INVESTIGATION OF THE STRUCTURAL COMPOSITION OF SEDIMENTARY ORGANIC MATTER TO ASSESS ITS FEEDSTOCK POTENTIAL FOR DEEP MICROBIAL POPULATIONS

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In recent years microorganisms are recognized to occur widely disseminated in the deep subsurface of the Earth, far away from any photosynthetic energy supply. This so-called deep biosphere must play a fundamental role in global biogeochemical cycles over both, short and long-time scales, because its mass is assumed to be equal to that of the surfaces biosphere (Whiteman et al., 1998). It has been stated that diverse microbial life appears to be present wherever a source of energy (substrate) is present (Kerr, 1997). In the zone of diagenetic alteration functional groups, containing oxygen, are lost from the sedimentary organic matter, partly in form of CO₂, acetic acid (acetate) or higher fatty acids. The idea is that these released products may provide a significant carbon and energy source for deep microbial populations like *Bacteria* and *Archaea*. For instance, Horsfield et al. (2006) were able to show an increase of microbial activity in a sedimentary section with increased thermally induced substrate release, which might indicate such a bio-geo coupling, although in an environment with a much higher thermal heatflow.

New Zealand represents a perfect natural laboratory to investigate this bio-geo coupling hypothesis. The so-called New Zealand coal band contains a coal series of almost continuous maturity from Cretaceous to Tertiary age and represents therefore different feeder potentials. Within the scope of the DEBITS (Deep Biosphere in Terrestrial Systems) project, coal samples of different maturity (ranging from 0.23 to 0.81 R₀) were gathered from various coal mines on the North and the South Island of New Zealand. Additionally, organic carbon rich samples including a rank range from lignites, brown coals to sub-bituminous coals were taken from the 148 m deep DEBITS-1 well, which was drilled in the Waikato coal area (Taranaki Basin, North Island, New Zealand) in February 2004. Thus, the collected sample set covers a maturity range that is consistent with significant generation, expulsion and migration of potential substrates.

The main goal of this study has been to elucidate the structural composition of the organic matter at different stages of maturity or different depth in the DEBITS-core by using several consecutive chemical degradation reactions, thereby providing insights into substrate generation.

After extraction of the soluble compounds with water and organic solvent the first chemical degradation step has been the cleavage of the ester bound moieties using KOH in methanol. First GC/MS results of a low mature coal sample ($R_0 = 0.45$) show a bimodal distribution (maxima at *n*-C₁₆ and *n*-C₂₆) of saturated and unsaturated fatty acids ($C_{10} - C_{31}$), as well as some methyl substituted fatty acids. However, one of the most important food sources for deep microbes might be short chain fatty acids, therefore, we will develop a sensitive method to analyse acetic acid (acetate) and other short chain fatty acids in small amounts. The next steps will be the acidic hydrolysis (HI) of ether bonds followed by cleavage of sulfide and polysulfide bonds using in situ generated Ni₂B. Finally, the oxidation of the kerogen skeleton using RuO₄ will give information about the basic structure of the kerogen. The released compounds and the remaining residues after each degradation step will be analysed using GC/MS and pyrolysis GC/MS techniques. Mass balancing will provide information about different feeding potentials of the selected samples of different maturity and sample depth. Here, we will present the first results of our investigation.



Figure 1. Gas chromatogram of a coal sample ($R_0 = 0.45$). *n*- C_x = carbon number of FA.

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