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# EFFECTS OF DIAGENESIS AND CATAGENESIS ON LADDERANE LIPIDS AS DETERMINED BY HYDROUS PYROLYSIS

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Ladderane lipids (Sinninghe Damsté *et al*., 2002) are characteristic membrane lipids of bacteria performing anaerobic ammonium oxidation (anammox), a process that was found to contribute significantly to the loss of inorganic nitrogen from the ocean. Ladderanes occur in a variety of different forms either ester or ether bound to the glycerol backbone, and contain three or five linearly fused cyclobutane rings, which is unprecedented in nature. They have been applied as biomarkers for anammox activity in oxygen depleted zones of the ocean (Kuypers *et al.*, 2005) and in marine sediments. However, to date no fossil remnants of ladderane lipids have been found in ancient sediments. Due to the highly strained conformation of the cyclobutane moieties, the structures of the ladderanes are probably altered by reactions during diagenesis. Opening of the cyclobutane rings (Sinninghe Damsté *et al.*, 2005) could eventually result in the formation of e.g. n-alkyl biphenyls (Fig. 1).

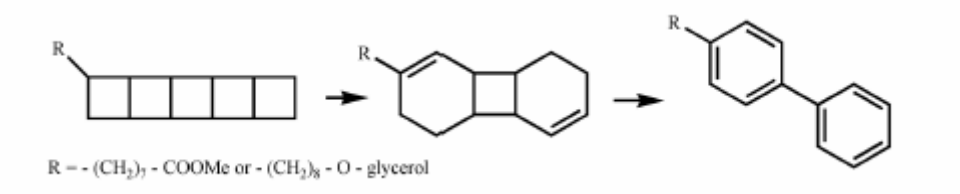


Figure 1. Hypothetical diagenetic pathway for ladderane lipids. Opening of the cyclobutane rings may result in the formation of biphenyls. The intermediate compound was formed during GC analysis and its structure was revealed by NMR studies (Sinninghe Damsté *et al.*, 2005).

Hydrous pyrolysis was applied to investigate the thermal stability of ladderane lipids as well as to elucidate their possible diagenetic and catagenetic products, which can then be used to trace past anammox activity. Artificial maturation was accomplished by isothermally heating anammox biomass derived from a wastewater treatment plant in Rotterdam (The Netherlands) at temperatures ranging from 120 to 365°C for 72 hours. To study the role of minerals in the thermal alteration of ladderane lipids, additional experiments were conducted with anammox biomass mixed with common sedimentary minerals (montmorrillonite, calcite)

as well as quartz-rich sediment from the North Sea. For each experiment all organic phases (i.e., aqueous, gas, oil and residue) were quantitatively collected and analyzed by GC and GC-MS. The generated gases contained mainly $CO_2$, but at temperatures >240°C production of hydrogen gas and $C_1$-$C_5$ hydrocarbons was observed. Generation of an immiscible oil started at 240°C, with a maximum yield at 335°C that was followed by a rapid decrease at higher temperatures.

The objective is to identify degradation products of ladderane lipids that will, in combination with their highly $^{13}C$-depleted carbon isotopic signature (Schouten *et al.*, 2004), provide a suitable biomarker to assess possible anammox activitiy in the geological past. Currently, we are studying the composition of the hydrous pyrolysates with GC-MS and LC-MS. In addition, detailed information on the diagenetic and catagenetic pathways of bacteriohopanepolyols will be obtained because anammox bacteria were found to synthesize these lipids (Sinninghe Damsté *et al.*, 2004). Indeed, at temperatures >300°C significant production of hopanes was observed.

**REFERENCES**

Sinninghe Damsté, J. S., Strous, M., Rijpstra, W. I. C., Hopmans, E. C., Geenevasen, J. A. J., van Duin, A. C. T., van Niftrik, L. A. and Jetten, M. S. M., 2002. Linearly concatenated cyclobutane lipids form a dense bacterial membrane. *Nature* **419**, 708-712.

Kuypers, M. M. M., Lavik, G., Woebken, D., Schmid, M., Fuchs, B. M., Amann, R., Jørgensen, B. B., Jetten, M. S. M., 2005. Massive nitrogen loss from the Benguela upwelling system through anaerobic ammonium oxidation. *PNAS* **102**, 6478-6483.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Geenevasen, J. A. J., Strous, M., Jetten, M. S. M., 2005. Structural identification of ladderane and other membrane lipids of planctomycetes capable of anaerobic ammonium oxidation (anammox). *FEBS* **272**, 4270-4283.

Schouten, S., Strous, M., Kuypers, M. M., Rijpstra, W. I. C., Baas, M., Schubert, C. J., Jetten, M. S. M., Sinninghe Damsté, J. S., 2004. Stable carbon isotopic fractionations associated with inorganic carbon fixation by ammonium-oxidizing bacteria. *Appl. Environ. Microbiol.* **70** (6), 3785-3788.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Schouten, S., Fuerst, J. A., Jetten, M. S. M., Strous, M., 2004. The occurrence of hopanoids in planctomycetes: implications for the biomarker record. *Org. Geochem.* **35**, 561-566.