Report on sequestration of Eu(III), Se(IV,VI), and Np(V) by Calcite

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANAGEMENT

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SEQUESTRATION OF EU(III), SE(IV,VI), AND NP(V) BY CALCITE

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Introduction

Calcite is the most common polymorph of calcium carbonate and the thermodynamically most stable at standard conditions (room temperature and atmospheric pressure). It is abundant in many environmental settings and plays a key role in controlling the geochemical milieu (pH, alkalinity) of soils and ground water. In the surroundings of potential nuclear waste disposal sites calcite is e.g. present as a mineral constituent in clay formations (up to 20 % in some cases), as fracture filling material in granitic rocks, or as a corrosion product of concrete based materials in the technical barrier. Due to the high reactivity of its surface and its tendency to tolerate considerable variation in its chemical composition, calcite has often been considered as a mineral phase with a high potential for the sequestration of toxic metals.

Selenium and Neptunium are of direct concern for save nuclear waste disposal due to the long half-life of the isotopes [79]Se and [237]Np and the expected high mobility of the corresponding oxidized species. [79]Se is present in nuclear waste as a fission and decay product and [237]Np is a minor actinide, which is produced in nuclear reactors by neutron activation of [235]U or by alpha decay of [241]Am. Europium itself has only little relevance as a fission and decay product. It is studied as a chemical homologue for trivalent minor actinides Pu(III), Am(III), and Cm(III), which dominate the radiotoxicity of nuclear waste on long time scales.

In this report we will focus on new experimental results on Eu(III). Concerning Se(VI), we recently showed that it does neither interact significantly with the calcite surface, nor

does it coprecipitate with calcite in significant amounts at surface controlled crystal growth conditions (Heberling et al., (submitted)-a). Only starting from highly supersaturated solutions, Se(VI) coprecipitation with calcite has been reported (Staudt et al., 1994). About Se(IV) we reported in the previous annual workshop proceedings (JUEL-4364, 2013), and recently submitted a manuscript on an adsorption / entrapment model (Heberling et al., (submitted)-b). This model is based on the observations that Se(IV) adsorbs in small but significant amounts at the calcite surface and that this adsorption is equivalent to the formation of a surface monolayer solid solution with a partition coefficient of D = 0.016±0.012. At elevated supersaturation this surface solid solution can be entrapped by growing calcite, keeping its composition. However, the precipitated solid solution reflects non-equilibrium conditions. Equilibrium incorporation of Se(IV) into calcite is virtually impossible, $D \approx 10^{-9}$.

Concerning Np(V), we previously showed that upon coprecipitation Np(V) is structurally incorporated into calcite (Heberling et al., 2008b), Np(V) adsorbs quite strongly at the calcite surface (Heberling et al., 2008a), and the presence of surface adsorbed Np(V) has significant impact on the calcite growth rate (Heberling et al., 2011). After the very promising results of aragonite to calcite recrystallization experiments in the presence of Se(IV) (Heberling et al., (submitted)-b) and Eu(III) (this work) we launched similar experiments in the presence of Np(V). Experiments aim at Np(V) coprecipitation with calcite at very low supersaturation (SI(calcite) = 0.14) as a function of ionic strength and comparing two different background electrolytes (NaCl and KCl) and correspondingly different cations, which may provide charge compensation upon structural incorporation. However as calcite growth at these experimental conditions is extremely slow, the experiments are still ongoing and conclusive results cannot yet be reported.

Back to Eu(III), we report here aragonite to calcite recrystallization experiments in the presence of 1 µmol/L Eu(III) at two solid to liquid ratios, 20 g/L and 0.2 g/L, and a laser fluorescence spectroscopic investigation of the corresponding reaction products. The results allow us to identify the most relevant substitution mechanism for Eu(III) in calcite and to narrow down the Gibbs free energy of a possible virtual $NaEu(CO_3)_2$ endmember of the dilute $NaEu(CO_3)_2$-calcite solid solution. Interestingly, incorporation species observed in this study agree only partly with those observed before upon Eu coprecipitation with calcite at higher supersaturation (Marques Fernandes et al., 2008;

Schmidt et al., 2008; Schmidt et al., 2010), highlighting the importance of experiments at close to equilibrium conditions.

