

**PHOSPHOLIPIDS AND ARCHAEOOL AS LIFE MARKERS:
INSIGHTS INTO THEIR THERMAL STABILITY USING PYROLYSIS**

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Phospholipids (PLs) are abundant constituents of biological tissues and are known to quickly degrade after death of an organism or a cell respectively (White et al., 1979). However, experiments to date were carried out over non-geological time periods and under laboratory conditions and focused on the enzymatic biodegradation of phospholipids. To give evidence for the abiotic thermal decay over geological time spans we combined pyrolysis experiments on synthetic standard compounds with LC-MS and GC-MS analyses of its products and residues. On-line open system pyrolysis experiments using the Source Rock Analyser (SRA; 0.7, 2.0, 5.0K/min) provided the input data for the bulk kinetic model from which half-lives for bulk thermal degradation of PLs were calculated. Both open- and closed system (MSSV) experiments were also conducted in preparative mode to ascertain which compositional changes accompanied thermal degradation. Four temperature endpoints were selected for SRA analysis (222, 270, 300, 309°C) and 6 for MSSV pyrolysis (200, 250, 300, 350, 400, 450°C) using a heating rate of 0.7K/min. Heated samples were then extracted with organic solvents, split into two equal aliquots and analysed by LC-MS and GC-MS. Unheated samples and blanks were analysed in parallel for comparison.

Results are striking in that they show rapid thermal decay of intact PL (diacylphosphatidylcholine, -ethanolamine, -glycerol) already at a temperature of 200°C under the stated laboratory conditions. As well as residual intact compounds, thermal products such as lyso-PLs and diglyceride core lipids are present (Fig. 1). Interestingly, also intermediate fragments (loss of methyl groups at polar head group) are detected in low abundance demonstrating the stepwise degradation of the intact PL. Higher temperatures, reflecting increased maturation, yield in succession increasing diglyceride derivatives and cracking products of diglycerides (Fig. 1). It should also be noted that cleavage occurs at molecular positions identical to those susceptible to biological degradation. Main products of thermal breakdown detected by GC-MS of extracts as well as by Py-GC-MS are the phospholipid fatty acids (PLFAs) stemming from the side-chains of PLs, increasing at lower temperature and decreasing from 350°C towards higher temperatures. As expected, higher temperatures

enhance the formation of short-chain hydrocarbons (C_1 to C_5 ; C_6 to C_{14}) reflected by closed pyrolysis analyses.

Experiments on archaeol, a disubstituted triglyceride alcohol, demonstrates a higher stability during maturation; decreasing signal of the intact compound is clearly detectable until 300°C , beyond 300°C thermal decay accelerates but no characteristic cleavage fragments have been detected by LC-MS of extracts of heated samples. On the other hand, between 300 and 400°C Py-GC-MS and GC-MS show increasing formation of degradation products such as phytene, phytol, and several adducts.

In conclusion, both decay of intact membrane lipids and generation of its products during maturation can be followed concordantly by the combination of LC-MS and (Py-)GC-MS. Kinetic modelling of PL decay results in a half-life of $10^4 - 10^5$ years at 50°C but of only 1 - 50 years at 100°C , thereby supporting the hypothesis that phospholipids are utilisable as „life markers“ especially in the deep HOT biosphere.

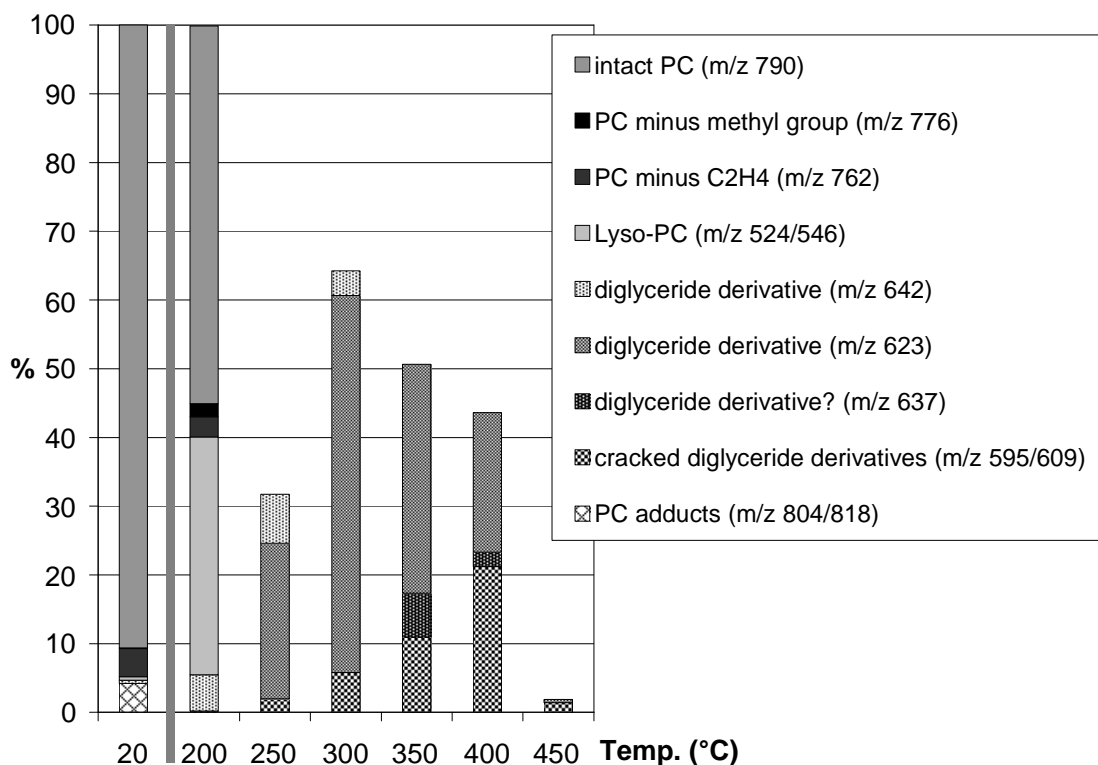


Figure 1. Percentage distribution of PC thermal degradation products from LC-MS analysis after MSSV-Pyrolysis; sample at 200°C was set to 100% in comparison to all heated samples.

REFERENCE

White, D. C., Davies, W. M., Nickels, J. S., King, J. D. and Bobbie, R. J. (1979) Determination of the sedimentary microbial biomass by extractible lipid phosphate. *Oecologia* **40**, 51-62.