

Modelling rare earth element complexes in aqueous solutions

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Rare earth elements (REEs) are important metals for the manufacture of modern technological devices. Since the supply of REEs—particularly Nd and the heavy REEs—has been identified as ‘critical’ [1], new methods for their sustainable extraction and processing must be identified. It has been shown that REEs can be mobilised and concentrated to economic levels in hydrothermal fluids [2,3]. Therefore, fractionating REEs from solution offers a potentially cheap way to maximise yield from ore deposits.

Here, we report the results of *in silico* studies of the stabilities and mobilities of REE complexes in aqueous solutions. 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. Ligand exchange reactions, such as

$$[\text{REE}(\text{H}_2\text{O})_x]^{3+} + \text{Cl}^- \rightarrow [\text{REE}(\text{Cl})(\text{H}_2\text{O})_y]^{2+} + (x-y)\text{H}_2\text{O},$$
were simulated using advanced sampling methods, and complex stability constants were calculated based on binding free energies. Ligands include organic acids (e.g. oxalates) which have been highlighted to play important roles in the accumulation of REEs [4]. In addition, we report on the stability and structure of REE complexes at raised temperatures and over a range of salt concentrations.

Our results extend the catalogue of thermodynamic data on aqueous REE species and provide atomic scale mechanistic insights into ligand exchange. In addition, we provide information about the role of background ions in REE complexing and the significance of these species for REE fractionation.

[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] A. Migdisov *et al.* (2016), *Chem. Geo.* **439**, 13-42.

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