Experimental Details

In this study calcite precipitation is induced by aragonite dissolution / recrystallization. This reaction is based on the principle that aragonite is more soluble than calcite at standard conditions, with the solubility products (K_{SP}) being $\log_{10}(K_{SP}(aragonite)) = -8.34$ and $\log_{10}(K_{SP}(calcite)) = -8.48$, respectively. Therefore, an aragonite equilibrated solution is at standard conditions always supersaturated with respect to calcite with SI(calcite) = 0.14. This gives us the possibility to perform very simple batch type calcite growth experiments at very stable low supersaturation conditions, which are hardly achievable in classical precipitation experiments.

The aragonite we use is synthesized by mixing 0.5 molar Na_2CO_3 solution and 0.5 molar $CaCl_2$ solution at 90 °C. After two to three minutes the precipitated powder is separated from solution by filtration and dried in an oven at 105 °C. The resulting aragonite contains traces of calcite (~0.3%) and halite (<1%). The BET surface area of the aragonite powder is 4 m^2/g.

In a kinetic experiment 1 g of aragonite is brought in contact with 50 mL of 0.1 molar NaCl solution containing 1 μmol/L Eu^{3+} (S/L = 20 g/L), and in a second series of "equilibrium" experiments 0.2 g of aragonite are exposed to 1000 mL of 0.1 molar NaCl solution containing 1 μmol/L Eu^{3+} (S/L = 0.2 g/L). The kinetic experiment is planned as a multisampling experiment, with the aim to monitor the reaction progress, while the "equilibrium" experiments at low S/L ratio are planned as single point measurements, originally aiming at the determination of a Eu-calcite partition coefficient. The kinetic experiment is sampled after: 1, 4, 11, 48, 97, 193, and 420 days. With each sampling the suspension is thoroughly agitated and 5mL of homogeneous suspension are pipetted directly onto a filter membrane. The separated powder is dried in an oven at 105 °C , and analysed by powder XRD on a Bruker D8 advance powder diffractometer. For the quantitative analysis of the aragonite and calcite content of the powder we use the Topas 4.2 Rietveld refinement software from Bruker AXS. By comparison to a parallel kinetic experiment without Eu^{3+} (Heberling et al., (submitted)-b) we can learn about the influence of Eu^{3+} on the recrystallization kinetics.
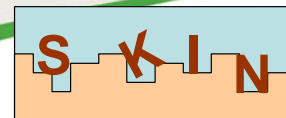
The "equilibrium" experiments are sampled after 580 days. The dried powders are analysed by powder XRD as described above and the solutions are analysed for Ca^{2+} and Eu^{3+} by ICP-MS.

Samples of the kinetic experiments after one day and after 400 days and one sample of the "equilibrium" experiment are investigated by site selective time resolved laser fluorescence spectroscopy (TRLFS). We perform TRLFS measurements on a Nd-YAG laser pumped optical parametric oscillator (OPO) laser system. The wavelength of the laser light is tuned with a resolution of 0.01 nm. The sample is cooled to 20 K during the measurements. First we record an excitation spectrum by scanning the excitation wavelength from 575 nm to 582 nm and recording the total fluorescence yield. In this excitation spectrum each Eu-species with a distinct chemical environment produces an individual peak at a certain wavelength, which corresponds to the energy level of the species' $^7F_0$ - $^5D_0$ transition. In a second set of measurements we directly excite the $^7F_0$ - $^5D_0$ transitions of the species and record the corresponding fluorescence emission spectra. The ground state splitting of the fluorescence emission allows us to draw conclusions about the symmetry of the coordination environment around a certain species (cf. e.g. (Schmidt et al., 2008)) or can be used like a fingerprint to identify similar species in different samples.

