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Crystal growth of the barite (001)-surface in aqueous solution via a hybrid DFT- continuum solvation approach

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^{226}Ra is a major constituent of naturally occurring radioactive materials (NORM) and readily forms solid solutions with barite. In some scenarios for the direct disposal of spent nuclear fuel, ^{226}Ra dominates the dose after 100,000 years. Several studies have shown that upon contact with ^{226}Ra, original pure barite is replaced by the $(Ba,Ra)SO_4$ solid solution, which lowers the radium aqueous solubility by several orders of magnitude [1]. Recrystallization experiments indicate a wide range of 3 to 16,900 years until full equilibration [2]. While the thermodynamic aspects of the $(Ba,Ra)SO_4$ solid-solution have been extensively studied, the details of the molecular scale mechanisms controlling the Ra-uptake kinetics are not well understood.

Here we harness advanced methods of computational quantum mechanics: a hybrid Density Functional Theory (DFT) and Self Consistent Continuum Solvation (SCCS) approach for computation of barite-aqueous phase interface, and a Nudged Elastic Band (NEB) approach for computation of activation energies, to shed the light on the barite crystal growth process. The applied first principles-based approach represents an advancement comparing to previous atomistic modelling studies of Stack et al. [3], which apply a simplified, force-field-based description of interatomic interactions. We computed the activation energies for Ba^{2+}, Ra^{2+} and SO_4^{2-} attachment and incorporation into barite at relevant surface sites, allowing for a detailed understanding of the structural and kinetic aspects of barite crystal growth. In particular we characterized the Ba^{2+}, Ra^{2+} and SO_4^{2-} attachment on the barite (001) surface and the role of the aqueous phase in the process, focusing on "Kink-site-nucleation" [3]. The obtained results are compared to existing experimental data [4] and results of previous computational studies [3]. Similarities and differences between Ra and Ba uptake will be highlighted. In addition, we will discuss the stability of the nine most relevant barite-surface terminations. We will elucidate the challenges associated with applying atomistic simulations for understanding the details of crystal growth.

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