Theoretical study on isotope fractionation in multistep biotic uranium reduction reaction

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Metabolically varied microorganisms can reduce the hexavalent uranium (U(VI)) to the tetravalent uranium (U(IV)). During this biotic reduction, the heavier isotope (^{238}U) is enriched in U(IV) and the apparent isotope fractionation coefficient Δ was obtained as 0.85–0.88‰.[1] However, its mechanism has not been well uncovered. By introducing the steady-state model for multistep reaction,[2] we could derive the representation of Δ as below.

$$\Delta = \left(\varepsilon_{ab} + \alpha_{ba}\tilde{\mathrm{X}}_b\right) + \left(\varepsilon_{bc} + \alpha_{cb}\tilde{\mathrm{X}}_c\right)\mathrm{X}_b + \left(\varepsilon_{cd} + \alpha_{dc}\tilde{\mathrm{X}}_d\right)\mathrm{X}_b\mathrm{X}_c + \left(\varepsilon_{de} + \alpha_{ed}\tilde{\mathrm{X}}_e\right)\mathrm{X}_b\mathrm{X}_c\mathrm{X}_d + \left(\varepsilon_{ef} + \alpha_{fe}\tilde{\mathrm{X}}_f\right)\mathrm{X}_b\mathrm{X}_c\mathrm{X}_d\mathrm{X}_e + \left(\varepsilon_{fg} + \alpha_{gf}\tilde{\mathrm{X}}_g\right)\mathrm{X}_b\mathrm{X}_c\mathrm{X}_d\mathrm{X}_e\mathrm{X}_f + \alpha_{gh}\mathrm{X}_b\mathrm{X}_c\mathrm{X}_d\mathrm{X}_e\mathrm{X}_f\mathrm{X}_g \quad (1)$$

Here, ε and α are the equilibrium and kinetic isotope fractionation coefficients for each reaction step, respectively. X is the flux ratio and $\tilde{\mathrm{X}}$ is defined as 1–X. The reaction is in equilibrium when X is 1, and it is irreversible when X is 0. In this study, we calculated ε for each reaction step in the biotic uranium reduction pathway[3] (Fig. 1). Because the nuclear volume term, the dominant term of ε in uranium,[4] is highly affected by relativity, we used *ab-initio* methods based on the relativistic quantum chemical theory.[5]

Because ε_{bc} is larger than the experimental Δ value[1] (Fig. 1), the contribution of the second term in Eq. 1 must be decreased. Thus, either X_b is smaller than one, $\tilde{\mathrm{X}}_c$ is non-zero with a negative α_{cb}, or both. These conditions mean that the binding of the substrate to an enzyme (A→B) or the reduction of U(VI) to U(V) (B→C) is not in equilibrium.

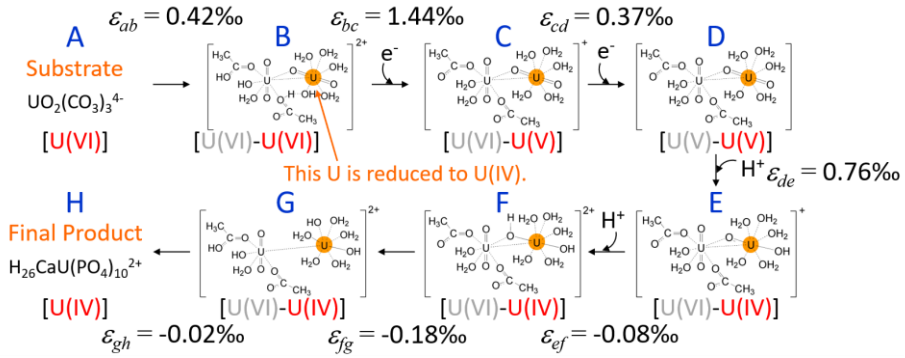

Fig. 1. Model of biotic uranium reduction pathway and obtained ε for each reaction step.

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