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Nanoconfinement facilitates the precipitation of iron hydroxides in porous amorphous aluminum oxides

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In nature, nanoscale spaces where molecules are confined are ubiquitous in pores and fractures in rock, sediments, clays, mineral aggregates, biofilms and biological cells. Reactions that occur in these nanoscale domains are often subject to unique constraints arising from steric restrictions on solvation, ion mobility, and charge distributions. For example, it is well known that constraints on water structure due to nanoconfinement decrease its dielectric constant locally, impacting its ability to screen charge and solvate ions and mineral surfaces. Consequently, relative to that in bulk fluid, reaction rates are typically assumed to be slower due to lower diffusivities and mass transfer. Here, we explore confinement effects on a mineral replacement reaction involving nanoporous amorphous aluminum oxide that when contacted with acidic ferric chloride solution precipitates iron oxyhydroxide while also dissolving the pore walls. Consumption of protons and release of Al^{3+} yield supersaturation that deposits 2-5 nm Al-doped ferrihydrite and akageneite nanoparticles heterogeneously nucleated on the surface of aluminum oxide pores, as characterized by SEM-EDS, TEM-EDS, XRD, and Mössbauer spectroscopy. Surface area normalized coupled dissolution/reprecipitation rates exhibit an exponential increase of two orders of magnitude as pore diameter linearly decreases from 200 nm to 30 nm. This increasing trend of reaction rate with decreasing pore size aligns quantitatively with the principle of heterogenous nucleation of ferric hydroxides on curved surfaces. These results underscore the notion that nanoconfined space can accelerate reaction rates by reducing the energy barrier to nucleation of stable end products. Our results shield light on the underestimated and significant role of confined spaces on mineral replacement reactions in subsurface environments displaced far from equilibrium, such as in acid mine drainage or enhanced geothermal systems.