



Determination of thermal stability of specific biomarker lipids of the freshwater fern *Azolla* through hydrous pyrolysis

Merel Sap (1), Eveline N. Speelman (1), Michael D. Lewan (2), Jaap S. Sinninghe Damsté (1,3), Gert-Jan Reichart (1,4)

(1) Utrecht University, Faculty of Geosciences, P.O. box 80021, Utrecht, The Netherlands (m.sap1@students.uu.nl), (2) U.S. Geological Survey, Box 25046, MS 977, Denver, CO 80225, United States, (3) Netherlands Institute for Sea Research (NIOZ), P.O. Box 5, Texel, The Netherlands, (4) Alfred Wegener Institute for Polar and Marine Research (AWI), Am Handelshafen 12, 27570, Bremerhaven, Germany

Enormous blooms of the free-floating freshwater fern *Azolla* occurred within the Arctic Basin during an extended period of ~ 1.2 Ma during the middle Eocene (Brinkhuis et al. 2006; Speelman et al., GB, 2009). The sustained growth of *Azolla*, currently ranking among the fastest growing plants on Earth, in a major anoxic basin may have substantially contributed to decreasing atmospheric CO₂ levels by burial of *Azolla*-derived organic matter. Speelman et al. (OG, 2009) reported biomarkers for *Azolla* (1,w20 C32 - C36 diols, structurally related C29 20,21 diols, C29 1,20,21 triols, C29 dihydroxy fatty acids as well as a series of wax esters containing these mono- and dihydroxy lipids), which can be used to reconstruct palaeo-environmental conditions. Here we assess the thermal stability of these compounds, to extend their biomarker potential.

We specifically focused on the thermal stability of the *Azolla* biomarkers using hydrous pyrolysis in order to determine which burial conditions allow reconstruction of past occurrences of *Azolla*. In addition, hydrous pyrolysis was also performed on samples from the Eocene Arctic Ocean (ACEX core), to test if and how the biomarkers change under higher temperatures and pressures in situ. During hydrous pyrolysis, the biomass was heated under high pressure at temperatures ranging between 220 and 365°C for 72 hours. Four experiments were also run using different durations to explore the kinetics of biomarker degradation at specific temperatures. First results indicate that the *Azolla* specific diols are still present at 220°C, while the corresponding wax esters are already absent. At 300°C all *Azolla* specific biomarkers are destroyed. More specific determination of the different biomarkers' stability and kinetics would potentially allow the reconstruction of the temperature and pressure history of *Azolla* deposits.

Literature:

- Brinkhuis, H., Schouten, S., Collinson, M. E., Sluijs, A., Sinninghe Damsté, J. S., Dickens, G. R., Huber, M., Cronin, T. M., Onodera, J., Takahashi, K., Bujak, J. P., Stein, R., van der Burgh, J., Eldrett, J. S., Harding, I. C., Lotter, A. F., Sangiorgi, F., van Konijnenburg-van Cittert, H., de Leeuw, J. W., Matthiessen, J., Backman, J., Moran, K. (2006), Episodic fresh surface waters in the Eocene Arctic Ocean, *Nature* 441, 606-609.
- Speelman, E. N., M. M. L. van Kempen, J. Barke, H. Brinkhuis, G. J. Reichart, A. J. P. Smolders, J. G. M. Roelofs, F. Sangiorgi, J. W. de Leeuw, A. F. Lotter, J. S. Sinninghe Damsté (2009), The Eocene Arctic *Azolla* bloom: environmental conditions, productivity and carbon drawdown, *Geobiology*, 7, 155-170.
- Speelman, E. N., G.-J. Reichart, J.W. de Leeuw, W. I. C. Rijpstra, Jaap S. Sinninghe Damsté (2009), Biomarker lipids of the freshwater fern *Azolla* and its fossil counterpart from the Eocene Arctic Ocean, *Organic Geochemistry*, 40, 628-637.