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Ion ordering and microphase separation at charged mineral-water interfaces.

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We have systematically studied the pH-dependent adsorption and precipitation of varied metal cations onto muscovite mica. Using *in situ* atomic force microscopy and streaming potential measurements, we have discovered distinct modes of ion adsorption and interfacial precipitation. The outcomes are primarily determined by the cation valency, with trivalent cations showing remarkably complex behaviors.

For divalent cations (i.e. Mg^{2+}, Co^{2+}, and Ni^{2+}), the behavior was consistent with common expectations. At lower pH values they showed modest adsorption, and they formed continuous hydroxide monolayers via a classical ‘birth and spread’ process as the pH was raised toward the saturation point. However, the trivalent cations (i.e. Al^{3+}, Fe^{3+}, Cr^{3+}) showed much more complex behavior. At lower pH, the trivalent ions form ordered ion networks (OINs), with nanometer-scale correlations between ions. When the pH was increased, the ions formed hydroxide films, but instead of forming continuous films, they created a 2D network of islands and gaps. This was accompanied by abrupt changes in the interfacial potential, indicating that electrostatic forces play a key role in the film formation.

To better understand the trivalent cation’s complex adsorption modes, we developed a new Monte Carlo lattice model that integrates key aspects of canonical models for phase transformation (i.e. the 2D Ising model) and adsorption (i.e. surface completion models) into a single unified model. Importantly, the new model combines a short-range interaction term that captures the tendency of ions to form clusters (e.g. via hydroxyl bridges) with a long-range repulsive interaction term that approximates the screened electrostatic forces. Because these terms are opposed, the result is a ‘charge-frustrated' system. With this model, we show that the OINs and nanostructured films can be understood as ‘microphase separated states’. The balance of interfacial-binding energies and surface potentials causes the ions to partially cover the surface. Subsequently, the balance of short-range attraction and long-range repulsion drives the spontaneous assembly of ions into clusters and islands with characteristic length-scales. The result cannot be understood as simple ion adsorption, nor bulk nucleation, but is instead a unique phase that is specific to the interface.