Sulfate reduction in peatlands – Ecophysiology of a rare microorganism that contributes to a process with increasing importance for the global climate

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Methane emission from peatlands contributes substantially to global warming but is significantly reduced by sulfate reduction, which is fuelled by globally increasing aerial sulfur pollution. However, the biology behind sulfate reduction in terrestrial ecosystems is not well understood and the key players for this process as well as their abundance remained unidentified. Linking (phylo)genetic information, obtained through gene-specific or metagenomic/-transcriptomic surveys, to the ecosystem process sulfate reduction is notoriously difficult because (i) known sulfate reducers are phylogenetically intermingled with non sulfate reducers and (ii) marker genes for sulfate reduction [such as *dsrAB*, encoding subunits of dissimilatory (bi)sulfite reductase] are also present and transcribed in some bacteria that lack the capability for sulfate reduction. Here we demonstrate, by comparative 16S rRNA gene stable isotope probing in the presence and absence of sulfate, that a *Desulfosporosinus* species, which constitutes only 0.006% of the total microbial community, is a main sulfate reducer at a long-term study peatland. Parallel stable isotope probing of *dsrAB*, confirmed that no other microorganisms contributed substantially to sulfate reduction in the incubations supplied with *in situ* concentrations of short-chained fatty acids and lactate. Subsequent single substrate incubations revealed that sulfate reduction was stimulated best with lactate, propionate, and butyrate, but not with acetate or formate. For the identified *Desulfosporosinus* species a high cell-specific sulfate reduction rate of 341 fmol SO_4^{2-} $cell^{-1}$ day^{-1} was determined. Thus, the small *Desulfosporosinus* population has the potential to reduce sulfate *in situ* at a rate of 4.0-36.8 nmol (g soil w. $wt.)^{-1}$ day^{-1}, sufficient to account for a considerable part of sulfate reduction in the peat soil. These data show that the identified *Desulfosporosinus* species, despite being a member of the 'rare biosphere', contributes to an important biogeochemical process that diverts the carbon flow in peatlands from methane to CO_2 and, thus, alters their contribution to global warming.

Abiogenic formation of carbon species at hydrothermal conditions using a novel flow apparatus

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We present an experimental configuration that permits constant high-pressure flow through hydrothermal cells while at the same time maintaining uniform concentrations of multiple dissolved gases. This system provides an additional benefit for kinetic studies as it allows precise redox control without the presence of mineral buffers or the need to rely on the hydothermal breakdown of unstable intermediates in the source fluid. Steady-state equilibrium can be determined when a target species concentration no longer changes with increasing residence time at equivalent temperature, pressure and source fluid composition. For example, we have calibrated the equilibrium constant for the water-gas shift (WGS) reaction ($CO_2 + H_2 = CO + H_2O$) in pure water between 225-374°C and 220-325 bars, including the critical point. In this region the log K_{WGS} is linear with respect to water density. These equilibrium constants, as well as those for formic acid (thought to be the WGS reaction intermediate) are in good agreement with those derived from the HKF equation of state if recent updates for the involved species are incorporated. This is especially noteworthy due to the uncertainty of thermodynamic calculations near the critical point of water with implications for modeling natural hydrothermal systems.

While the low concentrations of CO appear in equilbrium with the WGS reaction, controls on the appreciably higher concentrations of methane in deep-sea hydrothermal fluids are still unclear. However, this methane is often thought abiogenic and CO_2 is the dominant source of carbon. This is an important consideration when studying the kinetically prohibitive synthesis of reduced hydrocarbon species (e.g. $CO_2 + 4H_2 = CH_4 + 2H_2O$). Using a source fluid containing geologically relevant concentrations of H_2 and CO_2, we have observed the formation of C1-C3 hydrocarbons in reaction cells constructed of both titanium and gold, with and without the presence of magnetite, between 200-400°C. Methane generation is linear with respect to residence time in the cells and synthesis is maximized at temperatures near 300°C. Our results demonstrate that hydrocarbon formation is enhanced as much as 200X in the gold cell relative to the titanium cell, while magnetite appears relatively ineffectual as a catalyst for hydrocarbon formation.