

## Can organic haze and O<sub>2</sub> plumes explain patterns of sulfur mass-independent fractionation during the Archean?

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The existence of mass-independently fractionated sulfur in Archean rocks is almost universally accepted as evidence for low atmospheric O<sub>2</sub> and O<sub>3</sub> concentrations at that time. But the detailed patterns of the  $\Delta^{33}\text{S}$  values and of the ratios  $\Delta^{33}\text{S}/\delta^{34}\text{S}$  and  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  remain to be explained, and the mechanism for producing the mass-independent fractionation remains controversial. Here, we explore the hypothesis that the relatively low  $\Delta^{33}\text{S}$  values seen during the Mid-Archean, 2.7-3.5 Ga, were caused by the presence of organic haze produced from photolysis of methane. This haze helped shield SO<sub>2</sub> from photolysis, while at the same time providing surfaces on which unfractionated short-chain sulfur species could condense. The evolution of oxygenic photosynthesis, and the concomitant disappearance of organic haze towards the end of the Archean allowed more negatively fractionated S<sub>4</sub> and S<sub>8</sub> to form, thereby generating large positive fractionations in other sulfur species, including sulfate and H<sub>2</sub>S. Reduction of this sulfate to H<sub>2</sub>S by bacteria, followed by incorporation of H<sub>2</sub>S into pyrite, produced the large positive  $\Delta^{33}\text{S}$  values observed in the Neoproterozoic rock record, 2.5-2.7 Ga.

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