# Theoretical modeling of uranium isotope fractionation in multi-step biotic reduction

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Uranium (U) isotope fractionation induced by the biotic reduction mediated by microorganisms is attractive as a tool to clarify the evolution of life in the earth's history [1]. However, its mechanism has not been uncovered and under debate. In the present study, we calculated the equilibrium isotope fractionation coefficient ($\varepsilon$) for each reaction step in the biotic U reduction pathway [2] (Fig. 1) using *ab initio* quantum chemical methods.

The obtained $\varepsilon$ values are shown with the reduction pathway in Fig. 1. Based on the steady-state model for multi-step reaction [3], we could derive the representation of the apparent isotope fractionation coefficient ($\Delta$) as below.

$$\Delta = \left(\varepsilon_{ab} + \alpha_{ba}\right) \cdots + \left(\varepsilon_{ef} + \alpha_{fe}\right) \cdots \varepsilon_{gh} X_b X_c X_d X_e X_f X_g \quad (1)$$

where $\varepsilon$ and $\alpha$ are the equilibrium and kinetic isotope fractionation coefficients for each reaction step, respectively. X is the flux ratio, and $\tilde{X}$ is defined as 1–X. When X is 1, the reaction is in equilibrium, and when X is 0, it is irreversible. Because $\varepsilon_{bc}$ is (1.44‰) is larger than the experimental value ($\Delta$ = 0.85–0.88‰) [1], the contribution of the second term in Eq. 1 must be decreased. Thus, either $X_b$ is smaller than one, or $\tilde{X}_c$ is non-zero with a negative value of $\alpha_{cb}$. 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.

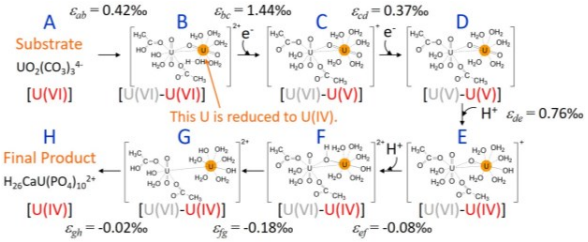


**Figure 1:** Model of biotic U reduction pathway and calculated $\varepsilon$ values for each reaction step.

[1]Stylo *et al.* (2015) *PNAS.* **112**, 5619-5624. [2] Sundararajan *et al.* (2008) *JPCA.* **112**, 4451-4457. [3] Rees (1973) *GCA.* **37**, 1141-1162.