The quadruple sulfur isotope analysis of lake water

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Sulfur isotope geochemistry has focused on 34S/32S ratio since 1960's. Recent high precision measurements of quadruple sulfur isotope system (32S/33S/34S/36S) demonstrated the potential to provide additional information not only for photochemically induced non-mass-dependent fractionations, but also for terrestrial mass-dependent processes such as mass-transfer and isotopic fractionation in metabolic and biogeochemical reaction networks (Farquhar et al. 2003, Ono et al., 2003, Johnston et al.,2005). Previous analysis of multiple sulfur isotopes has focused on sulfate reducing bacteria cultured in laboratory experiments, though no investigation on natural environment has been reported. It is important to document quadruple sulfur isotopic variation in nature.

We measured quadruple sulfur isotope ratios of sulfate and sulfide in a small monomictic lake Fukami-ike, central Japan, having a maximum depth of 8.0m, and 2200 m^2 of the lake surface area. The lake is eutrophic and is stratified from March to October, when green and purple sulfur bacteria (anaerobic photosynthesis) are active at oxic-anoxic boundary layer, and sulfate reducing bacteria produces hydrogen sulfide accumulated in an anoxic hypolimnion (Saijo 1981, 1992; Yagi 1996). Such variety and activity of sulfur metabolisms may be partly due to relatively high concentration of sulfate compare to general freshwater lake.

We analyzed the lake water at 8 depths in August and November, when the lake was stratified. In August, sulfate concentration decreased from oxic-anoxic interface at 5 m to the bottom with gradual increase of d34S value from -12 to +5 permil. Moreover, D33S value of sulfate was uniform (+0.04 permil) in oxic epilimnion and systematically decreased from +0.04 to -0.08 permil in anoxic hypolimnion. On the other hand, sulfide concentration increased from oxic-anoxic boundary to the bottom. Dissolved sulfides at all depths show 34S-depletion by about 27 permil relative to coexisting sulfate and show uniform D33S of about +0.15 permil, which is significantly higher than that of sulfate. These systematic profiles indicate activity of sulfate reduction within a water column above sediment-water interface. Simple calculation assuming Rayleigh process yields a fractionation factor for 34S/32S (alpha-34) of 0.980, and mass dependent exponents (lambda-33 and -36) of 0.5053 and 1.934, respectively. Both the estimated lambda values are similar to those observed in the laboratory experiments of microbial sulfate reduction (Johnston et al., 2007), but significantly different from those of equilibrium fractionation (0.515 and 1.90; Hulston and Thode, 1965). On the other hand, in November, oxic epilimnion developed down to 1m above sediment-water interface. The d34S, D33S and D36S values of sulfate and sulfide show only small variation probably because sulfate reduction only occurred within the bottom sediment. Interestingly, linear D33S and D36S relationship for all the samples exhibited slope of -3.49 in August and -18.96 in November. These D36S/D33S slopes are different from that of simple mass balance or equilibrium (-6.85; Ono et al.,2006). The slope in November is comparable to some of microbial sulfate reduction (-11; Johnston et al., 2007), whereas the D36S/D33S slope in August (-3.49) is higher than -7, which have not yet described in the culture experiments of sulfate reducers. This character may have resulted from oxidative recycling of sulfur due to activities of anaerobic photosynthesis flourishing in August. Hence, our results indicate that D33S and D36S signatures are potential indicators not only for microbial sulfate reduction but also for different sulfur metabolisms or cycles.