

## Microbial sulfate reduction within the Iheya North subseafloor hydrothermal system constrained by quadruple sulfur isoto

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Subseafloor hydrothermal system may host active and abundant microbial community. Sulfate reduction may be one of the dominant microbial metabolisms among the subseafloor ecosystem. In order to demonstrate and quantify the potential sulfate reducing activity, we analyzed sulfur isotopes ( $^{32}\text{S}/^{33}\text{S}/^{34}\text{S}/^{36}\text{S}$ ) of pore water sulfate extracted from core samples at the Iheya North hydrothermal system in the Okinawa drilled by CHIKYU, 2009 (IODP Leg 331). After drilling, core samples were divided into several sections. Then, pore water was extracted on board, and stored with cadmium chloride for fixing hydrogen sulfide. In our laboratory, the samples were first divided into sulfide precipitate and supernatant liquid by centrifugation. Then, dissolved sulfate was precipitated as  $\text{BaSO}_4$  by addition of barium chloride into the supernatant liquid. After weighing, the barium sulfate was converted into silver sulfide and subsequently sulfur hexafluoride, which was purified by GC and then introduced into mass spectrometer (MAT253) through newly developed microvolume inlet for precisely determining quadruple sulfur isotopic composition.

Based on pore water chemistry and temperature profile, the subseafloor environment are divided into Unit-1, -2 and -3 with depth below surface. In Unit-1 (0-10 mbsf), fresh seawater is circulated, whereas in Unit-3 (>40 mbsf), hot hydrothermal fluid (>150°C) is stored below anhydrite cap. The Unit-2 is the mixing zone between the hydrothermal fluid and seawater.

We found that the  $\delta^{34}\text{S}$  value of sulfate in the mixing zone was higher than those expected by simple mixing between seawater sulfate in Unit-1 (-20 permil) and the hydrothermal component in Unit-3 (-16 permil). The observed  $^{34}\text{S}$ -enrichment and decreased sulfate concentration suggest sulfate reduction took place in this hydrothermal system. Based on our model calculation assuming the mixing and reduction, apparent isotope effect for  $^{33}\text{S}$ ,  $^{34}\text{S}$  and  $^{36}\text{S}$  are estimated to be -16.5 permil, -32.2 permil and -62.5 permil, respectively. These large fractionations together with slight  $\text{D}^{33}\text{S}$  enrichment and  $\text{D}^{36}\text{S}$  depletion all suggest that the sulfate reduction is microbial and not thermochemical process. Our numerical simulation also indicates that the sulfate is reduced before mixing with high temperature fluid, probably within the recharge zone of seawater. Based on these results, we will discuss microbial sulfur cycling in this subseafloor environment.

Keywords: Microbial sulfate reduction, quadruple sulfur isotope, subseafloor hydrothermal system, Iheya North hydrothermal system in the Okinawa