

## Biogeochemistry of trace metals during a coastal bloom in the Baltic Sea

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Ultrafiltration was performed before and during spring-bloom, using filters with six different cut-offs (1kD, 3kD, 5kD, 10kD, 100 kD and 0.22µm).

By early May, phytoplankton production was the important source of particulate carbon. POC to chlorophyll-a decreased from 200 to 50,  $\delta^{13}\text{C}$ -POC increased from -30‰ to -22‰, and TEP (Transparent Exopolymeric Particles, reflecting sugar-rich exudates from mainly diatoms) increased around 8 times. COC (1kD-0.22µm) was around 30% and POC 5% of TOC before plankton production started. During bloom COC increased to about 45% and POC up to 10% of TOC.

The unfiltered Cu, Ni and Co concentrations remained relatively stable throughout the sampling period (around 30, 34 and 1.5 nM, respectively). Furthermore, the colloidal fractions remained relatively constant for these three elements. Approximately 60% of colloidal Cu was found in the 5-10kD fraction and around 25% in the 1-5kD fraction, both before and during bloom. However, a distinct decrease in the solution (<1kd)/colloidal ratio was observed during bloom.

The Fe data showed that the LMW fraction was reduced from 50nM down below 7nM during bloom, in spite of the fact that the total Fe concentration was around 600 nM. This slow transfer may induce iron-stressed conditions for certain plankton species during bloom.

Data indicate a slow transfer of low molecular trace metals (directly bioavailable) from particulate and colloidal phases. Most of the decrease in the solution fraction (LMW fraction) reflects uptake in the particulate fraction.

Three different mechanisms could explain this phase change. Active uptake of LMW trace metals by living plankton, uptake by TEP and scavenging by Mn-rich particles (which were formed during bloom).

About 75% of the unfiltered Al concentration was retained by the 0.22 µm filter before bloom and 90% during bloom. The LMW/colloidal ratio decreased from 8 down to 1 during the sampling period. These data indicate an uptake of LMW Al into the particulate fraction during plankton bloom. Active uptake of Al by plankton appears to be a less likely explanation for this phase change. Association of LMW Al with TEP is a more reasonable explanation.

## Modelling of catalytic abiogenic synthesis of the hydrocarbons in the Earth's crust

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The problems of the hydrocarbon deposits origin are being considered for a long period of time. The most conventional models imply biogenic mechanisms of oil-gas lenses formation in the Earth's crust.

The present paper summarizes the research results of the lab-scale and pilot synthesis of hydrocarbons from CO,  $\text{C}_2$  and  $\text{C}_2$  over bifunctional metal-containing catalysts (covering Fe, Ni, Co, Mo etc.) mixed with clays,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and zeolites. The compositions of the synthesised hydrocarbon mixtures are compared with those of the natural gas-condensate deposits.

The conclusion was made that the modern technologies of abiogenic hydrocarbon synthesis on bifunctional catalysts allow obtaining the natural variations of hydrocarbon mixtures – from predominantly methane to the liquid hydrocarbon mixtures (up to  $\text{C}_{20+}$ ) with various contents of olefins, n-alkanes, iso-paraffins, and aromatic hydrocarbons.

The supposition is analysed that the processes of hydrocarbons synthesis from  $\text{C}_2$ ,  $\text{C}_4$  and  $\text{C}_2$  mixtures over inorganic catalysts may simulate the macro-geochemical processes having proceeded in the Earth's crust at different stages of its geochemical history.

The possible geochemical schemes for the abiogenic synthesis of hydrocarbon mixtures are proposed.

It was taken into account that the biogenic version of hydrocarbon synthesis has a low thermodynamic probability: the carbon dioxide and water bonding reactions proceed in the endothermic way, requiring an energy source. Their intensity in the oxygen-free atmosphere would be negligible. However in case of the abiogenic hydrocarbon syntheses the reactions proceed with a considerable heat release and thermodynamically are very highly probable. The intensity and probability of these processes under the primary atmosphere conditions must have been quite high.

### References

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