Results and Discussion

The results of the powder diffraction analyses concerning the calcite content of the samples taken during the kinetic experiment are summarized in Figure 1. Figure 1 clearly shows that in the kinetic experiment at high S/L ratio the recrystallization rates in absence and presence of Eu^{3+} are very similar, i.e. Eu^{3+} has no significant influence on the recrystallization rate. A decreased reaction rate at the beginning and the end of the experiment is observable. If we assume that the period between 97 and 193 days represents a steady state regime, we can approximate the reaction rate, R, during this period to be R=$2 \cdot 10^{-10}$ mol/($m^2 \cdot$ s), which is indeed very slow compared to other calcite precipitation experiments (Curti, 1999). This value is only a rough approximate because we do not know exactly, which is the relevant reactive surface area, that should be considered. As a first approximation we use the surface area of the original aragonite in this calculation.
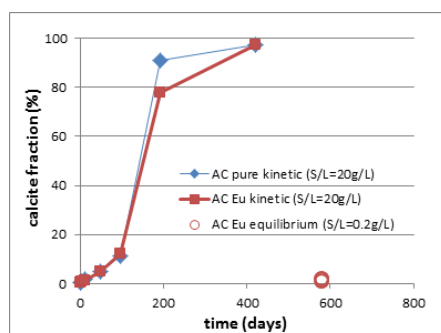
Figure 1: Calcite content of the samples from kinetic (AC Eu kinetic) and "equilibrium" experiments (AC Eu equilibrium) as obtained from the analysis of powder diffraction data. The kinetic experiment in the presence of Eu^{3+} is compared to data obtained in Eu^{3+}-free experiments (AC pure kinetic) (Heberling et al., (submitted)-b).

The TRLFS spectra of the almost pure Eu doped calcite (97.5 %) after 400 days of the kinetic experiment reveals that the Eu-speciation in this sample is dominated by one species, which is excited at 579.55 nm. Two minor species are excited at 579.65 nm and 579.75 nm, respectively (Figure 2a).
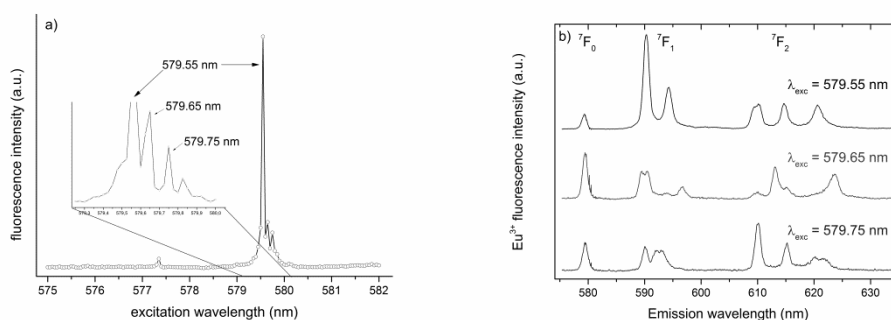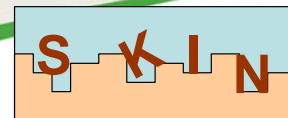

Figure 2: TRLFS excitation (a) and emission (b) spectra of Eu-doped calcite after 400 days of recrystallization.

Small peaks at 577.80 nm and 579.85 nm are likely not indicative for a particular Eu-species, as no distinct emission spectra were detectable upon excitation into these bands. Emission spectra of the three confirmed Eu-species are shown in Figure 2b. The

species at 579.55 nm can be clearly identified as the well-ordered incorporation species reported earlier (Marques Fernandes et al., 2008; Schmidt et al., 2008). A direct comparison between the emission spectrum recorded in this study and that of the earlier studies is shown in Figure 3. Marques Fernandes et al. and Schmidt et al. showed that there is clear evidence that this species is related to Eu^{3+} incorporated into the calcite structure according to a coupled substitution mechanism, in which two Ca^{2+} are substituted by one Eu^{3+} and one Na^{+}.

