

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, ClO₄⁻ 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:

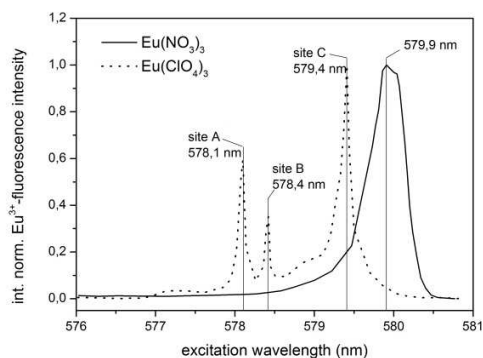
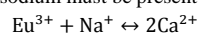


Figure 1: TRLFS excitation spectra of Eu³⁺ doped calcite with nitrate (one site) and perchlorate (three sites) as counterion

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 lanthanide ion (Horrock's equation^[2]). As no other sites could be found, a new mechanism of Eu incorporation in the presence of NO₃⁻ -ions has to be assumed. Therefore, the uptake of Eu³⁺ by calcite is strongly influenced by the presence of trace amounts of NO₃⁻. Considering the ubiquity of nitrate in the geosphere, this will highly affect modelling calculations for long term safety of nuclear waste deposits.

Reference

- [1] Schmidt (2008) *Angew. Chem. Int. Ed* 47, 5846–5850
- [2] Horrocks (1979) *J. Am. Chem. Soc.* 101, 334