# Kinetic isotope fractionation of ionic species in $D_2O$ and methanol

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Certain kinetic processes, such as the self-diffusion and desolvation of ions in aqueous solution, have been shown via experiments[1,2] and molecular dynamics (MD) simulations[2,3,4] to fractionate $Li^+$, $K^+$, and $Ca^{2+}$ isotopes. Both the self-diffusivities and desolvation rates of these isotopes in pure water follow an inverse power-law dependence on isotopic mass. In other words, lighter isotopes diffuse faster and exchange water molecules between their first hydration shell and the bulk liquid more quickly than heavier isotopes of the same species. In order to better elucidate the mechanism(s) responsible for kinetic fractionations associated with these processes, we performed MD simulations of ions in $D_2O$ and diffusion experiments of ions in methanol comparable to previous experiments and simulations of the same ionic species in pure $H_2O$.

MD simulations involved one cation and 550 $D_2O$ molecules in a periodically replicated cell at 298 K. Heavy water was modeled by altering the mass of SPC/E water but leaving all other model parameters unchanged. Simulation results indicate that both self-diffusion and desolvation of $Li^+$ and $K^+$ in $D_2O$ produce larger isotopic fractionations compared to those determined for the same species in pure $H_2O$. For $Ca^{2+}$, ion desolvation rates in $D_2O$ had no isotopic mass dependence, whereas data obtained in $H_2O$ showed $^{44/40}$Ca kinetic fractionations of order 3 ‰[4,5]. Kinetic isotope fractionations associated with self-diffusion of $Ca^{2+}$ isotopes in $D_2O$ are ambiguous at best due to the magnitude of the errors: simulation results predict diffusive fractionations between $^{44}$Ca and $^{40}$Ca of ca. 0.8 ± 5 ‰; by comparison, $^{44/40}$Ca kinetic isotope fractionation by diffusion in $H_2O$ is 0.43 ± 0.05 ‰[2]. Experimental corroboration of our $D_2O$ simulation results is forthcoming.

Preliminary experimental results indicate that diffusion of $K^+$ in methanol produces larger isotopic fractionations than diffusion in pure $H_2O$. We are currently testing appropriate force field models for MD simulations of $Li^+$, $K^+$, and $Ca^{2+}$ in methanol. Together, these observations reveal how properties of the solvent (and, hence, kinetic processes that chemically couple the solute to the solvent) may play a critical role in the isotopic fractionation of cations in solution.

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# Influence of nitrate on the Eu(III) uptake by calcite: A TRLFS study

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## Introduction

Calcite is present up to high amounts in clay minerals which are being discussed as a host rock formation and is formed by the degradation of cementitious material as a secondary phase. Furthermore, nitrate is very common in the geological environment and can influence the sorption behaviour of radionuclides. Because of the high impact of trivalent actinides (Pu, Am, Cm) on the radiotoxicity on long time scales, we used Europium as a homologue due to its spectroscopical properties and chemically similar behaviour. Earlier studies[1] have shown that Eu forms solid solutions with calcite under moderate conditions (T=25°C, IS=0.01M, $ClO_4^-$ trace concentration). Three different sites were determined by TRLFS (dotted line, fig.1). By measurement of the fluorescence lifetimes after direct on-site excitation, these have been identified as one sorption (site A) and two incorporation species (sites B and C). For charge compensation, sodium must be present:

$$\mathrm{Eu^{3+} + Na^{+} \leftrightarrow 2Ca^{2+}}$$

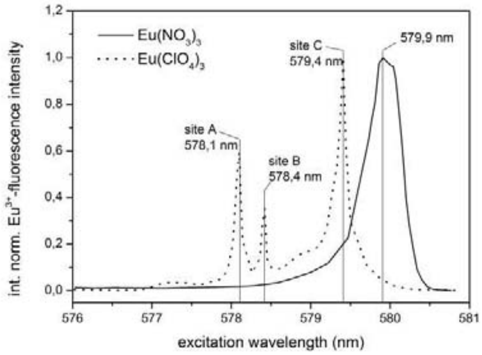

**Figure 1:** TRLFS excitation spectra of $Eu^{3+}$ doped calcite with nitrate (one site) and perchlorate (three sites) as counterion

## Results and Conclusion

By using 2 µM europium nitrate (T=25°C, IS=0.02M) instead of a perchlorate solution, a bathochromic shift of the emission maximum of about 0.5 nm was observed (solid line, fig.1). The long emission lifetime of this species (602 ± 59 µs) indicates that there are no water molecules left in the first coordination sphere of the lanthanaide ion (Horrock's equation[2]). As no other sites could be found, a new mechanism of Eu incorporation in the presence of $NO_3^-$ -ions has to be assumed. Therefore, the uptake of $Eu^{3+}$ by calcite is stongly influenced by the presence of trace amounts of $NO_3^-$. Considering the ubiquity of nitrate in the geosphere, this will highly affect modelling calculations for long term safety of nuclear waste deposits.

## Reference

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