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Poster Session Day 1

Increase of microbial fractionation factor at the end of Proterozoic inferred from high precision quadruple sulfur isotope analysis

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Microbial Sulfate Reduction (MSR) is important for sulfur cycle. The apparent isotopic fractionation between sulfide and sulfate has increased at two global oxygenation event (GOE; Great oxidation event and NOE; Neoproterozoic oxidation event) potentially in response to increase of the fractionation for MSR. However, accurate estimate of the fractionation factors of MSR has been challenging due to the lack of sulfate minerals particularly in the Precambrian period. Hence, interpretation of large isotopic variations observed in sedimentary pyrites is often ambiguous. Here, we report the fractionation factors of MSR throughout the Proterozoic by re-evaluation of multiple sulfur isotope records of sedimentary pyrites. Our previous analysis of Paleoproterozoic black shale from the Francevillian succession demonstrated that a distinct negative correlation between $\delta^{34}S$ and $\Delta^{33}S$ values of different generations of pyrite was created by MSR within sediment. Using the observed relationship, we can estimate fractionation factor ($^{34}\alpha = {}^{34}R_{sufide}/{}^{34}R_{sufate}$), mass-dependent exponent ($^{33}\lambda = \ln({}^{33}R_{sufide}/{}^{33}R_{sufate}) / \ln({}^{34}R_{sufide}/{}^{34}R_{sufate})$) as well as the $\delta^{34}S$ value of initial sulfate ($\delta^{34}S_i$) without analyzing sulfate. This method was validated using some lake sediments, where the estimated $\delta^{34}S_i$ values from sulfides are consistent with measured $\delta^{34}S$ values of sulfate in the water column. Utilizing the same approach, small fractionation ($^{34}\alpha$ from 0.978 to 0.997) and low $^{33}\lambda$ (< 0.512) were estimated from Proterozoic sedimentary pyrites. In contrast, marine pyrites after the Ediacaran show larger fractionation ($^{34}\alpha$ from 0.955 to 0.965) and higher $^{33}\lambda$ (> 0.512), though lake sediments show smaller fractionation ($^{34}\alpha$ from 0.981 to 0.987). This increased value of fractionation factors from the Ediacaran is close to the equilibrium fractionation at room temperature, suggesting a slowing of the microbial sulfate reduction rate. Based on these findings, one explanation is that the appearance of multicellular animals during the Ediacaran may have promoted the decomposition and recycling of organic matter, limiting the supply of organic matter available to SRB.