



Effect of background electrolytes on gypsum dissolution

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Knowledge of the dissolution behaviour of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in aqueous solutions is of primary importance in many natural and technological processes (Pachon-Rodriguez and Colombani, 2007), including the weathering of rocks and gypsum karst formations, deformation of gypsum-bearing rocks, the quality of drinking water, amelioration of soil acidity, scale formation in the oil and gas industry or measurement of water motion in oceanography.

Specific ions in aqueous solutions can play important but very different roles on mineral dissolution. For example, the dissolution rates and the morphology of dissolution features may be considerably modified by the presence of the foreign ions in the solution, which adsorb at the surface and hinder the detachment of the ions building the crystal.

Dissolution processes in the aqueous environment are closely related to the rearrangement of water molecules around solute ions and the interaction between the solvent molecules themselves. The rearrangement of water molecules with respect to solute species has been recognized as the main kinetic barrier for crystal dissolution in many systems (Davis, 2000; De Yoreo and Dove 2004; Wasylenki et al. 2005). Current research suggest that the control that electrolytes exert on water structure is limited to the local environment surrounding the ions and is not related to long-range electric fields emanating from the ions but results from effects associated with the hydration shell(s) of the ions (Collins et al. 2007) and the ions' capacity to break or structure water (i.e. chaotropic and kosmotropic ions, respectively). These effects will ultimately affect the kinetics of crystal dissolution, and could be correlated with the water affinity of the respective background ions following a trend known as the lyotropic or Hofmeister series (Kunz et al. 2004; Dove and Craven, 2005).

In situ macroscopic and Atomic Force Microscopy (AFM) flow-through dissolution experiments were conducted at a constant undersaturation and ionic strength, on gypsum cleavage surfaces in the presence of different 1:1 salts. pH and calcium concentration were measured using position-sensitive pH and calcium selective microelectrodes at different dissolution times. Dissolution rates were determined from both free Ca measurements and the spread velocity of the etch pits in the AFM images and were found to depend on the nature of the background ions used.

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