

## Abiotic Formation of Dissolved Organic Sulfur in Anoxic Sediment of Santa Barbara Basin

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Sulfurization of organic matter is an effective mechanism to enhance organic matter preservation and petroleum formation in marine sediments. The burial of sulfur in sediments as organic sulfur versus pyrite may also affect atmospheric oxygen levels over geologic time. However, a comprehensive understanding of abiotic sulfurization mechanisms is lacking. In this study, we analyzed the dissolved organic matter composition of 28 pore water samples from the top 4.5 m of the anoxic sediments of Santa Barbara Basin (SBB) by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS). We investigated: 1) Formation mechanisms of dissolved organic sulfur (DOS) compounds in pore waters, 2) Types of chemical formulas that promote the formation of DOS compounds abiotically, and 3) The possible fates of these DOS compounds after they form in the pore water.

Our results indicate that nucleophilic addition reactions of hydrogen sulfide ( $\text{HS}^-$ ) and polysulfide ( $\text{HS}_x^-$ ) are the major pathways for the abiotic formation of organic sulfur compounds in anoxic sediments of SBB. Between the two sulfur incorporation pathways, we identified 2,124 unique DOS formulas that are produced through abiotic sulfurization, which account for ~70% of all DOS formulas detected in the samples analyzed. Of the reactant formulas involved in abiotic sulfurization, 64% are CHO formulas while the remaining (34%) are dissolved organic nitrogen (DON) formulas. Our results reveal high sulfurization reactivity for many of the CHO and DON formulas that fall in the carboxyl-rich alicyclic molecules (CRAM) region. This specific class of formulas could be responsible for the formation of a major fraction of organic sulfur compounds in anoxic and sulfide-rich ecosystems.