

U(V) is an intermediate in the reduction of U(VI) by *Shewanella oneidensis* MR-1

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The metal-reducing bacteria *Shewanella oneidensis* MR-1 reduces soluble and mobile hexavalent U(VI) to less mobile tetravalent U(IV), as uraninite or non-crystalline U(IV). However, the exact mechanism of transfer of two electrons to U(VI) is not fully understood. Pentavalent uranium U(V) is expected as an intermediate due to a single electron transfer to U(VI). However, because of its lack of stability in aqueous systems, and the difficulty in distinguishing it from other uranium valence states with conventional tools, it has not been evidenced during reduction by *S. oneidensis* MR-1.

We harnessed the U(V) stabilizing properties of an aqueous ligand (DPAEA) [1] to trap uranyl(V) in solution during the reduction of solid phase U(VI)-DPAEA by the microorganism. As the reaction of U(VI)-DPAEA proceeded, U was solubilized, suggesting reduction, which was confirmed by a resin-based separation of U(VI) and U(IV). Furthermore, we probed the system by M4-edge High Energy Resolved Fluorescence Detected X-ray Absorption Near Edge Structure (HERFD-XANES) to resolve the U(V) valence from others [2]. We observed the predominance of U(V) in solution while residual U(VI) and some U(IV) were identified in the solid phase. Thus, we show convincingly that U(V) is an intermediate in enzymatic U(VI) reduction.

We currently seek to determine whether the further reduction of U(V) is due to disproportionation of U(V) to U(VI) and U(IV) or to a second one-electron transfer to U(V), generating U(IV).

[1] Faizova (2018) *J. Am. Chem. Soc.* **140**, 13554–13557. [2] Pivchenko et al. (2018), *Environ. Sci. & Technol.*, 51 (4), 2217–2225.