine and the groundwater are very similar showing a strong negative Ce anomaly and *HREE* enrichment. Only the river Rhine has a strong positive Gd anomaly which is of anthropogenic origin. The dissolved load *REE* distribution patterns of the low-pH Vosges streams are very different from those of the plain rivers and much more varied. A comparison of the dissolved load *REE* distribution patterns with those of the principal lithologies in the corresponding drainage basins illustrates some similarities and close relationships between both of them. Especially the Eu anomaly is strongly lithology dependent.

Different physicochemical parameters control the *LREE* enrichment in the low pH Vosges and high pH plain rivers. Only the plain rivers including river Rhine and groundwater show a pH controlled *LREE* enrichment similar to the world's major rivers. Therefore, also the shape of the *REE* distribution patterns of these solutions are pH dependent. An additional parameter controlling the *HREE/LREE* fractionation is the dissolved organic carbon concentration in the solution. However, the Sm/Nd ratios of these evolved and mature water systems have not been significantly fractionated with respect to average continental crust as documented by the

correlation between ϵNd and Sm/Nd.

The Sm/Nd ratios and corresponding ϵNd values of the dissolved load of the river Rhine and the groundwater are low and close to values for the terrigenous clay-rich Mesozoic schists from the Rhine's catchment basin. These schists are thought to correspond closely to the average isotopic composition of the continental crust in the studied area and therefore also of the alluvial deposits in the Rhine valley. This, however, is not the case for the less evolved, non-mature and low-pH Vosges streams. Chemical alteration of accessory, probably *LREE* depleted minerals in the catchment area control the *REE* abundances of these waters. The high Sm/Nd ratios and the associated and, compared to average crust, significantly higher ϵNd values but lower Sr isotopic composition values of these dissolved loads support this suggestion.

Thus, the mature water systems such as the river Rhine and the groundwater incorporated the Sm-Nd isotope characteristics of average continental crust whereas the less evolved and mature Vosges rivers incorporated the isotope characteristics of *REE* carrying minerals from the different lithologies in the different catchment areas. Thus, the least mature streams provide most important information about chemical alteration especially concerning differences in weathering resistance between minerals and fractionation of their *REE* patterns during weathering.

The Ce anomaly in the dissolved load of the non-mature Vosges streams and of the evolved plain rivers including Rhine and groundwater, however, is neither controlled by the source rock characteristics nor directly by the pH. Most probably it is oxidative scavenging of Ce by Al bearing colloids which leads to decreasing Ce* values and Al concentrations in the

dissolved phase as pH increases.

The *REE* distribution patterns of the suspended load leachates have no similarities with those of the corresponding dissolved load indicating that they contain not only *REE* adsorbed on the suspended particles but also *REE* from minerals at least partly leachable in 1N HCl. The Sr and Nd isotope data support this suggestion. Their $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios are always higher and lower, respectively, than those of their corresponding dissolved loads. The leachates show *MREE* enriched distribution patterns very similar to those of the corresponding residual phases but are more strongly depleted in light and heavy *REE*. Leachable and residual phases show very different Sr and Nd isotopic composition values indicating that both of them relate to very different mineral phases. The

humpshaped *REE* distribution patterns of the leachates are typical of diagenetically altered apatite. With the exception of the Eu anomaly the *REE* distribution patterns of the suspended loads do not mirror the characteristics of the basin lithologies. The patterns are, however, similar to those of alteration products like clay-minerals which is supported by the very high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic composition values and Sm/Nd ratios. Leachates and corresponding residual phases define alignments in the Sm/Nd isochron diagram whose slopes define ages ranging between 200 and 390 m.y. indicating that the mineral phases in the suspended load retained some memory of their primary precursor minerals originating from the Hercynian granitic rocks.