Linking molecular-level processes on crystal surfaces and macroscopic thermodynamics and kinetics modeling of reactions

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The doping of [137]Ba in the initial experimental solutions enabled us to measure unidirectional fluxes near solubility equilibrium in batch reactors [1]. Both attachment and detachment fluxes increase with [Ba]/[SO$_4$] ratios. As expected, since the solutions were near solubility equilibrium, the attachment and detachment fluxes were nearly equal. The experimental data can be fit accurately using the Zhang and Nancollas (1998) (ZN98) process-based AB crystal growth model, which describes crystal growth and dissolution through nucleation and propagation of kink sites. Simultaneous fitting step velocity data in the literature significantly reduced the number of non-uniqueness solutions. The remarkable fit implies that barite recrystallization at room temperature near equilibrium and moderate supersaturation occurs via ion-by-ion addition and removal, rather than the formation of amorphous precursors or aggregation of particles. The model is best fit using different detachment frequencies for Ba and SO$_4$, suggesting the ZN98 assumption that detachment frequencies should be the same for the constituent ions does not apply to barite. Based on experimental data and model fitting, Ba attachment and detachment fluxes at a fixed saturation state increase with [Ba]/[SO$_4$] ratios monotonically.

[1] Kang, J.T., J.N. Bracco, J.D. Rimstidt, G.H. Zhu, F. Huang, and C. Zhu. 2022. Ba attachment and detachment fluxes to and from barite surfaces in Ba-137-enriched solutions with variable Ba2+ / SO4(2-) ratios near solubility equilibrium. Geochimica Et Cosmochimica Acta 317: 180-200.