Enrichment of ^{34}S in the intracellular sulfate during dissimilatory sulfate reduction

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Sulfur isotope fractionation during microbial sulfate reduction has been widely used to probe the elemental cycling in present and past ecosystems. However, little is known about sub-cellular mechanisms by which environmental factors affect microbial isotope fractionation, fundamentally limiting our ability to generate the interpretation of sulfur isotope signatures based on microbial physiology. Here we present the isotopic composition of intracellular sulfur metabolites and provide a direct means of probing the isotope fractionation mechanism at sub-cellular levels. With lactate as an electron donor, *D. multivorans* and *D. alaskensis* show ^{34}S enrichment in the intracellular sulfate relative to the extracellular sulfate. Interestingly, the larger the magnitude of overall isotope effect, the greater the enrichment of $^{34}SO_4^{2-}$ in the cell. This reflects the isotope mass-balance principle when a stronger sulfur isotope effect is not accompanied by a more reversible sulfate transport. Our results also confirm that a strong preference for light sulfur isotopes during dissimilatory sulfate reduction is driven by intracellular enzymatic reactions rather than sulfate transport across the cell membrane. Although extremely small quantities of other sulfur metabolites (e.g. APS, sulfite, and thiosulfate) make the isotopic measurement without the interference from contaminant sulfur challenging, APS recovered from *D. alaskensis* cells is isotopically lighter than intracellular sulfate. This observation may necessitate the sulfur isotope fractionation between sulfate and APS, which has been assumed to be zero.