

# The effect of $\text{Se(IV)O}_3^{2-}$ and $\text{Np(V)O}_2^+$ on calcite growth

LUKAS ZUNFTMEISTER<sup>1</sup>, EVA SOBALLA<sup>2</sup>, DIETER SCHILD<sup>3</sup> AND FRANK HEBERLING<sup>3</sup>

<sup>1</sup>KIT

<sup>2</sup>KIT - INE

<sup>3</sup>Karlsruhe Institute of Technology

Presenting Author: Lukas.Zunftmeister@kit.edu

In natural systems, calcite is subject to dynamic dissolution and re-precipitation processes. These yield a substantial retention potential for contaminants if impurity uptake is involved. In this study we investigate the recrystallization of aragonite into its polymorph calcite in presence of the impurity ions  $\text{Se(IV)}$  ( $\text{SeO}_3^{2-}$ ) and  $\text{Np(V)}$  ( $\text{NpO}_2^+$ ). Selenium and Neptunium are part of spent nuclear fuel. Due to the long half-lives of  $^{79}\text{Se}$  ( $3.8 \times 10^5$  a) and  $^{237}\text{Np}$  ( $2.1 \times 10^6$  a) and the expected mobility of selenium and neptunyl, retention of these isotopes by calcite crystals in the host rock may be relevant for the long-term safety of nuclear waste repositories. Under thermodynamic considerations, recrystallization of aragonite into calcite should happen spontaneously. Experiments indicate that in pure systems kinetics are rather fast ( $< 1$  a). However, both  $\text{SeO}_3^{2-}$  and  $\text{NpO}_2^+$  inhibit this process while at the same time being taken up at calcite and/or aragonite surfaces. For Se, a concentration dependent reduction of calcite crystallization rates was observed (Figure 1). At Se-concentrations above  $50 \mu\text{mol/L}$ , the recrystallization of aragonite into calcite is inhibited. The growth inhibition through  $^{237}\text{Np}$  was found to be even more effective. In the presence of  $1 \mu\text{mol/L}$   $^{237}\text{Np}$ ,  $< 2\%$  of the aragonite powder (100 mg solid/ 1L liquid) recrystallized into calcite after 2886 days when NaCl (0.1 mol/L) was used as electrolyte ( $\sim 5\%$  for 0.1 mol/L KCl). EXAFS results suggest an uptake of  $^{237}\text{Np}$  into aragonite, likely at the surface, and that uptake in the small amount of growing calcite plays no significant role.

The uptake of  $\text{SeO}_3^{2-}$  has been described as an entrapment process<sup>1</sup>, where at sufficiently high supersaturations, an impurity that is not compatible with the bulk crystal gets forced into the crystal through entrapment of a stable surface species. Recrystallization experiments conducted in this study provide complementary data on selenite uptake at low supersaturations ( $\text{SI}(\text{calcite}) \sim 0.14$ ) that are used to test and refine predicted excess enthalpies and partitioning coefficients for a virtual  $\text{CaSeO}_3$  solid-solution endmember.

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<sup>1</sup>Heberling, Frank; Vinograd, Viktor; Polly, Robert et al. (2014): *Geochimica et Cosmochimica Acta* 134, S.16–38.

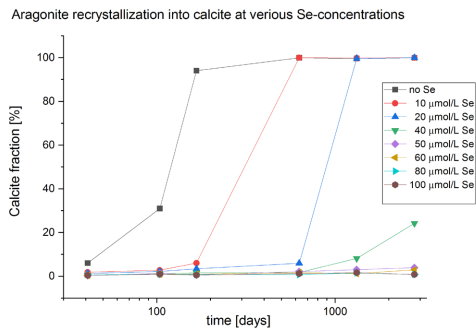


Figure 1: Recrystallization from aragonite to calcite in the presence of various amounts of aqueous selenite.