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Vanadate Partitioning During Schwertmannite Precipitation and Transformation

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Schwertmannite ($Fe_8O_8(OH)_{8-2x}(SO_4)_x \cdot nH_2O$, where ($1 < x < 1.75$) (Swm) abundantly forms in acid mine drainage (AMD)-impacted environments, where it sequesters oxyanionic species. Over time and under oxic conditions, this poorly crystalline iron(III) oxyhydroxysulfate mineral transforms into crystalline goethite (Gth) phase, depending on the chemical conditions of the environment and the presence of adsorbed species. We conducted a series of experiments in which Swm formed in the presence of varying vanadate concentrations (0-125% stoichiometric replacement of SO_4 at constant Fe:(SO_4+V) molar ratio). Time-resolved pair distribution function (PDF) measurements were used to monitor the effects of V concentration and oxic stress on the poorly crystalline Swm phase. At low V concentrations, vanadate replaces sulfate in both surface and tunnel sites without inhibiting Swm formation or its subsequent transformation into Gth. However, high V directs Swm toward amorphous Fe phases. *Ab initio* molecular dynamics (AIMD) simulations of both surface and tunnel environments capture the dynamics of vanadate at the Swm–water interface, with simulated PDFs in agreement with experimental measurements. AIMD shows that adsorbed vanadate interacts with Swm through directional hydrogen bonding, forming V-surface oxygen and V-Fe bonds at 1.85 Å and 3.23 Å, respectively, in tunnel structures. On the surface of Swm, vanadate forms directly bonded inner-sphere (IS) complexes with surface oxygens at 1.95 Å, and fully hydrated outer-sphere (OS) V-surface oxygen bonds at 3.24 Å.

