

The behaviour of rare earths in solution and at clay/water interfaces: insights from computer simulation.

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Given their importance as ‘critical minerals’ [1], new and sustainable extraction, processing and recycling methods for rare earth elements (REEs) must be identified. Since REEs can be mobilised and concentrated in hydrothermal fluids [2] and from easily leachable clays [3], fractionating REEs from solution offers a cheap way to increase their yield from deposits. In the present study, density functional theory and classical force field molecular dynamics have been applied to investigate the solvation structure and mobility of Nd³⁺, Gd³⁺ and Er³⁺ in water and on the kaolinite surface.

Ligand exchange reactions involving chloride were simulated using advanced sampling methods, and stability constants for the complexes were calculated. Analysis of the free energy surfaces for these systems allows us to characterise mechanisms of ligand exchange. Organic acids (citrate, oxalate, gluconate)—known to remove REEs from solution [4]—were also considered. Our results show that REE ion size is crucial for these types of ligand exchange mechanisms.

We have also used density functional methods to simulate the energy of binding of REE chlorides to both terminations of the (001) surface of kaolinite - chosen as an example of an important component of many clays.

These simulations provide new information both about REE complexation in solution and the mechanisms of absorption onto flat clay surfaces. Our work highlights the ability of simulations to elucidate processes important in the recovery of REEs from easily-leachable deposits.

[1] European Commission, Critical Raw Materials for the EU, EU Commission Enterprise and Industry Report (2010).

[2] C. H. Gammons *et al.* (1996), *Geochim. Cosmochim. Acta* **60**, 4615-4630.

[3] G. A. Moldoveanu and V. G. Pagangelakis (2013), *Hydrometallurgy*, **131-132**, 158-166.

[4] K. W. Goyne *et al.* (2010), *Chem. Geo.* **278**, 1-14