Interestingly, in earlier studies, in which calcite was precipitated at higher supersaturation compared to this work, this incorporation species was always accompanied by two further species at 578.1 nm and 578.4 nm, which were interpreted as a surface species and a low symmetry incorporation species (Marques Fernandes et al., 2008; Schmidt et al., 2008). These species are absent in our present study. The two minor species we observed at wavelengths higher than 579.55 nm have not been reported before.
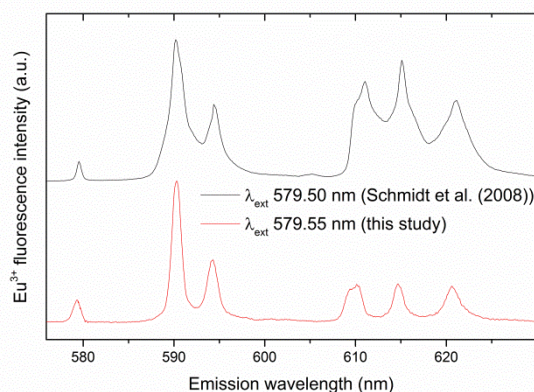

Figure 3: *Comparison of emission spectra of the main species identified in Eu-doped calcite in this study and the well-ordered incorporation species reported earlier (Schmidt et al., 2008).*

Due to technical problems we could not perform fluorescence lifetime measurements and prove structural incorporation of the Eu-species during this study, but due to the similarity of the emission spectra (Figure 3) we interpret our main species in analogy to Marques Fernandes et al., 2008 as $NaEu(CO_3)_2$ in calcite. The two minor species at
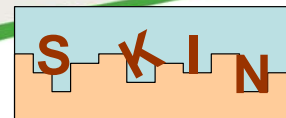
579.65 nm and 579.75 nm are, due to the strong red shift and the fluorescence emission spectra, likely less ordered incorporation species. The fact that the main species in our experiment can be attributed to a $NaEu(CO_3)_2$-calcite solid solution, provides us with important information for further quantitative modelling of the incorporation process.

A first surprising result is observed in TRLFS spectra measured on aragonite contacted with Eu^{3+} containing solution for one day during the kinetic experiment (Figure 4). Only one Eu-species can be identified. This species coincides perfectly with a structural incorporation species of Eu^{3+} in aragonite reported earlier (Schmidt et al., 2009). The broad shoulder from 578.0 to 579.2 nm is possibly caused by minor Eu^{3+} species which could not be further resolved and characterized.
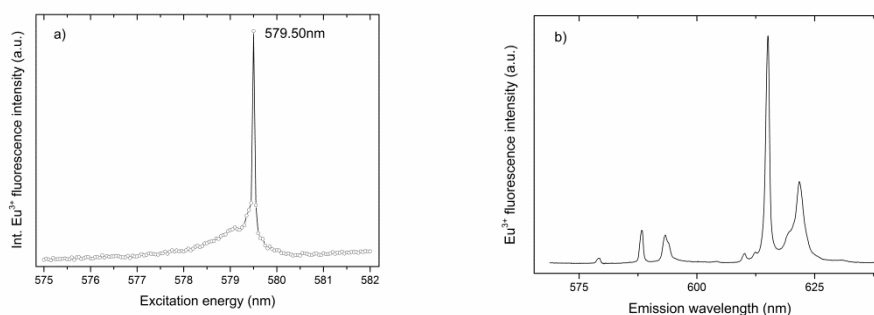

Figure 4: *Excitation and emission spectrum of Eu^{3+} in aragonite.*

Accordingly, aragonite does not only dissolve to form calcite, but undergoes as well a surface recrystallization, which leads to Eu^{3+} incorporation into aragonite within 24 h.

The biggest surprise, however, is certainly that in the "equilibrium" experiments at low S/L ratio we observe virtually no formation of calcite. The calcite content of three independent samples increased during the reaction period only from initially 0.3 % to 1.0 % to 1.9 % after 580 days. The TRLFS spectrum of the aragonite after 580 days in the "equilibrium" experiment (not shown here) is quasi identical to the one observed in the kinetic experiment after one day (Figure 4).

