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URANIUM REDUCTION BY MAGNETITE: AB INITIO THERMODYNAMICS OF NANOWIRE FORMATION AND STABILITY

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In anoxic environments, the reduction of soluble hexavalent U(VI) species to sparingly soluble tetravalent U(IV) species results in uranium immobilization through decreased aqueous solubility. Reduction by the mixed-valence iron oxide magnetite (Fe_3O_4) has been shown to produce crystalline uranium in the form of UO_2. The details of the underlying reduction mechanism remain unknown but are of critical importance to explain variability in uranium biogeochemical behavior. Investigations of the progressive reaction revealed the emergence of uranium oxide nanocrystals (1–5 nm) of intermediate valence, followed by their self-assembly into nanowires extending away from the magnetite surface. Our proposed conceptual model suggests that the surface energy of the U(V)-bearing nanoparticles is minimized by nanowire formation and that nanowire growth continues through the attachment of further nanoparticles. U(V) reduction ultimately leads to nanowires collapse and formation of UO_2 nanoclusters.

This work focuses on understanding why nanowires form, how they grow, why they collapse, and how uranium valence states evolve. To address these questions, we first use *ab initio* thermodynamics (AIT) combined with density functional theory (DFT) to determine the Gibbs free energies of bulk uranium oxide polymorphs as a function of environmentally relevant conditions. This approach provides a first-principles description of the relative bulk phase stability of uranium polymorphs and associated redox energetics.

We further evaluated how the nanoparticle size influences the relative thermodynamic stability by calculating the Gibbs free energy of hydroxylated surfaces for different surface orientations. To capture nanoparticle effects, particularly the contribution of surface energy to the stability of the nanoparticle, we used METADISE, a classical force-field–based approach for modeling hydroxylated semi-infinite slabs. This method enables the calculation of surface Gibbs free energies for relevant crystallographic orientations in aqueous conditions.

Combining DFT-derived bulk free energies and METADISE-derived surface energies provides a more complete picture of the thermodynamic behavior of uranium polymorphs as both 3D bulk systems and 0D nanoparticles. This complementary framework allows us to evaluate how particle size, hydration state, temperature, and water partial pressure influence the stabilization of intermediate-valence U(V) species and the thermodynamic driving forces governing nanowire growth and collapse under environmentally relevant conditions.