Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.18476

Molecular Network Analysis of the Geolipidome of Ancient Sediments

DANICA MITROVIC[1], SU DING[1], NICOLE J. BALE[1], ELLEN C. HOPMANS[1] AND STEFAN SCHOUTEN[1,2]

[1]NIOZ Royal Netherlands Institute for Sea Research
[2]Utrecht University

Presenting Author: danica.mitrovic@nioz.nl

Recent studies have demonstrated that combining ultra-high-pressure liquid chromatography high-resolution mass spectrometry (UHPLC-HRMS) with computational methods such as molecular networking provides new insights in the lipidomes of modern environments[1] and microbial cultures[2]. Here we describe the application of this methodology for the first time to geological samples in order to examine the "geolipidome", i.e. the collection of fossilized lipids. In this study, an organic rich oil shale core from Messel pit (62-115 m; Germany), an ancient maar crater lake of Mid-Eocene age (47.8 Ma[3]), was investigated. Historically, analysis of such sediments was focused on those molecules amenable to gas chromatography, missing larger, more polar compounds.

The molecular network of the Messel oil shale comprised >9500 ion components which could be separated into tens of sub-networks and numerous individual components (i.e., singletons) based on their MS^2 spectral similarity (Fig. 1). The two sub-networks that contain most lipid species comprised sterols and bacteriohopanepolyols (BHPs), of which C30-sterol and anhydro-bacteriohopanetetrol (anhydro-BHT) were the most abundant lipid species within their respective subnetworks. Isoprenoid and branched glycerol dialkyl glycerol tetraethers (i.e., isoGDGTs and brGDGTs) clusters comprise other important sub-networks, while less abundant sub-networks included a series of bacterial diether glycerol lipids (DEGs), archaeal derived *sn*-2,3-diphytanyl glycerol diethers (DGDs), with archaeol (AR) as the main lipid, and long chain ketones. A number of subnetworks and singletons containing only unknown lipids were also found. Interestingly, more than half of total components in this network are singletons (~60%), meaning they do not share spectral similarity with each other. Among the cluster-components, so far we have been able to identify only ~10% of clusters, leaving a vast majority unknown.

The use of molecular networking allowed us to study compound's down-core variation/diversity even without structural identification. Future efforts will be focused on unravelling the compounds from the unknown clusters and assessing their variability in connection to changes in organic matter input and paleoenvironmental change.

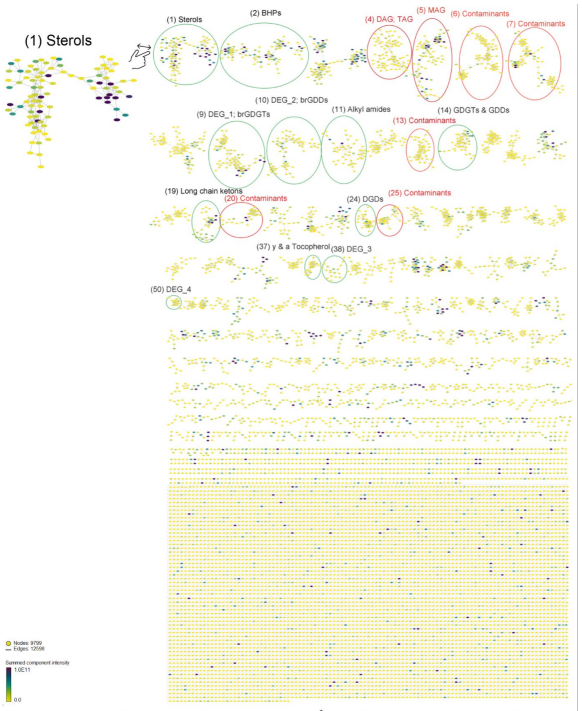

Fig. 1. Molecular network of the oil shale core of Messel. Nodes represent MS^2 spectra of ion components which are connected based on spectral similarity (cosine > 0.5). Nodes are colored from light yellow to dark blue with increasing summed intensity among all the sediment core samples (18 depths). Annotated lipid classes (clusters) are either (tentatively) identified in this study or have been reported previously[1]. Around 60% of all nodes are singletons (i.e., individual boxes in the lower half of the figure).
Legend: BHPs - bacteriohopanepolyols; MAGs - monoacylglycerols; DAGs - diacylglycerols; TAGs - triacylglycerols; DEGs - dietherglycerols; GDGTs - glycerol dialkyl glycerol tetraethers; GDDs - dialkyl glycerol diethers; brGDGTs - branched glycerol dialkyl glycerol tetraethers; brGDDs - branched dialkyl glycerol diethers; DGDs - diphytanyl glycerol diethers.

[1]Ding, S., et al. 2021. *Frontiers in Microbiology*: doi.org/10.3389/fmicb.2021.659315.

[2]Ding, S., et al. 2022. *ISME Communications*: doi.org/10.1038/s43705-022-00207-3.

[3]Mertz, D.F. and Renne, P.R. 2005. *Courier Forschungsinstitut Senckenberg* 255, 67–75.