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Quadruple sulfur isotope analysis of seasonal sulfur cycle change

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Sulfur is one of the main light elements which compose a living body and ecosystem. There are many kinds of naturally occurring sulfur compounds. Also many kinds of bacteria which metabolize these compounds have existed from the early Earth. Sulfur cycle is supported by many bacteria. For example, sulfur reducing bacteria produces hydrogen sulfide from sulfate and photosynthetic sulfur bacteria oxidize it. Until recently, the study of sulfur cycle is mainly discussed with $^{34}S/^{32}S$. But from these data, we can only discuss about a few processes of metabolism that have large fractionation of $d^{34}S$(small delta notation), such as dissimilatory sulfate reduction and sulfur disproportionation.

Recently, quadruple sulfur isotope system ($^{32}S/^{33}S/^{34}S/^{36}S$) has been focused, because it provides a way to distinguish the signatures of different sulfur metabolisms, even when $d^{34}S$ fractionations are identical (Ono et al., 2006). The capital delta notations of less abundant isotopes show minor deviation from mass-dependent fractionation. And we also use 'lambda' to express observed mass-dependent fractionation in logarithmic form. When the reaction is a simple equilibrium reaction, the values of 33- and 36-lambda become 0.515 and 1.90 respectively. But un identical chemical or physical processes can fractionate sulfur isotopes with values of lambda more variable and the range is about 0.500 to 0.516(Young et al.,2002). These quadruple sulfur values have a potential of a new tracer not only for photochemically-induced non-mass-dependent reactions, but also for mass-dependent processes including biogeochemical reactions (Farquhar et al.,2003; Johnston et al., 2007). The works with quadruple sulfur isotopes has been reported on ancient rocks as well as incubation experiments of sulfate reducing and disproportionating bacteria for simulating fractionation.

The modern stratified lake system has been studied on the basis of the knowledge of this biological fractionation. We tried to determine multiple sulfur isotope fractionation factors of microbial sulfate reduction in nature. We have studied quadruple sulfur isotope ratios of sulfate and sulfide in a small monomictic lake, Fukami-ike, central Japan, having a maximum depth of 8.0 m. The lake is eutrophic and is stratified from April to November, when green and purple sulfur bacteria (anaerobic photosynthesizer) are active at oxic-anoxic boundary layer, and sulfate reducing bacteria produces hydrogen sulfide accumulated in an anoxic hypolimnion (Yagi 1983, 1996).

In August, systematic changes of $d^{34}S$ as well as $D^{33}S$ and $D^{36}S$ values were observed both for sulfate and sulfide in anoxic hypolimnion. Simple calculation assuming Rayleigh process yielded fractionation factors for $^{34}S/^{32}S$ (alpha-34), and mass dependent exponents (lambda-33 and 36). The results are consistent with sulfate reduction within a water column of the lake. The results are clearly different from equilibrium isotope exchange and are within the range of the incubation experiment of sulfate reducing bacteria (Johnston et al., 2007). So, these results indicate that the effect of the quadruple sulfur isotope fractionation by sulfate reducing bacteria is large and the behavior is almost the same for both pure culture and natural environment.

However, there is a difference about the relations of each isotope ratios. For example, the plot of $D^{36}S/D^{33}S$ shows different trends between pure culture microbial sulfate reduction and the results of August. The slope found in August is much larger than that of the laboratory experiments. If the process is equilibrium, the slope is -6.85(Ono et al., 2006). The higher slope $>$ -6.85 haven't been observed in the laboratory experiments (Johnston et al., 2007) and may be reflected the kinds of microbial metabolisms in the lake where both reduction and oxidation processes are included. Moreover, seasonal variation of $D^{36}S/D^{33}S$ relationship demonstrated that ^{33}S and ^{36}S signatures are potential indicators not only for microbial sulfate reduction but also for different sulfur metabolisms or cycles.