

Kinetics of ^{226}Ra incorporation into (Ba,Ra) SO_4 solid solutions

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(Ba,Ra) SO_4 solid solution formation is relevant as a retention mechanism for the safety assessment of deep geological repositories for nuclear waste. Earlier studies show that ^{226}Ra in contact with pure barite will be replaced by the (Ba,Ra) SO_4 solid solution during recrystallization, lowering the solubility of ^{226}Ra by several orders of magnitude compared to pure RaSO_4 [1]. However, a fundamental theoretical understanding of the Ra-uptake process in barite is still missing.

Accurate description of the hydrated ion and the mineral-water interface is a challenge when simulating barite crystal growth. The aim of our study is to determine the role of Ba^{2+} , Ra^{2+} , and SO_4^{2-} -ion attachment processes by computing activation energies for the kink-site-nucleation at the [120]-steps at the most relevant (001)-surface. We applied a combined hybrid density-functional theory (DFT) and soft-sphere continuum solvation (SSCS) approach to simulate barite-water interfaces and the nudged elastic band (NEB) approach to compute activation energies for the attachment-detachment processes. A set of models of the stepped barite (001)-surface structure, considering all relevant positions for kink-site-nucleation was constructed and verified by comparison with the available experimental data.

Ba^{2+} -ion attachment to this is a complex process mainly determined by bond formation of the ion with the surface and stepwise dehydration. The rate-limiting steps are the formation of the first bond to the barite surface and the complete uptake into the step – forming the new kink. The completely attached Ba^{2+} -ion is the configuration with the lowest energy. The energy pathway can explain barite growth exclusively by surface processes, which are also responsible for the experimentally observed anisotropic barite (001)-surface growth [2]. We discuss the obtained results against previous studies which applied classical force-fields [3]. Simulations show differences between Ra^{2+} and Ba^{2+} attachment to the barite (001)-surface caused by different coordination numbers of the hydrating water for Ra^{2+} and Ba^{2+} . Thus, Ra^{2+} uptake appears to be kinetically favored during recrystallization by easier dehydration.

[1] Brandt et al. 2020, *Minerals*, 10, 812. [2] de Antonio Gomez et al., *Cryst. Growth Des.* 13, 2840-2845. [3] Stack et al. 2012, *J. Am. Soc.*, 134, 11-14.