

The impact of solution stoichiometry on crystal formation: Stability of charged triple-ion clusters

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When crystals form in natural aquatic systems such as seawater, pore fluids, and body fluids, nuclei form from solutions with widely diverging ratios of the crystal-building ions. One or both ions is generally externally controlled by e.g., weathering rates, redox conditions, physiology, or pH. However, laboratory as well as theoretical studies investigated crystal nucleation in fluids where the ion ratio matches that of the crystal lattice or vary in titration experiments. For existing crystals, it is known that growth rate depends strongly on the solution's ionic ratio, even if degree of supersaturation is kept constant (Kowacz et al., 2007; Wolthers et al., 2012). For nucleation, almost all experiments have been conducted at ideal ionic ratio, i.e., the cation:anion ratio of the uncharged final crystal. Nuclei, that form at these conditions are expectedly charge neutral, and their formation can be described with nucleation theories based on uncharged gas condensation into droplets (Benning & Waychunas, 2008). Recently, it was shown for CaCO₃ that the solution ionic ratio impacts nucleation asymmetrically (Seepma et al., 2021). Here, we test the hypothesis that, when there is a shortage of one lattice-building ion, it is more likely that the main nucleation path is through the formation of charged triple-ion clusters. This triple-ion cluster can be positive (with two cations and one anion) or negatively charged (with two anions and one cation). To investigate if there is a difference in stability and lifetime of the triple-ion-clusters, we performed classical molecular dynamics with metadynamics. Results indicate a possible cause of the asymmetrical behaviour when nucleation occurs under non-stoichiometric conditions for some mineral systems.

References

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