Quadruple sulfur isotope fractionation of microbial sulfur reduction in pure culture

Atsushi Tada[1]; Yuichiro Ueno[2]; Ken Takai[3]; Naohiro Yoshida[4]

[1] Interdisciplinary Grad. School of Sci. and Eng., Titech; [2] Global Edge Inst., Tokyo Tech.; [3] SUGAR Program, JAMSTEC; [4] IGSSE, Tokyo Institute of Technology

The reduction of elemental sulfur (S^0) to hydrogen sulfide, utilizing either H_2 or organic compound as an electron donor, is widespread within both the Domains Archaea and Bacteria (Stetter, 1990; 1996; Schauder and Kroger, 1993). The S^0-reducers represent sorts of the most deeply-branching hyperthermophiles, suggesting that this metabolism may be one of the most primitive metabolisms among all the extent life (Stetter and Gaag, 1983; Canfield and Raiswell, 1999), though it is still unknown when the S^0 reduction appeared on the Earth. In order to detect the activity of this metabolism from geological record, sulfur isotope geochemistry might be useful. Recent multiple sulfur isotope analysis has suggested that microbial S^0-reduction may have played a role for deposition of some Archean sedimentary pyrites with positive $D^{33}S$ anomaly (Farquhar et al., 2001; Mojzsis et al., 2003; Ono et al., 2003). Isotopic effects by microbial sulfur reduction, however, have not yet been determined even for $^{34}S/^{32}S$ ratio. Here, we first report quadruple sulfur isotope effects ($^{32}S/^{33}S/^{34}S/^{36}S$) of microbial sulfur reduction by pure culture experiments of four sulfidogenic Bacteria and Archaeon. Our experiments demonstrated that the hydrogen sulfide is depleted in ^{34}S relative to substrate sulfur by -0.65 to -0.16 permil for *Deferribacter* and *Desulfurobacterium* species, whereas enriched by +0.60 to +1.46 permil for *Thermococcus* and *Lebetimonas* species. No significant change has been observed for $D^{33}S$ and $D^{36}S$ values for all the culture experiments. The small effects of fractionation observed (-1˜+1 permil for $d^{34}S$) may be partly due to isotope exchange between hydrogen sulfide and elemental sulfur. An additional experiment of abiotic isotope exchange reaction indicates that the isotope exchange proceedes in a period of the culture experiment (˜1 day), but does not reach in equilibrium. Comparing the results of isotope exchange reactions and time-course analysis of sulfur reducers, we concluded that *Thermococcus* promotes the isotope exchange reaction resulting in isotope equilibrium within 4 hours. However, *Deferribacter* and *Desulfurobacterium* shows an opposite direction of isotope fractionation to that of equilibrium effect, suggesting that their metabolic pathways are different from that of *Thermococcus* and may have larger kinetic isotope effects than the apparent fractionation observed in the culture experiments.