Experimental and theoretical treatment of molecular-scale mechanisms of crystal growth on baryte

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We have used Atomic Force Microscopy in a fluid cell with close to molecular resolution to observe different growth types such as two-dimensional nucleation, anisotropic effects during layer-by-layer growth and spiral growth with structure-induced self-inhibition on different faces of baryte. In combination with computer simulations, we were able to resolve these growth mechanisms and their relative importance for overall growth at an atomic level. This knowledge allows us to critically test the relevance of classical crystal growth theories, specifically the relationship between crystal growth mechanisms and fluid supersaturation as well as the effect of surface crystal structure on growth morphology. According to the classical Burton-Cabrera-Frank (BCF) theory, we found that spiral growth is the predominant mechanism at the lowest supersaturation, whereas two-dimensional nucleation prevails at somewhat higher supersaturations. Even though Periodic-Bond-Chain (PBC) theory can explain some of the directions of terminating steps of growth islands, computer simulations involving ionic attachment energies are necessary to explain anisotropic effects into different growth directions and finally explain the sector-like shape of these islands. We also demonstrate that this effect leads to a self-inhibition of spiral growth on baryte, although spiral growth is widely regarded as the most important growth mechanism under near-equilibrium conditions.

In order to understand the mechanisms of crystal growth at different conditions (e.g. supersaturation, pH), for different minerals and in the presence of different growth inhibitors/chelators, it is necessary to be able to model these processes by using dynamic molecular modelling techniques. In addition to the deterministic approach that explains the shape of the growth islands, we developed a semistatistical Monte-Carlo model which allows to calculate growth of processes such as dynamic attachment/dissolution, surface diffusion, relaxation of the surface structure and migration of ions in the near-surface region. The difference between the different minerals ($BaSO_4$, $SrSO_4$, $PbSO_4$) then only arises from applying the respective sets of ionic potentials that were derived from structural data, elastic properties and phonon frequencies of the respective minerals.

Once crystal growth in a pure $BaSO_4$ solution is calculated, we introduced the presence of different organic growth inhibitors and chelators as an additional parameter. These play a crucial role in nature and for geotechnical applications. Molecular modelling techniques can be applied to calculate the surface sites to which the organic molecules will be bonded. These processes influence the rates of growth and dissolution and change the shape of growth islands and etch pits as can be verified by using AFM.