Interaction of Eu(III) with calcite surfaces in presence of $NaNO_3$

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Calcite is one of the most abundant minerals in the earth's crust, playing an important role as a geochemical barrier in nuclear waste deposits. It is known to adsorb and even incoporate many metal ions including lanthanides and actinides [1, 2]. In this study, we present the influence of $NaNO_3$ on the calcite surface and the uptake of Eu(III), investigated by site-selective time resolved laser fluorescence spectroscopy (TRLFS) and atomic force microscopy (AFM).

Discussion of results

TRLFS measurements with Eu(III) as a molecular probe showed that the lanthanide ion is not incorporated into the calcite crystal itself. Excitation and emission spectra (Fig. 1) differ considerably from the well-known Eu^{3+}/calcite solid solution [3]. The fluorescence lifetime of this Eu^{3+}/NO_3^- /calcite species was determined to be $630 \pm 50\ \mu s$, indicating the presence of only one water molecule in the first coordination shell of Eu.

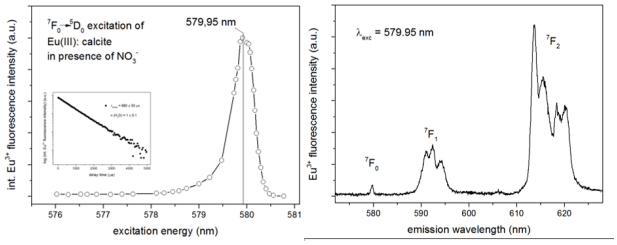

Figure 1: TRLFS excitation and emission spectra.

For further characterization of the influence of $NaNO_3$, calcite single crystals were equilibrated in aqueous $NaNO_3$ solutions (10^{-7} to 10^{-2} M) and measured *in situ* with AFM. Images of these samples reveal critical changes of the surface morphology (roughening of the facets and rounding of step edges). An amorphous, soft layer forms rapidly on top of the calcite lattice. Europium seems to be incorporated into this layer, which is about 0.8 ± 0.1 nm thick.

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Using compound-specific isotope analysis to assess biodegradation of nitroaromatic explosives in the subsurface

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Assessing the fate of nitroaromatic explosives in soils and sediments is challenging because these contaminants are present in different phases, that is bound to the organic and mineral matrix or as solid-phase residues, and transformation takes place via several competing pathways over time-scales of decades. To infer the type and extent of biotransformation of nitroaromatic compounds (NACs) from the combined evaluation of their C, N, and H isotope signatures, we have developed procedures for compound-specific analysis of 2,4,6-trinitrotoluene (TNT), dinitrotoluene isomers (2,4-DNT and 2,6-DNT), and mono-nitrotoluenes in subsurface material from a contaminated site.

Because of repeated spill events during decades of site operation as well as the perturbed subsurface at the study site, neither concentration nor $\delta^{13}C$, $\delta^{2}H$, or $\delta^{15}N$ profiles provided evidence for transformation. Correlation of N vs. C and H vs. C isotope fractionation, in contrast, enabled to the identification of three biodegradation routes.

Indicative trends of $\Delta\delta^{15}N$ vs. $\Delta\delta^{13}C$ and $\Delta\delta^{2}H$ vs. $\Delta\delta^{13}C$ were obtained from laboratory model systems with pure cultures for reaction pathways initiated via (i) dioxygenation, (ii) reduction, and (iii) CH_3-group oxidation. The comparison of $\Delta\delta^{15}N$ vs. $\Delta\delta^{13}C$ from field and laboratory data enabled a distinction of reductive and oxidative transformation of TNT, 2,4-DNT, and 2,6-DNT while $\Delta\delta^{2}H$ vs. $\Delta\delta^{13}C$ was used to quantify the relative shares of dioxygenation and CH_3-group oxidation. Based on the apparent kinetic isotope effects of the three biodegradation routes, our data imply that 86-89% of 2,4-DNT transformation in the field was due to dioxygenation while TNT was mostly reduced to aminonitrotoluenes and 2,6-DNT reacted via a combination of reduction and CH_3-group oxidation. Isotopic and historic site information suggest biodegradation of 2,4-DNT with half-lives of up to 9 to 17 years compared to 18 to 34 years for co-metabolic transformation of TNT and 2,6-DNT.

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