Tracking intermediate redox species of sulfur

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The intermediate redox species of sulfur are vital for early diagenetic processes involving sulfur, iron, and carbon. Intermediate sulfur species serve as substrates for the microbial oxidation, reduction, and disproportionation of sulfur. However, preserving and quantifying these intermediates has been particularly difficult due in large part to the rapid chemical and biologic rates of reactions. We have developed a methodology using the fluorescent compound bromobimane that preserves sulfur intermediates. Using an Ultra Performance Liquid Chromatographer (UPLC) connected to a Time of Flight Mass Spectrometer (TofMS), we were able to rapidly separate, quantify, and perform compound specific isotope analysis (CSIA) for sulfur intermediates. Our methodology provided quantification for samples containing millimolar to nanomolar concentrations of sulfur, with detection limits of femtomoles. We applied our methods to pure cultures of sulfur oxidizing (*Sulfurovum lithotrophicum* and *Thiobacillus thioparus*) and reducing bacteria (*Desulfococcus multivorans* and *Desulfovibrio desulfuricans*), as well as co-cultures of these bacteria to elucidate important sulfur intermediates. This methodology proved to be very effective in stable isotope probing (SIP) experiments where ^{34}S and ^{33}S labeled substrates were provided to pure cultures and sediment incubations. We have collected individual fractions from the LC in order to obtain high precision CSIA on a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) for natural abundance sulfur isotope fractionation.