

Impact of Solution Stoichiometry on BaSO₄ and CaCO₃ Nucleation and Growth

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When ionic minerals like BaSO₄ and CaCO₃ form in natural or engineered aqueous environments, they commonly do so from non-stoichiometric solutions. Here, we studied the impact of solution stoichiometry on BaSO₄ and CaCO₃ nucleation and growth experimentally and computationally.

The first step of (pre)nucleation in non-stoichiometric conditions likely is the formation of (charged)-triple-ion clusters (CTIC) via the addition of a constituent ion that is in excess to an ion pair of BaSO₄ or CaCO₃ [1,2]. For the latter, this results in the formation of Ca₂CO₃²⁺ or Ca(CO₃)₂²⁻ CTIC. The free energy landscape of CTIC formation was investigated using Molecular Dynamics and metadynamics [2], revealing that the energies and lifetimes for positive and negative CTICs vary differently for BaSO₄ and CaCO₃.

Dynamic-Light Scattering and Zeta-potential measurements revealed that for both mineral phases, solution stoichiometry affects nanoparticle size and charge evolution asymmetrically [2-5]. Electron microscopy imaging of the particles formed further suggested that the morphology of the particles forming is distinct [3,4]. Solution transmission and optical light microscopy showed that a large excess of either cation or anion inhibits the nucleation and growth of both mineral phases also at longer time and length scales [5,6]. The dependence of barite nucleation and growth rates on supersaturation and solution stoichiometry was captured by a semi-empirical rate model [6] that combines scattering theory with two-step crystallization via nucleation and growth.

These results show that the solution stoichiometry is a highly relevant parameter to fundamentally understand BaSO₄ and CaCO₃ (pre-)nucleation and growth. Moreover, our results may help to improve the tailoring of ionic mineral formation in environmental, industrial and engineered settings.

References

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