

Review of:

Zerkle, Aubrey L., Mark W. Claire, Shawn D. Domagal-Goldman, James Farquhar, and Simon W. Poulton. (2012) *A bistable organic-rich atmosphere on the Neoproterozoic Earth*. *Nature Geoscience* DOI: 10.1038/NGEO1425

Primary Question

What was the Earth's atmosphere like prior to the Great Oxidation Event? Did it have an organic haze?

Methods of Addressing this Question

1. geochemical proxies from sediment cores
2. photochemical models

Why is this important in the larger perspective?

They find that the Earth could have been alternating between two stable states: a haze-free atmosphere and an atmosphere with an organic haze. Understanding the concentrations of organics in the atmosphere constrains the reaction pathways and exit channels that are involved in sulfur MIF.

1. Haze Free CH_4 : $\text{CO}_2 < 0.1$
SOURCE: SO_2 photolysis is the major source of sulfur MIF
EXIT CHANNELS: For the haze-free state, increasing CH_4 allows elemental sulfur to polymerize, promoting S_8 as the reducing exit channel. At the same time, SO_2 becomes the dominant oxidized exit channel.
2. Thin Organic Haze CH_4 : $\text{CO}_2 \sim 0.2$
SOURCE: Opacity of haze lowered the rates of SO_2 photolysis in the lower atmosphere, but SO_2 photolysis still was a likely source of sulfur MIF. In addition, symmetry dependent de-excitation of SO_2 could have also been an important S-MIF source.
EXIT CHANNELS: SO_2 and other minor channels.

Switching between these two states could explain the slope changes in the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$.

Weakness

They are not able to explain why rotation of the data array on the $\Delta^{33}\text{S}$ v. $\Delta^{36}\text{S}$ plot is happening. They say that "a rotation of the arrays to different slopes instead implies a change in the nature of the primary S-MIF signature, either due to a change in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ for a single atmospheric signal, or due to variable amounts of mixing between atmospheric sources with different $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ " (pg. 2). However, they are not able to specify which sources could produce the signal that is demonstrated in the plot.

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