



The effect of specific background electrolytes on water structure and solute hydration: consequences for crystal dissolution and growth

M. Kowacz, A. Putnis

Institut für Mineralogie, University of Münster, Germany

We use barium sulfate as a model system to illustrate how solution composition can affect the thermodynamic and kinetic properties of a precipitating/dissolving crystal. We show that solubility, rates of reactions, modes of growth and morphological features can be modified by the introduction of simple ionic salts, due to the effects of these electrolytes on water structure dynamics and solute and surface hydration which in turn influence electrostatic interactions in the reacting system.

Based on the results of AFM *in situ* experiments we show that the kinetics of growth and dissolution of barium sulfate changes under conditions of constant thermodynamic driving force (supersaturation) and constant ionic strength (IS) depending on the background electrolyte used to adjust IS. Salt-specific effects on reaction dynamics exhibit systematic behavior that correlates with the energy gain of barium cation-water interaction and solute-surface Coulombic attraction that have been modified by the presence of respective sodium or chloride 1:1 salts. Rates of two-dimensional nucleation under constant supersaturation are determined by the activation energy of closest water molecule exchange around Ba^{2+} , which is given by the difference in the energy of ion-water and water-water interactions and defines the frequency of water exchange. Morphology of growth and dissolution features is also shown to depend on characteristics of solute hydration and solvent structure. This conclusion is supported by the fact that the same morphology changes that were observed in the presence of different background electrolytes can be obtained just by modification of water temperature that exerts a similar effect on water structure to respective salt addition.

Knowledge about dependence of ion properties on solution composition and dependence of crystal behavior on ion properties can help us to understand phenomena such as growth and dissolution in the presence of organic additives or impurity incorporation. We show that incorporation of the same foreign ion differs depending on its properties in solution. A sodium cation can therefore enter into the barite structure when present at low concentration as the fluoride or sulfate salt but not when present in the form of chloride salts.

Our investigations give a phenomenological description and theoretical explanation of the role of fluid structure and properties of solute and surface solvation on thermodynamics and kinetics of crystal dissolution and growth. Simple ionic salts used to modify the solvation environment give insight into principles, which can be subsequently extended to more complex systems.