PALAEOCLIMATE CONDITIONS OF PLIOCENE AND PLEISTOCENE SEDIMENTS FROM MULTIPLE BIOMARKER ANALYSIS

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The targeted analysis of organic matter in soils is useful to evaluate palaeoenvironmental conditions, as specific compounds (called biological markers or biomarkers), may be directly linked to organisms or to the conditions in which they thrived. The variation in amounts and presence of certain biomarkers is a powerful tool for changes in palaeoenvironmental climate conditions. Given their fundamental connection to carbon fixation, photosynthetic pigments are among the most important of the sedimentary "molecular fossils" that reflect the biological communities inhabiting aquatic environments at the time of sediment deposition. As photosynthetic pigments relate directly to CO_2 uptake, understanding what controls pigment abundances in aquatic sediments is essential, not only to profile environmental change in times past, but also to inform future climate scenarios. While it is evident that abundance levels are linked to the intensity of primary production, environmental conditions also play a significant role in controlling preservation potential. Other proxies include lipids such as *n*-alkanes (which can be useful to differentiate between higher plants and algal and bacterial inputs), and the side chain length and nature of substituents in sterol and hopanol structures can distinguish contributions from different sources. The sterol side chain length can be specific of different groups: C_{27} chain length in zooplankton, C_{28} in diatoms and C_{29} in higher plants. Moreover, particular substituents are markers for specific primary producers, for example, gramisterol (Fig. 1a) is a marker for mosses and dinosterol (Fig. 1b) is synthesised by dinoflagellates (Volkman, 1986).

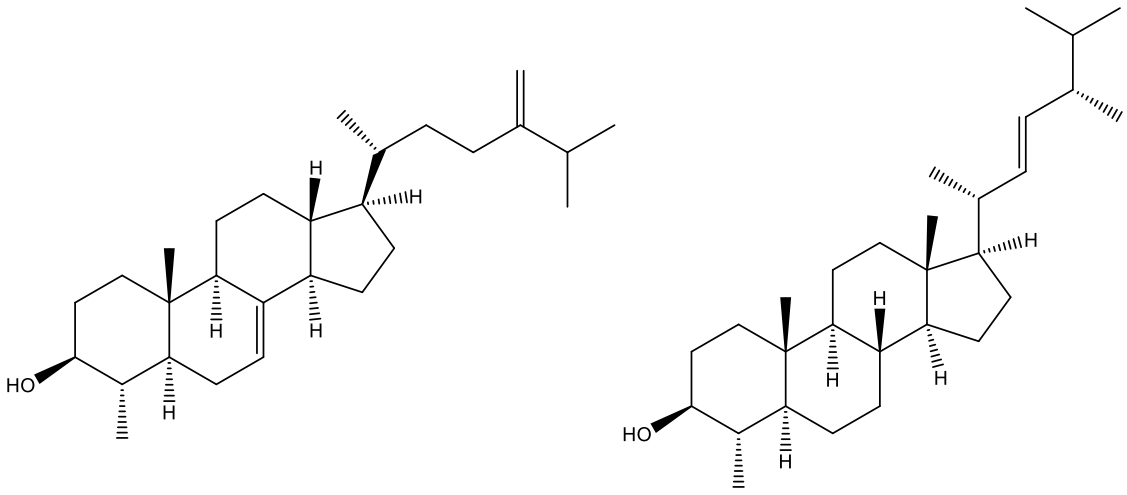
This project examines sediment sequences of Pliocene lake and Pleistocene coastal deposits. The Pleistocene records encompass sediments cycling between estuarine and marine conditions spanning several sea-level changes, and benefit from detailed chronologies using amino acid and luminescence dating. By linking the pigment, climate proxy and chronological records, the impacts of climate change on the primary producer communities and preservation of molecular signatures will be assessed over transgressive and regressive phases of sea-level change.

A multiple biomarker approach was applied on these Pliocene and Pleistocene sediments, with analysis of chlorophyll pigments and lipids: the former were analysed with a new UHPLC-DAD method (Saesaengseerung, 2013) and the latter with GC-FID and GC-MS. Key results are presented here - for example, in the Pliocene Willershausen lake basin, the presence of DPEP (desoxophylloerythroaetioporphyrin) in the bottom part of the lake sediments indicates anoxic conditions, while in the surface sediments, pheophorbide a methyl ester suggests oxygenating conditions. Long chain *n*-alkanes were dominant, indicating a predominance of higher plants, rather than algae, compatible with the anoxic, alkaline conditions of the basin. β-amyrin, which was also found in the sediments, is a biomarker for

angiosperms, plants that thrive in temperate conditions. Considering the location of the lake in the Harz Mountains, it is therefore possible that in the Pliocene the site experienced temperatures warmer than today's.

In Loch of Stenness, early oxidation diagenesis products of chlorophyll a were found, indicating that the sediments are immature and the lake was oxygenated. Also present were chlorin e and chlorophyllone; in the laboratory, these two pigments are formed by base treatment, hence it is possible that part of the lake was alkaline.

This study showed that this multi-proxy investigation was able to yield valuable palaeoenvironmental information from a range of sediment types.



a) Gramisterol b) Dinosterol

Figure 1. *a) Gramisterol and b) Dinosterol, examples of sterol markers for mosses and dinoflagellates, respectively*

References

Saesaengseerung, N., 2013. High-throughput Methods for the Analysis of Pigments in Aquatic Sediments. PhD Thesis, University of York

Volkman, J.K., 1986. A Review of Sterol Markers for Marine and Terrigenous Organic Matter. Organic Geochemistry 9, 83–99