Structural incorporation of Eu(III) into calcite, Aragonite and Vaterite: A comparative TRLFS study

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The behaviour of actinides in the environment is to a large extent governed by reactions like adsorption, ion exchange and incorporation processes. Especially the incorporation of actinides into secondary phases and the formation of "solid solutions" play a key role in the retardation process. In this presentation we will focus on the interaction of Eu(III) taken as a chemical homologue to trivalent actinides with calcium carbonates, with special emphasis on structural incorporation.

Calcium carbonates homogeneously doped with Eu^{3+} were synthesized in a mixed-flow-reactor. All three stable polymorphs - calcite, aragonite and vaterite – were investigated.

Site-selective time resolved laser fluorescence spectroscopy (TRLFS) on Eu^{3+} at low temperatures (< 20K) was used because the non-degeneracy of Eu^{3+} fluorescing states ($^5D_0 \rightarrow {}^7F_0$) gives rise to a single emission line for each species and facilitates determination of the number of non-equivalent sites. Furthermore, this selective excitation allows to record emission spectra of different sites in a sample separately with high selectivity. In particular the coordination symmetry of each site can be identified since the splitting of the $^7F_2$ state is very sensitive to changes in the ligand field. Moreover, the number of water molecules in the first coordination sphere of the metal ion was determined by measuring the fluorescence intensity as a function of time after excitation.

Eu^{3+} exhibits different sorption behavior on all three investigated mineral phases. In the aragonite and vaterite system Ca^{2+} substitution by Eu(III) is the only observed form of interaction, which is evident by the corresponding emission spectra and fluorescence lifetimes. In contrast, in calcite two incorporated species of different coordination symmetry and one partly hydrated surface species were identified.

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Noble gas radionuclides and ATTA in hydrology: State of the art

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The Atom Trap Trace Analysis (ATTA) method was first demonstrated for pure Kr gas in 1999 with an efficiency of 10^{-7} [1]. Since then its efficiency has been improved by a factor of 10^3 and enabled us to measure radiokrypton isotopes, ^{81}Kr ($t_{½}$ = 229,000 yr, isotopic abundance in air ~10^{-12}) and ^{85}Kr ($t_{½}$ = 10.8 yr, isotopic abundance in air ~10^{-11}), in Kr extracted from samples of air and water [2, 3]. ^{81}Kr measurements of air samples showed no measurable difference in the $^{81}Kr/Kr$ ratio of pre-bomb and post-bomb air [2]. Measurements of Kr extracted from large (> 2,000 L) groundwater samples from the Nubian Aquifer in the Western Desert of Egypt showed ^{81}Kr residence times approaching one million years, in good agreement with ^{36}Cl data and numerical hydrodynamic models [3]. A number of other hydrologic studies using ATTA are currently in progress. Improvements have been made in methods of dissolved gas extraction from large water samples (using hydrophobic membranes) and in purification of Kr from the resulting large gas samples [4]. Recent advances in ATTA design will increase both its counting rate and efficiency, and may allow measurement of ^{39}Ar. At 1% efficiency, the required sample size for ^{81}Kr measurements is only ~10 L of water or ice, enabling a much wider range of applications in the earth and environmental sciences.

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