

Competition for sulfide in marine sediments: Electrogenic Filamentous Bacteria versus *Beggiatoa*

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Recently, a novel mechanism of sulfide oxidation has been described from marine sediments, whereby long filamentous bacteria (ElectroFilaments) couple the reduction of oxygen at the surface to the oxidation of sulfide at centimeters depth via electrical currents. This creates a wide suboxic zone similar to that created by the large sulphur bacteria of the genus *Beggiatoa*. These latter bacteria are motile and capable of intracellular nitrate storage, and in this way, *Beggiatoa* can transport nitrate to deeper sediment layers to oxidize H₂S. In the seasonally hypoxic Lake Grevelingen, The Netherlands, both types of sulfur oxidizing bacteria have recently been observed. This rises the question how these different modes of microbial sulfide oxidation compete?

We conducted a yearlong study of monthly sampling campaigns in Lake Grevelingen. Microsensor profiling of O₂, pH and H₂S revealed the geochemical fingerprint of the dominant microbial process over time (both mechanisms generate a very distinct pH profile). In addition, FISH tagging for *Desulphobulbus* and microscopic counting of *Beggiatoa* allowed to quantify the abundance of the two competing bacteria. Our results show that both modes of microbial sulfide oxidation follow a predictable seasonal succession, where *Beggiatoa* are dominant in autumn right after summer hypoxia, while Electrofilaments become dominant in spring. Field data and additional mesocosm experiments suggest that bottom water oxygenation, nitrate availability and physical disturbance are the main environmental factors controlling the outcome of this microbial competition. These two competing microbial pathways of sulfur oxidation strongly affect the biogeochemical cycling, but in a very different way, and so, the predominance of either mechanism can have a strong impact on the elemental cycling in coastal sediments.

Tracing the origin of sulphur in Darzila karst cave, NE Iraq

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Darzila cave, located in the Sangaw district in Northern Iraq, develops by the dissolution of limestone by sulphuric acid through oxidation of H₂S. The hydrogen sulphide may either originate from oil-rich reservoirs, such as the nearby Kirkuk oil field, or from gypsum of the Lower Fars Formation.

Samples from these possible endmembers were subject to isotopic analyses ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$). The water of three prominent floor feeders inside the cave was analyzed for its content of major ions, trace elements, total organic carbon, as well as for the stable isotopic composition of water (δD , $\delta^{18}\text{O}$), dissolved sulphate ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$) and sulphide ($\delta^{34}\text{S}$).

Investigations of water samples pointed towards a potential influence of hydrocarbon-bearing layers at two sites. Indices were significantly elevated SO₄²⁻/Ca²⁺ ratios, an increased content of total dissolved solids (10-31 g/L) and dissolved organic carbon (14-20 mg/L), and relative enrichments of trace elements such as Cr, Be, Ga, Ni, Co, Mn, and V. The isotopic investigations confirmed the influence of H₂S affluxes from hydrocarbons ($\delta^{34}\text{S} \approx -9\text{‰}$ VCDT) at these sites. Further evidence was given by depleted $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in sulphate, small differences between the sulphur isotopic signature of sulphate and sulphide, as well as elevated δD values in ambient water.

The third floor feeder had an entirely different isotopic signature, showing distinct signs of bacterial sulphate reduction and therefore pointing towards primary gypsum from the Lower Fars Formation ($\delta^{34}\text{S} \approx +22\text{‰}$ VCDT) as sulphur source. Main indications were a $\delta^{34}\text{S}$ value of sulphate above that of gypsum and strongly depleted sulphide. However, it appears that sulphate reduction was superimposed by several secondary transformation processes.