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Molecular characterisation of the organic matter at the Mallik 5L-38 Research Well: Implications for depositional environment and the Deep Biosphere

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Living microbial communities have been documented in numerous gas hydrates from marine settings [1]. By contrast, almost nothing is known about microorganisms which may live within terrestrial gas hydrates and their surrounding strata. In this contribution, we show how biogeochemistry has been used in search for the existence of a so-called Deep Biosphere in the gas hydrate zone of the Mallik 5L-38 Gas Hydrate Research Well, Mackenzie Delta (Northwest Territories, Canada). Also, we outline the ecosystems of the Kugmallit Sequence at the time of its deposition (Oligocene) at the Mallik site. Therefore, core samples of different lithologies (shales, sandstones, siltstones, and lignites) covering the depth interval 898-1145m in the Mallik 5L-38 Well were investigated with regard to their biomarker composition using GC-MS and LC-ESI-MS-MS. A series of terrestrial biomarkers (such as isopimarane, α -phyllocladane, β -amyrine etc.) indicates the predominantly terrigenous character of the organic matter. The *n*-alkane distributions of the lignites with a maximum at $n-C_{23}$, characteristic for Sphagnum sp., and of the interbedded coarser-grained sediments with a maximum at n-C₂₉, characteristic for higher land plants, suggest an alteration of a swampy milieu with a fluviatile sedimentation within an overall deltaic setting.

Phospholipids were our target compounds in the search for viable microbial ecosystems in the subsurface of the Mallik site. Because they are rapidly degraded after cell death, their occurrence can be taken as an indicator for living microbial cells. Intact phospholipids have been found in Mallik sediments, which is the first molecular indication for the existence of deep microbials communities not only at the Mallik site but for terrestrial gas hydrates in general. A series of compounds interpreted as lyso-phosphatidyl-ethers by their MS-MS fragmentation patterns were detected in almost all samples investigated. Ether lipids are known to occur in archaeal biomass. Thus, their presence may indicate the existence of archaeal communities in the subsurface at the Mallik site.

Reference

[1] Wellsbury et al. (2000) *Proceedings of the ODP*, *Scientific Results* **164**, 379-391.

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Deep biosphere in terrestrial systems (DEBITS): The New Zealand coal band

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Bacterial gas is known from isotopic and chemical considerations to occur to thousands of metres depth. How methanogenic bacteria can be active in such deep and ancient formations, where substrates and nutrients should have been long ago removed, is puzzling. However, the thermal maturation of terrigenous organic matter can produce substances which are known to be substrates for methanogens, namely carbon dioxide, acetate and methanol. In addition, aromatisation of organic compounds may produce molecular hydrogen enabling autotrophic reactions to occur, including H_2/CO_2 methanogenesis and acetogenesis. This temperature activation of buried organic matter could stimulate bacterial activity at depth and at the same time result in reactions and products, previously thought to be abiotic.

We have drilled a continuous core (170 metres; 6" diameter) in New Zealand under strictly controlled conditions to sample the deep biosphere in a terrestrial setting. The Cenozoic sedimentary section of the Taranaki Basin (New Zealand) contains potential "feeders" in the form of coals and coaly shales and closely juxtaposed coarse grained sediments, which may act as a habitat for microorganisms. The sediments have experienced significant burial and uplift resulting in a rank range that is consistent with significant generation, expulsion and migration of potential substrates. Additionally, surrounding localities display a wide range of coalification encompassing peats, brown coal and sub-bituminous coal.

We are delineating living microbial populations in coarse grained lithologies using "Life Markers" such as the intact phospholipids. Genetic diversity within the microbial ecosystem is being determined using nucleic acid probes. The role of abiotic diagenetic reactions in generating potential substrates is being addressed from the organic geochemistry of macromolecules and the composition and occurrence of low molecular weight functionalised compounds. Changes in the chemical composition of the sediment due to microbial activity is also being examined using laboratory incubation experiments.

In this communication we present initial results from the drilling and research programme.