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Quantifying rare earth element distribution and isotope fractionation in hydrous systems using density functional theory and speciation modelling

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Rare earth elements (REE) are important tracers for paleoenvironmental conditions like redox, reservoir mixing, or geochronology. However, so far only REE element patterns and radiogenic Nd isotopes have been widely applied.

We have calculated a novel dataset of reduced partition functions (as 1000lnβ) for numerous aqueous species of stable La, Ce, and Nd isotopes that are applicable to a range of hydrous systems. We combined our results with speciation modelling of simplified seawater and hydrothermal fluids at variable pH and temperature. REE elements show a high affinity for carbonate complexes at circumneutral conditions in seawater, but they are mostly absent at lower pH. The presence of major anions such as carbonate and sulphate significantly change the isotopic composition of hydrated ‘free’ species for adsorption on sediments. Minor anions like phosphate have no considerable effect on the isotopic composition of free species.

Fluoride and chloride become more important ligands at elevated temperature in hydrothermal fluids. Their destabilization through changes in fluid conditions might leave a distinct isotopic composition in minerals. Isotope fractionation is proportional to $1/T^2$ and therefore the magnitude of fractionation approaches current analytical uncertainties at high temperatures (>300 ºC). Consequently, ratios between isotopologues with small mass differences simply reflect the bulk composition. To overcome this problem, larger mass differences between stable isotopes are required such as $^{148\text{-}144}$Nd which show a Δ1000lnβ (≈$\Delta^{148\text{-}144}$Nd) of 0.1 at 300 ºC (Fig. 1).

Ce(IV) is insoluble at low temperatures and its speciation in aqueous solution is mostly unknown. However, calculations show that isotope fractionation between aqueous Ce(III) and Ce(IV) is significant (Δ1000lnβ=0.5) which makes it a suitable tracer for palaeoredox conditions since Ce anomalies are prone to fluid overprinting.

Our models represent a new approach of how environmental changes are potentially traceable through isotopic signatures in sediments and it can be used to support experimental data.

Figure 1