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Multiple sulfur isotope geochemistry of pyrites in Paleoproterozoic black shales from Francevillian succession, Gabon

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Sulfur isotopes have been utilized to monitor sulfur cycle through the Earth history. In general, variation of $d^{34}S$ values of sulfides gradually increased from the Archean to the Phanerozoic, which have been interpreted to monitor gradual increase of microbial sulfate reduction (MSR) in response to oxygenation of atmosphere-ocean system [1]. However, fractionation between sulfate and sulfide in the Archean and Paleoproterozoic remains largely unknown because original sulfates are poorly preserved. Therefore, isotope ratios of seawater sulfate at that time are largely uncertain, and it is difficult to determine actual fractionation factor for MSR only from sulfide.

In this study, we report multiple sulfur isotope analysis for various forms of pyrites in the Paleoproterozoic Francevillian succession, Gabon. Based on petrological observation, the pyrites in black shales were classified into five types. The sulfur isotope analysis revealed that these pyrites exhibit large variation of $d^{34}S$ values more than 50‰. Importantly, oval pyrite nodules formed before compaction have low $d^{34}S$ down to -15‰, while those formed later (authigenic pyrites crosscutting the laminations) show high $d^{34}S$ up to +40‰. Furthermore, a clear negative correlation between their $d^{34}S$ and $D^{33}S$ values were found from the different types of pyrites within a single rock sample. The observed co-relation can be explained by the Rayleigh distillation model. As a result of the model calculation, the isotope fractionation factor (34-alpha), the mass-dependent exponent (33-lambda) and initial $d^{34}S$ value of porewater sulfate were estimated. The calculated 34-alpha and 33-lambda values were consistent with previous incubation experiments of MSR [2] [3] [4]. Furthermore, the estimated microbial fractionation in the Paleoproterozoic (<25‰) were smaller than those in the Phanerozoic. The newly developed approach is useful to estimate the fractionation factor only from sulfide sulfur isotopes, which provides a new insights into sulfur cycling in the Precambrian period.

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