ICP-MS measurements revealed that 99.4 % of the Eu^{3+} sorbs at aragonite. As mentioned above, TRLFS identified an incorporation species for Eu^{3+} sorbed at aragonite. If correspondingly we interpret the sorption as a solid solution formation
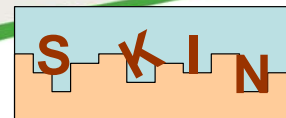
process and assume that, as in calcite, coupled substitution of sodium provides charge balance, the partition coefficient of $NaEu(CO_3)_2$ in aragonite would be D(aragonite) = 1350. If we interpret the sorption as a surface recrystallization reaction and quantify the result in terms of an adsorption K_D, the corresponding value would be K_D = 200 L/m^2, and the observed surface coverage would correspond to about 10% of a monolayer.

The fact that Eu^{3+} sorbs at aragonite offers us the possibility of a tentative explanation, why we observe aragonite dissolution and consecutive formation of calcite only at high solid to liquid ratio. According to spectroscopy results Eu^{3+} incorporation into calcite may be described as a solid solution between $NaEu(CO_3)_2$ and $Ca_2(CO_3)_2$. A phase similar to the Eu-endmember $NaEu(CO_3)_2 \cdot 6 H_2O$ has a solubility product of $\log_{10}(K_{SP}(NaEu(CO_3)_2 \cdot 6 H_2O))$ = -20.5 (Curti et al., 2005; Fannin et al., 2002). Analogously to the approach we applied previously (Heberling et al., (submitted)-b) we assume that the dilute solid solution obeys Henry's law and we can describe the Eu^{3+} incorporation into calcite as a virtual pseudo-ideal solid solution between a virtual $NaEu(CO_3)_2$ endmember and $Ca_2(CO_3)_2$. The solubility product of the virtual endmember is defined such that the virtual solid solution is ideal by definition and describes the real behaviour of a $Na_XEu_X,Ca_{(2-2X)}(CO_3)_2$ solid solution in a limited range of $NaEu(CO_3)_2$ content in calcite.

Model calculations show that, if we consider thermodynamics of whole system involved, i.e. the total amount of solid and liquid, the calcite solid-solution is in any case more stable than aragonite, no matter how we choose the solubility of the virtual $NaEu(CO_3)_2$ endmember. Therefore, we may rule out any simple thermodynamic explanation. On the other hand, the kinetic experiment indicates that Eu^{3+} incorporation has no significant impact on the calcite growth or aragonite dissolution rate. This makes a kinetic inhibition effect as an explanation unlikely as well. However, if we assume that in order to grow calcite we need an initial small amount of Na,Eu-calcite solid solution, e.g. a growth nucleus, which is in partial equilibrium with the aqueous solution, it is possible to show that such initial small nuclei become unstable relative to aragonite at low solid to liquid ratio, if $\log_{10}(K_{SP}(NaEu(CO_3)_2:virtual)) \leq$ -21.3. According to such a scenario the system of a 0.2 g/L aragonite in suspension and $4.8 \cdot 10^{-9}$ mol/L Eu^{3+} in solution (after adsorption of 99.4% of the Eu^{3+} at the aragonite surface) remains in a metastable state and calcite cannot form, because any initial calcite nuclei must contain a high amount of Eu^{3+} and this destabilizes them relative to aragonite. This relation is illustrated in Figure 5.
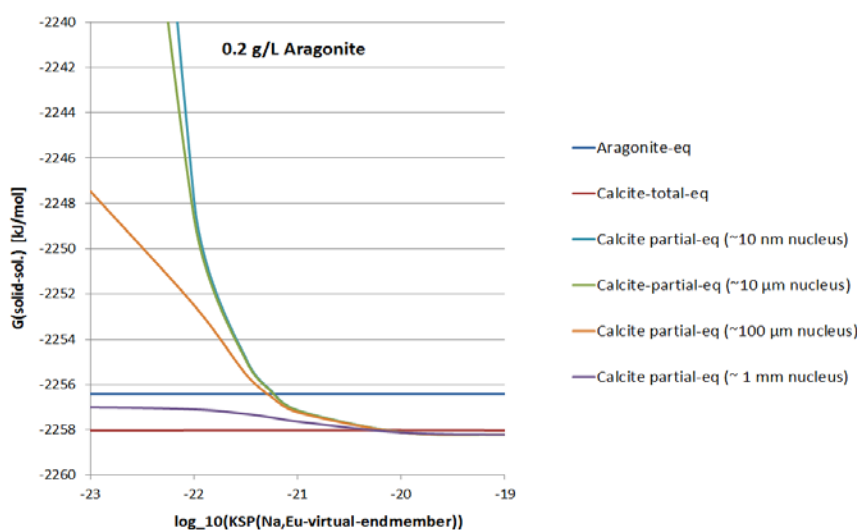
Figure 5: Gibbs free energy of single Na,Eu-calcite solid solution particles in partial equilibrium with aqueous solution as a function of the solubility product of the virtual NaEu(CO₃)₂ endmember. Shown are a series of nuclei of various sizes and total calcite and aragonite equilibria for comparison. For $log_{10}(K_{SP}(NaEu(CO_3)_2:virtual)) \leq -21.3$ small solid solution nuclei are unstable relative to aragonite. Recrystallization could in such a scenario only occur if large amounts of calcite, corresponding to a ~1 mm nucleus, would form instantaneously. This is extremely unlikely. On the other hand, for $log_{10}(K_{SP}(NaEu(CO_3)_2:virtual)) \geq -21.2$ a corresponding metastable situation cannot be achieved at all.

