Laser micropyrolysis-GC/MS of biomarkers in authigenic carbonates

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Miniaturised, extract-based biomarker techniques have recently proven applicable to analyse distinct mineral phases of microbially mediated, authigenic carbonates. However, laboratory sample contamination is a concern in with this technique, and the mechanical treatment of the rocks limits lateral resolution. Laser pyrolysis (LaPy) and/or thermal extraction of biomarkers from close to the surface could potentially overcome this risk.

In this study, we compared data acquired by interfacing a near-IR laser microprobe to a gas chromatograph / mass spectrometer (GC/MS) to biomarker distributions collected from the same samples using extract-based techniques.

Very few sample preparation steps are needed for LaPy-GC/MS, which minimises contamination risk. The size of pyrolysis craters depends on laser power settings and radiation adsorption of the target region. This allows for probing recent and fossil microbialites in the sub-mm range.

Since the high power of a focused near-IR laser beam leads to thermal cleavage of carbon bonds, low-molecular-weight compounds were predominantly pyrolysis products. Nonetheless, significant biomarkers including *n*-alkanes, phytanol, and crocetane could be detected. Their distribution, however, did not match the more comprehensive patterns obtained using liquid extraction-GC/MS. At this stage, the laser-based extraction method does not offer a satisfactory alternative to the extract-based technique.



Figure 1: Laser micropyrolysis-GC/MS results obtained from the authigenic carbonate sample pictured top left (*).

Geochemistry of rift valley sediments and hydrothermal fluids at the ultraslow spreading S. Knipovich Ridge

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The rift valley of the ultra-slow spreading southern Knipovich Ridge in the Norwegian-Greenland Sea (73°N) is partly buried by a thick sediment cover. These glacial and post-glacial sediments (12-20 ky), derived from the nearby Bear Island fan, likely act as a thermal and hydrogeological boundary to heat and fluid flow and influence hydrothermal fluid compositions. Geochemical studies of the rift valley sediments and the hydrothermal vent fluids of the recently discovered black smoker vent field Loki's Castle provide insights into the origin of the hydrothermal vent fluids and their interaction with the sediments. Here we present an overview of preliminary data on the carbon and sulphur geochemistry of the sedimentary and hydrothermal components at Loki's Castle and compare these with other sedimented and un-sedimented mid-ocean ridge hydrothermal systems. The vent fluids have a pH of \sim 5 and are characterized by elevated concentrations of hydrogen and methane. Ammonia concentrations are also high compared to unsedimented ridge environments and point to a sedimentary input. Vent fluid S-isotope data reflect mixing of a MORB source with sulphide derived from reduced seawater sulphate. $\delta^{13}C_{DIC}$ (dissolved inorganic carbon) are depleted relative to mantle carbon values, consistent with an organic carbon input.

Short gravity cores of the rift valley sediments have relatively constant organic carbon contents (TOC) of ~0.5 wt%, but are locally as high as 1.5 wt%, and yield $\delta^{13}C_{TOC}$ values typical of marine organic matter. In two cores north of Loki's Castle, extracted sediment pore fluids show an increase in alkalinity and DIC concentrations with increasing burial depth. The corresponding $\delta^{13}C_{DIC}$ values show a clear depletion with increasing alkalinity and DIC concentrations, indicative of sulphate reduction at shallow depths within the sediment cover.