

Measurement of sulfur isotope fractionation by APS reductase and its biogeochemical implications

*Shawn E McGlynn¹, Min Sub Sim², Hideaki Ogata³, Jess F Adkins⁴, Alex L Sessions⁴, Victoria J Orphan⁴, Wolfgang Lubitz⁵

1. Tokyo Institute of Technology, 2. Seoul National University, 3. Hokkaido University, 4. California Institute of Technology, 5. Max Planck Institute for Chemical Energy Conversion

The fractionation of sulfur isotopes during microbial sulfate reduction (MSR) is a well-known example of kinetic isotope fractionation resulting from metabolic activity. Although data from cell cultures and sulfur minerals exist, an understanding of the enzyme-specific isotope effects associated with this process is lacking. Here we report for the first time the sulfur kinetic isotope effect of the enzyme adenosine phosphosulfate reductase (Apr), which is present in all known organisms conducting MSR. Implementing the newly determined value in a metabolic isotope-network model of MSR indicates that ^{34}S fractionation greater than 20‰ can occur only when there is a low energetic driving force for the Apr catalyzed step which leads to greater reaction reversibility. These results constrain the cellular states that result in large isotopic fractionations: small fractionations can be attributed to either low sulfate concentrations, high respiration rates, or combinations of these, but large fractionations greater than that of the Apr enzyme require reversibility at that step. Isotope fractionations greater than that of Apr are ubiquitous in modern environments but apparently lacking in Archean sediments, implying that ancient sulfate reducers had ample driving force for the Apr-catalyzed reaction. We also consider that electron donors available to sulfate reducers may have declined as aerobic competitors evolved.

Keywords: kinetic isotope effect, microbial sulfate reduction, archaean, equilibrium isotope effect, enzyme