In a similar scenario at higher solid to liquid ratio the Eu^{3+} concentration in solution is much lower because more Eu^{3+} is adsorbed at the aragonite surfaces. A corresponding calculation as depicted in Figure 5 is not shown for this scenario, but the resulting curves look identical only that the whole diagram is shifted to lower solubility products and the change to stable nuclei appears already at smaller nucleus sizes. Correspondingly, a metastable suspension is much less likely. For a precise calculation, the amount of Eu^{3+} sorption at 20 g/L aragonite needs to be known. Depending on the Eu^{3+} sorption mechanism, formation of an aragonite solid solution or adsorption, the estimated Eu^{3+} concentration in solution varies between 10^{-11} mol/L and 10^{-9} mol/L and
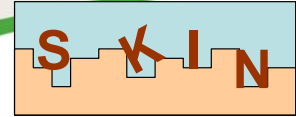
this uncertainty has a high impact on any model calculation. Nevertheless, due to sorption of Eu^{3+} at aragonite, the Eu^{3+} concentration in solution is always lower at the higher S/L ratio than at lower S/L ratio, and this likely explains the difference between the kinetic and the "equilibrium" experiments (which never reached equilibrium).

Conclusions and Future work

Experiments confirm the very high affinity of Eu^{3+} towards incorporation into $CaCO_3$ minerals aragonite and calcite.

Sorption at aragonite proceeds, depending which mechanism is assumed, with an adsorption $K_D = 200$ L/m^2 or a solid solution partition coefficient, $D = 1350$.

On Eu-reacted aragonite only incorporation species are detected by TRLFS.

At high solid to liquid ratio, Eu^{3+} incorporation into calcite has no significant impact on the calcite growth / aragonite dissolution rate.

TRLFS indicates that coupled substitution corresponding to the formation of a $Na_xEu_xCa_{(2-2x)}(CO_3)_2$ solid solution between $NaEu(CO_3)_2$ and $Ca_2(CO_3)_2$ endmembers, is the most relevant incorporation mechanism for Eu^{3+} in calcite involved in experiments in this study. Comparison to previous studies shows that this is not generally the case. In previous studies (Curti et al., 2005; Marques Fernandes et al., 2008; Schmidt et al., 2008) other mechanisms were identified to be most likely, or the Na,Eu incorporation species was accompanied by significant amounts of other species.

At low solid to liquid ratio a meta-stable situation can be achieved and calcite formation is inhibited. This phenomenon may only be explained for a solubility of the virtual $NaEu(CO_3)_2$ endmember of $\log_{10}(K_{SP}(NaEu(CO_3)_2:virtual)) \leq -21.3$.

In a next step we will investigate Eu^{3+} species in calcite and aragonite by EXAFS spectroscopy. Future experiments will aim at the substitution mechanism of Eu^{3+} in aragonite and will test the meta-stability of aragonite suspension at low S/L ratio in the presence of Eu^{3+}.

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