



## **A cryptic sulfur cycle driven by iron in the methane zone of marine sediment (Aarhus Bay, Denmark)**

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Many observations of the distribution of free sulfide in marine sediments show a net sink of sulfide below the sulfate-methane transition. The sulfide reacts with deeply buried Fe(III) and thereby undergoes a partial oxidation and conversion into pyrite. It was a goal of this study to understand whether sulfate may be generated by re-oxidation of sulfide throughout the sulfate and methane zones, which might explain the abundance of active sulfate reducers deep below the main sulfate zone. Sulfate reduction and sulfur-iron geochemistry were studied in 5-6 m deep gravity cores of Holocene mud from Aarhus Bay (Denmark). Sulfate penetrated down to 130 cm where methane started to build up and where the concentration of free sulfide peaked at 5.5 mM. Below this sulfate-methane transition, sulfide diffused downwards to a sulfidization front at 520 cm depth, below which dissolved iron, Fe<sup>2+</sup>, accumulated in the pore water. Sulfate reduction rates measured by <sup>35</sup>S-tracer incubations in the sulfate zone were high due to high concentrations of reactive organic matter. Within the sulfate-methane transition, sulfate reduction was distinctly stimulated by the anaerobic oxidation of methane. In the methane zone below, sulfate remained at positive “background” concentrations of <0.5 mM down to the sulfidization front. Sulfate reduction decreased steeply to rates which at 300-500 cm depth were 0.2-1 pmol SO<sub>4</sub><sup>2-</sup> cm<sup>-3</sup> d<sup>-1</sup>, i.e. four to five orders of magnitude lower than rates measured near the sediment surface. Sulfate reduction in the methane zone accounted for only 0.1% of sulfate reduction in the entire sediment column and was apparently limited by the low pore water concentration of sulfate and the low availability of organic substrates. Amendment of the sediment with both sulfate and organic substrates immediately caused a 10-40-fold higher, “potential sulfate reduction” which showed that a physiologically intact community of sulfate reducing bacteria was present. The “background” sulfate concentration appears to be generated from the reaction of downwards diffusing sulfide with deeply buried Fe(III) species, such as poorly-reactive iron oxides or iron bound in reactive silicates. The oxidation of sulfide to sulfate in the sulfidic sediment may involve the formation of elemental sulfur and thiosulfate and their further disproportionation to sulfide and sulfate. The net reaction of sulfide and Fe(III) to form pyrite requires an additional oxidant, irrespective of the formation of sulfate. This could be CO<sub>2</sub> which is reduced with H<sub>2</sub> to methane. The methane subsequently diffuses upwards to become re-oxidized at the sulfate-methane transition and thereby removes excess reducing power and enables the formation of excess sulfate. The combination of these well-established sulfur-iron-carbon reactions may lead to the deep formation of sulfate and drive a cryptic sulfur cycle. Processes similar to the ones described here probably occur widespread in marine sediments, in particular along the ocean margins.