

## Incorporation of Eu(III) into Calcite under different Recrystallization conditions

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Calcite is a ubiquitous mineral in the earth's crust. Its capacity to incorporate guest ions with similar ionic radius as  $\text{Ca}^{2+}$  (e.g.  $\text{Eu}^{3+}$ ,  $\text{Pu}^{3+}$ , and  $\text{Am}^{3+}$ ) makes it interesting for various environmental issues as well as for safety assessment of nuclear waste disposal sites. Here the trivalent later actinides with long half-lives (like Am and Cm) comprise the most of the long-term radiotoxicity.

For our experiments we used Eu as homologue because of its similar ionic charge and radius and its preferable luminescence properties [1]. We conducted batch studies with three calcite powders, which differ in their specific surface area (SSA) and recrystallization rates (Rr) (Fig. 1). The speciation of the incorporated Eu(III) was then investigated by site-selective time-resolved laser fluorescence spectroscopy. With increase of the recrystallization rate incorporation occurs faster and the speciation comes to be dominated by one species with its excitation maximum at 578.9 nm. Previous investigations of this process under growth [2] and phase transformation conditions [3] had not identified this species. A long lifetime of  $\sim 3000 \mu\text{s}$  demonstrates complete loss of hydration [4], consequently Eu must have been incorporated into the bulk crystal.

The results show a strong dependence of the incorporation kinetics on the recrystallization rate of the different calcites. The predominance of the newly identified species seems to be independent of this kinetic effect, however.

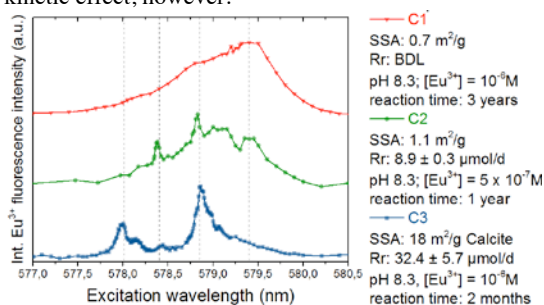


Fig. 1: Excitation spectra of calcite C1, C2 and C3 at different contact times

- [1] Binnemans (2015) *Coord. Chem. Rev.* 295, 1-45  
 [2] Schmidt (2008) *Angew. Chem., Int. Ed.* 47, 5846-5850  
 [3] Schmidt (2010) *J. Colloid Interface Sci.* 351, 50-56  
 [4] Horrocks (1979) *J. Am. Chem. Soc.* 101, 334.