Novel sulfur disproportionation of a deep-sea vent thermophile

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Sulfur disproportionation was first identified in sulfate-reducing bacteria isolated from anoxic sludges and marine sediments in 1987. Since the first discovery, 9 species have been known so far and all the sulfur-disproportinating bacteria (SurDB) are facultative sulfate-reducing bacteria (SateRB) within the *Deltaproteobacteria* and *Firmicutes* except for a strict sulfur-disproportionating bacterium. The ecological significance of SurDB in the local and global sulfur cycles in the present Earth is completely unknown. In addition, the energetics and the metabolic pathways of sulfur-disproportionation are poorly investigated. Nevertheless, the SurDB and their functions have attracted isotope geochemists investigating the sulfur cycles in the Archean Earth. It is probably because the SurDB are known to be the only phenotype other than the SateRB providing significant stable sulfur isotopic fractionation (^{34}S and ^{33}S). In the potentially ancient hydrothermal environments in the Pilbara (3.5 Ga), the sulfur isotopic signatures for the SurDB functions were suggested.

Based on the metabolic pathways recently being clarified in the sulfate-reducing prokaryotes (SateRP), sulfur-oxidizing prokaryotes (SurOP) and sulfur-reducing prokaryotes, however, we predict that the sulfur-disproportionation metabolism is substantially catalyzed by a combination of SOX (for SurOP) and reversible DSR systems for SateRP and SurOP). If this is true, the SurDB should have emerged (evolved) after the SurOP and SateRP, and the sulfur isotope signatures in the Pilbara would be more lilkely explained by the concurrent function of the SurOP and SateRP. Why did the SurOP dominate in the anoxic oceanfloor 3.5 billion-years ago? It also sounds unlikely. Anyhow, what is the most important is to clarify the metabolic pathways of the SurDB

We have isolated the first thermophilic SurDB from a deep-sea hydrothermal environment. It is also the first non-sulfate-reducing SurDB. We have characterized the physiological properties of the thermophilic SurDB that are significantly different from those of the previously known SurDB. The sulfur isotopic fractionations (^{34}S and ^{33}S) will be compared to the previous data. The genome sequence will provide an important insight into the pathways.

Identification of amides involved in Nitrogen sequestration in dissolved organic matter and sediments by ESI-FTICR-MS

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Nitrogen is a key component in global cycling. Fixed N is particularly important since it is the primary bioavailable form. Formation of fixed N is part of the N cycle which is co-dependent on other major elements including carbon, oxygen and phosphorus [1]. Two organic rich lacustrine sediments from Mud Lake, Florida and Mangrove Lake, Bermuda and dissolved organic matter from various pore waters and rivers were studied. Firstly, pyridine extracts of the sediments were analysed using two dimensional liquid state nuclear magnetic resonance (NMR) spectroscopy. Electrospray ionisation Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) was then used to characterise the pyridine extracts at the molecular level. In the case of dissolved organic matter from pore waters and rivers, electrodialysis was used to remove salts before MS analysis.

The ESI-FT-ICR-MS spectra of all samples show the presence of alkyl amides. Homologous series of alkyl amides and diamides are identified throughout both negative and positive ionisation mode spectra. Although the production of these alkyl amides and diamides could be via a lipase catalysed reaction with esters, abiological reactions are also possible. High concentrations of alkyl esters and ammonia in the lake sediments, pore waters, and riverine systems could lead to an amidation reaction. This reaction was tested by reacting sunflower oil with ammonium carbonate under environmental conditions. After four weeks alkyl amides were observed in the ESI-FT-ICR-MS spectrum. This proves that this reaction is a probable route to production of the alkyl amides and diamides observed in the two lake sediments.

To our knowledge this is the first observation of alkyl amides and diamides in immature organic rich sediments and riverine dissolved organic matter. These results could have a significant impact on current knowledge regarding N sequestration in sediments and in the water column.

[1] Zehr J. P., Ward B. B., (2002) *Appl. Environ. Micro.*, **68**, 1015-1024.