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Probing the interaction of Eu^{3+} and Cm^{3+} with $CaCO_3$ pre-nucleation clusters

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Since the first reports on stable $CaCO_3$ pre-nucleation clusters (*1, 2*), numerous studies invetigated the influence of such clusters on nucleation pathways (*3*). Not as much in the focus were their potential interactions with trace elements.

Here we report on laser luminescence spectroscopic investigations of Eu^{3+} and Cm^{3+}, which are used as highly sensitive homologue probes for trivalent Actinde elements, at conditions (pH, $c(Ca^{2+})$, $c(CO_3^{2-})$), at which we may expect the formation of $CaCO_3$ pre-nucleation clusters (*1*).

Spectra and fluorescence lifetimes recorded for defined Eu^{3+}- and Cm^{3+}-carbonato complexes and in corresponding solutions additionally containing Ca^{2+}, clearly indicated changes in Eu^{3+}- and Cm^{3+} speciation upon Ca^{2+} addition. This likely indicates the interaction of Eu^{3+} and Cm^{3+} with $CaCO_3$ pre-nucleation clusters. So far we can, however, not exclude the possibility, that the new species reflect rather a new type of ternary Eu^{3+}/Cm^{3+}-CO_3^{2-}-Ca^{2+} solution complexes.

Either way, the new species represent potential precursors for Eu^{3+} and Cm^{3+} co-precipitation with $CaCO_3$ minerals (calcite/aragonite/vaterite, cf. e.g. (*4, 5*)), and will need to be taken into account in future thermodynamic models for Eu^{3+}/Cm^{3+} incorporation into these mineral phases.

As solution species in general, these complexes are likely of minor importance, as they mainly exist in meta-stable solutions, which are significantly supersaturated with respect to calcite.

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