Complex microbial ecosystems recorded in sulfur and oxygen isotopes of carbonate associated sulfate in the Monterey Formation, California, U. S. A.

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$\delta^{34}S$ and $\delta^{18}O$ analyses of carbonate associated sulfate (CAS) and mineralogical evidence illustrate a complex microbial ecosystem within the phosphate-rich interval of the Miocene Monterey Formation. All $\delta^{34}S$ and $\delta^{18}O$ are below Miocene seawater values (~+22‰, VCDT and ~+12‰, VSMOW). $\delta^{34}S$ values range from +12.2‰ to +18.5‰ and $\delta^{18}O$ range from +2.7‰ to +17.7‰, demonstrating a positive linear correlation. $\delta^{34}S$ of insoluble sediments (combined pyrite and organic sulfur), used as a proxy for bacterially generated H_2S, range from 5.6‰ to 8.4‰. Sulfate reducing bacteria (SRB) drive the residual seawater sulfate pool to higher $\delta^{34}S$ values and generate low $\delta^{34}S$ H_2S (~14‰ lower than seawater sulfate). Initially, H_2S from SRB and Fe^{2+} produced by iron-reducing bacteria (FeRB) generated small amounts of pyrite until all available Fe^{3+} was consumed. With no available Fe^{2+}, H_2S reduced from sulfate by SRB diffused upward to the oxic-suboxic zone boundary where sulfide oxidizing bacteria (SOB) used molecular oxygen to re-oxidize H_2S to sulfate that retains the low $\delta^{34}S$ of the H_2S. Total sulfate $\delta^{18}O$ values produced by re-oxidation of H_2S record a mixture of the sulfate pool higher $\delta^{18}O$ and lower $\delta^{18}O$ of sulfate from oxidized H_2S. Observed $\delta^{34}S$ and $\delta^{18}O$ lower than seawater sulfate illustrate that the $\delta^{34}S$ versus $\delta^{18}O$ line defines a mixing line between the endmembers: total reduced sulfur $\delta^{34}S$ combined with fractionated atmospheric $\delta^{18}O$ [1], and Miocene seawater sulfate $\delta^{34}S$ and $\delta^{18}O$. This interpretation is supported by low $CaCO_3$ and high phosphate concentrations, whereby SOB promote decreasing seawater pH by production of a small amount of sulfuric acid, which inhibits the precipitation of $CaCO_3$ while promoting preservation of phosphate [2]. These results demonstrate that the phosphate-rich interval of the Monterey Formation records a complex suite of FeRB, SRB, and SOB, illustrated by $\delta^{34}S$ and $\delta^{18}O$ analyses of CAS.

[1] Ziegler (2008) *AGU Fall Meeting Abstracts*, P53D-03 [2] Nathan and Sass (1981) *Chem. Geol.* **34**, 103-111