



## **Structural incorporation of Eu(III) into calcite: process understanding on a molecular level**

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Demonstrating the geochemical aspects of the long term safety of a nuclear waste repository can significantly be improved by a molecular level understanding of the actinides behavior in the geosphere. In particular the interaction of radionuclides with minerals (adsorption, structural incorporation) strongly affects their mobility and retardation. In this presentation we will focus on the interaction of trivalent actinides and lanthanides with calcite, with special focus on the structural incorporation. Calcite ( $\text{CaCO}_3$ ) is an omnipresent mineral in many rocks which are discussed as potential host for a nuclear waste repository. Furthermore, many waste repository designs include cement based components. Calcite is one of the major secondary alteration products formed during the degradation of cement over geological timescales. Actinide and lanthanide partition data derived from co-precipitation experiments indicate a high sorption affinity of these elements to calcite but a comprehensive understanding of actinide and REE uptake by calcite is not yet available. From a geochemical perspective the molecular level substitution mechanism is of key interest. Trivalent actinides and lanthanides have a similar ionic radius compared to Ca, the charge compensation mechanism upon substitution is unclear despite various recent studies. We have studied synthetically doped calcite crystals with Time Resolved Laser Fluorescence Spectroscopy and Extended X-Ray Absorption Fine Structure Spectroscopy. The focus has primarily been on Eu(III), due to its fluorescence properties. The structural parameters of Am(III) doped calcites obtained by EXAFS confirm the substitu-

tion of  $\text{Ca}^{2+}$  within the calcite structure. Site-selective TRLFS measurements at temperatures  $< 20$  K show the presence of various incorporated molecular species. The incorporation into calcite involves several structurally distinguishable "sites". These sites may be due to local lattice distortions/relaxations around the metal ion in the calcite structure. These investigations give a mechanistic understanding of the incorporation process and show that the incorporation of trivalent metal ions is not a simple coupled substitution mechanism but involves complex substitution mechanisms.