Role of zero-valent sulfur in marine methane oxidation

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Sulfate is the main oxidant for seafloor methane, and the transition zones of methane and sulfate thus play a key role in the biogeochemical carbon cycling in methane-bearing marine sediments. Our recent results[1] suggest that the impact of anaerobic oxidation of methane (AOM) on the marine sulfur cycle might be just as important.

Using a suite of microbiological and experimental biogeochemical approaches, such as cultivation, stable- and radio-isotope labelling experiments and single-cell-based techniques, we have investigated microbial sulfur cycling associated with marine methane oxidation in microbial enrichment cultures. We could show that during AOM sulfate is only partially reduced to zero-valent sulfur, which is stored intracellularly as a mixture of cyclo-octasulfur and soluble polysulfides. The release of the produced sulfur from the cells provides a local source of zero-valent sulfur in sulphidic marine sediments. Furthermore, we could show that the produced zero-valent sulfur in a form of disulfide can be further disproportionated to sulfate and sulfide by bacteria associated with the methane-oxidizing archaea.

Our observations show an unexpectedly diverse metabolic potential of the AOM microorganisms and expand the physiological diversity of known microbial sulfur metabolisms. Moreover, our results suggest a solution to the long-standing mystery of a missing intermediate in AOM by suggesting a key role of zero-valent sulfur in this process. These new insights have important implications for the biogeochemical carbon and sulfur cycling in marine sediments.

[1] Milucka *et al.* (2012), *Nature 491*, 541–546.

Record of bacterial sulfate reduction during 50~210 kyr ago in the submarine hypersaline Meedee Lake, off Crete Island, Eastern Mediterranean Sea.

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Meedee Lake (2920m deep) is a submarine, hypersaline lake with its salinity >10 times higher than that of normal seawater, due to elution of submarine evaporites formed during Messinian Salinity Crisis 5.33 to 6 Ma ago. The density-stratified lake water has been kept anoxic due to consumption of dissolved O_2 by decomposition of organic matter sinking from the overlying water.

In order to understand changing redox state and microbial activity in the submarine extreme lake environment, sediment core was collected from the margin of the lake. The core shows alternation of pyrite-bearing light- and Fe-oxide-bearing dark-colored layers reflecting fluctuating redox during deposition [1].. The sulfate-rich lake hosted sulfate-reducing bacteria.

To obtain insight into biogeochemical S cycling in the lake, we measured abundance of S-bearing species by sequential extraction method. Five phases were separately quantified: (1) AVS (acid volatile sulfide), (2) pyrite, (3) sulfate, (4) organic-S, and (5) elemental S, by using a method of [2], a combination of [3, 4, 5]. Isotopic compositions of these phases were measured by EA-IRMS at Kyushu University.

Sulfate was found to be the most abundant species, accounting for 90% in both light and dark layers. The isotopic compositions ($\delta^{34}S_{SO4}$ vs. VCDT) vary greatly from +16‰ to +32‰. Such large fluctuations are most likely due to variable (a) degrees of sulfate utilization by sulfate-reducing bacteria (SRB) and/or (b) sulfate concentration. When activity of SRB was not enhanced, sulfate utilization by SRB was not complete, and/or sulfate concentration is reasonably high, then the $\delta^{34}S_{SO4}$ values would not have much changed from their original seawater value (+21‰). Contrary, when activity of SRB was enhanced and sulfate utilization was near complete, then the $\delta^{34}S_{SO4}$ values would have progressively increased from ~21‰ (i.e., Rayleigh fractionation).

Bacteriogenic pyrite would have gone by oxidation due to lowering of lake water level and invasion of oxic seawater, while sulfate minerals would have been preserved. This study demonstrates utility of sulfur isotope compositions of sulfate minerals in sediments to uncover past activity of SRB, even if bacteriogenic pyrite was not well preserved.

[1] Izumitani (2010) M.Sc,. Kochi Univ. [2] Kobayashi (2011) Senior Thesis,. Toho Univ. [3] Canfield *et al.* (1986) Chem, Geol, 54, 189, [4] Buckland & Boman. (2005). Agricul, Food Sci, 14, 70.

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