Goldschmidt 2024 Abstract
https://doi.org/10.46247/gold2024.24389

Small fractionation factors of microbial sulfate reduction in Proterozoic sediments inferred from high precision multiple sulfur isotope analysis of pyrite

ARU KURIHARA[1], YUSUKE SAWAKI[2], MATHIEU MOUSSAVOU[3], CHENGZHOU JIANG[4], MAYUKO NAKAGAWA[1], TOMOHIKO SATO[5] AND YUICHIRO UENO[1,6]

[1]Tokyo Institute of Technology
[2]The University of Tokyo
[3]Université des Sciences et Techniques de Masuku
[4]China University of Petroleum (Beijing), China
[5]Okayama University of Science
[6]JAMSTEC

Presenting Author: kurihara.a.ab@m.titech.ac.jp

Sulfur isotopes have been utilized to monitor sulfur cycle through the Earth's history. The apparent fractionation between sulfide and sulfate has increased through the Earth's history potentially in response to global oxygenation [1]. However, accurate estimate of the fractionation factors of microbial sulfate reduction (MSR) has been challenging due to the lack of sulfate particularly in the Precambrian period. Hence, interpretation of large isotopic variations observed in sedimentary sulfides is often ambiguous. Here, we report re-evaluation of multiple sulfur isotope records of Proterozoic, Phanerozoic, and modern sediment. Our previous analysis of Paleoproterozoic 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. Utilizing the same approach, almost Proterozoic pyrites give relatively small fractionation ($^{34}\alpha$ from 0.978 to 0.997) and low $^{33}\lambda$ (< 0.512). 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). The contrasting fractionation factors between Proterozoic and Phanerozoic marine sediments may reflect an increase of ocean sulfate level and/or change in the limiting factor for MSR at the end of Proterozoic, possibly due to the onset of quantitative consumption of organics by aerobic respiration.

[1] Fike et al. (2015) *Annual Review of Earth and Planetary Sciences*, 43, 593-622.