A biogeochemical and palynological investigation of late Cenozoic fluvial/ estuarine sediments, Western Cape, South Africa

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Background

Biomarkers (i.e. chemical "fossils") are widely used towards reconstructing marine and terrestrial palaeoenvironments and their evolution. For example, the distribution of certain classes of biomarkers in marine waters and organic-rich sediments has been found to be empirically related to sea surface temperature (SST) ($U^k_{37'}$ and TEX_{86}). Other biomarkers, in combination with their stable carbon isotope ratios, record water column conditions such as redox stratification, temporal salinity variations or euxinia (i.e. anoxic conditions in the presence of dissolved sulphide). Past climatic conditions from the terrestrial organic record can also be reconstructed using biomarkers derived, for instance, from higher plant waxes in combination with compound-specific carbon isotope data. The differences between the metabolic pathways and CO_2 sequestration strategies of C_3, C_4 and CAM plants result in a distinctive stable carbon isotope signature for each plant type, which in turn can be used to elucidate general climate trends to which the respective plants are adapted.

Proposed research

We propose to undertake a detailed organic geochemical study at the Langabaanweg fossil site, with the purpose of identifying organic matter sources and re-constructing the palaeoenvironment of deposition of the fossiliferous and adjacent horizons. The research can be carried out at PhD level. At the early stages, bulk organic carbon isotope analyses and conventional molecular analyses of organic matter will be carried out using standard gas-chromatography-mass spectrometry techniques at Rhodes University. These can be coupled with palynofacies analysis to be performed at the University of the Witwatersrand.

The latter part of the research would focus on a novel approach to reconstructing trends in mean annual temperature (MAT) and pH of the environment of deposition. This can be achieved using a specific class of compounds produced by yet unclassified soil bacteria that are thought to be anaerobic and thrive in environments such as peat bogs. These bacteria have the membrane-spanning lipids *glycerol dialkyl glycerol tetraethers* (GDGTs) which are more commonly found in archaea, yet possess branched features typical of bacteria. The various branched GDGT lipids differ in the amount of methyl groups attached to their alkyl chains, and in the amount of cyclopentyl moieties. Previous studies have demonstrated that the relative amount of cyclopentyl moieties is related to pH, whilst the relative amount of additional methyl branches at the C-5 and C-5' positions may be related to both pH and temperature. These allow for the use of these parameters as proxies for pH and past continental air temperatures.

Scientific relevance

Recent work carried out at the Netherlands Institute for Sea Research (NIOZ) has illustrated the use of biomarkers in deciphering the Miocene record of MAT and pH at selected sites from the northern hemisphere. Similar applications on organic sediments from the largely unresearched Langebaanweg site have therefore great potential to constrain local paleoenvironmental evolution, the palaeoclimate of the southern hemisphere during the same time period, and possibly will be an indicator for global-scale climate changes.

Potential for international collaboration

Subject to availability of funding, the proposed project will open avenues of long-term collaboration with NIOZ (Prof J.S.S. Damste, Dr S. Schouten, Dr E. Hopmans) and the University of Bristol, UK (Drs. R. Pancost & Johan Weijers). Both laboratories are world leaders in molecular organic geochemistry and will offer an unrivalled opportunity to the candidate in obtaining hands-on expertise in a completely new research niche in a South African context.

Analyses and sample requirements

Bulk organic carbon isotope and GC-MS analyses will be done at Rhodes University using in-house facilities. The analyses of GDGTs will require an approximately 4-6 month visit of the candidate to the premises of the NIOZ in Texel, the Netherlands. Samples will ideally be TOC-enriched (1-2 wt%) and relatively immature; 0.5 to 1 g of dry sample suffices for the analytical purposes of the project.

Methodology and protocol

Sample extraction can be done by soxhlet extraction, sonication or accelerated solvent extractor (ASE 200, DIONEX, available at NIOZ) using a solvent mixture of dichloromethane (DCM) and methanol. Purification of extracts is done over an activated Al_2O_3 column using solvent mixtures of hexane/DCM/ methanol. Finally, the extract is filtered over a 0.45 µm PTFE filter (Alltech) before analysis.

GDGTs are routinely analyzed and quantified by high performance liquid chromatography/ atmospheric pressure chemical ionization mass spectrometry (HPLC/APCI-MS). For separation, an Alltech Prevail Cyano column (150 mm × 2.1 mm; 3 µm) is used. Samples are run with a hexane:propanol (99:1, v/v) eluent. Low concentrations of GDGTs can be detected by MS analyses in a single ion monitoring (SIM) mode, which selectively scans for the masses of the compounds of interest. At NIOZ, an Agilent 1100 series/1100MSD series instrument, equipped with auto-injector and HP Chemstation software is available. A pure crenarchaeol standard is used to prepare a standard curve for quantification of the GDGT.