

Dynamics of interface-driven nucleation and assembly

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Heterogeneous distributions of ions and water at interfaces have a strong impact on processes of crystallization, aggregation and dissolution. Using a combination of *in situ* imaging techniques and computational methods, we are investigating these phenomena and their relationship to interfacial structure for a number of mineral systems in aqueous electrolyte solutions. Here I discuss two cases. In the first, we use high speed, atomically resolved AFM to directly observe gibbsite formation from AlCl_3 solutions on muscovite mica. We quantify the dynamics of sub-critical clusters and the transition to stable gibbsite films. We then compare the results to the predictions of classical nucleation theory and use density functional theory (DFT) and triple layer models to relate the behavior to the underlying ion distributions and surface interactions. In the second, we combine high temperature *in situ* TEM with classical DFT simulations to investigate the impact of organics on the transformation of ferrihydrite to hematite (Hm). We show that addition of oxalate induces interfacial gradients in ion concentration that cause nucleation to be restricted to an interfacial region about 1 nm away from any existing Hm particle, to which they then immediately attach. This process is repeated at regular orientation-specific rates, leading to the formation of complex mesocrystals that are self-similar at all times. Comparison to natural and synthetic systems suggests such interface-driven pathways are widespread.