

THE ISOTOPE GEOCHEMISTRY OF ARCHAEOAL LIPIDS IN THE BLACK SEA AND UNDERLYING SEDIMENTS CONSTRAINS THEIR SOURCES AND TURNOVER

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Introduction

Archaeal lipids in marine sediments have two principal sources: marine planktonic archaea (Schouten et al., 2013) and sedimentary benthic archaea (Lipp and Hinrichs, 2009). These lipids are present either as the comparatively labile intact polar lipids (IPLs) or as their more recalcitrant analogues, the core lipids (CLs), with the latter being frequently used for paleoenvironmental reconstruction. Stable isotopic compositions of these two lipid pools have the potential to constrain their sources and to provide information on their turnover. We therefore studied the stable carbon and hydrogen isotopes of archaeal IPLs and CLs by analyzing phytane and biphytane moieties in high resolution through the water column (N=5) and within an 8-m long sediment core (N=28) of the Black Sea that extends from the Holocene to the Last Glacial Maximum. The dataset is complemented by lipid abundance data and pore water geochemistry.

Results and Discussion

We measured $\delta^{13}\text{C}$ and δD values for archaeol-derived phytane and GDGT-derived biphytane-0 (BP-0; primarily derived from caldarchaeol) and BP-cren (derived from crenarchaeol) within the IPL and CL pools. In *Figure 1* we exemplarily present the BP-0 dataset. Comparing the carbon isotopic compositions of IPLs and CLs in both water column and sediments, archaea living in the lower suboxic zone apparently are the predominant contributor of lipids found in surface sediments. Interestingly, BP-0 in the sedimentary IPL pool is on average depleted in ^{13}C by 3‰ relative to the CL pool. This offset provides evidence for contributions of sedimentary heterotrophic archaea to the intact polar GDGT pool. Moreover, we observed a more negative signal in $\delta^{13}\text{C}$ of BP-0 in the CL pool in subsurface sediments between 100 and 600 cmbsf relative to the surface; this negative deviation is consistent with an addition of hydrolytic products in the form of core GDGTs from the ^{13}C -depleted IPL pool. Isotope mass balance calculations suggest that on average 14% of CL-caldarchaeol is derived from IPL degradation. The most negative carbon isotopic compositions of archaeal lipids are found in the sulfate-methane transition zone (SMTZ), indicating the contribution of methanotrophic archaea.

In the presentation, we will also highlight data from phytane and BP-cren and their relationship with geochemical contextual data. For example, we will provide evidence for the contribution of autotrophic methanogens to the CL and IPL pools and the recalcitrance of planktonic Thaumarchaeal IPLs. Moreover, we systematically analyzed the hydrogen isotopic compositions of archaeal lipids, which show notable contrasts between the lacustrine and marine sedimentary facies. We will discuss to what degree these contrasts are related to the paleoenvironmental history of the basin as well as to the metabolic shifts of the major archaeal lipid producers.

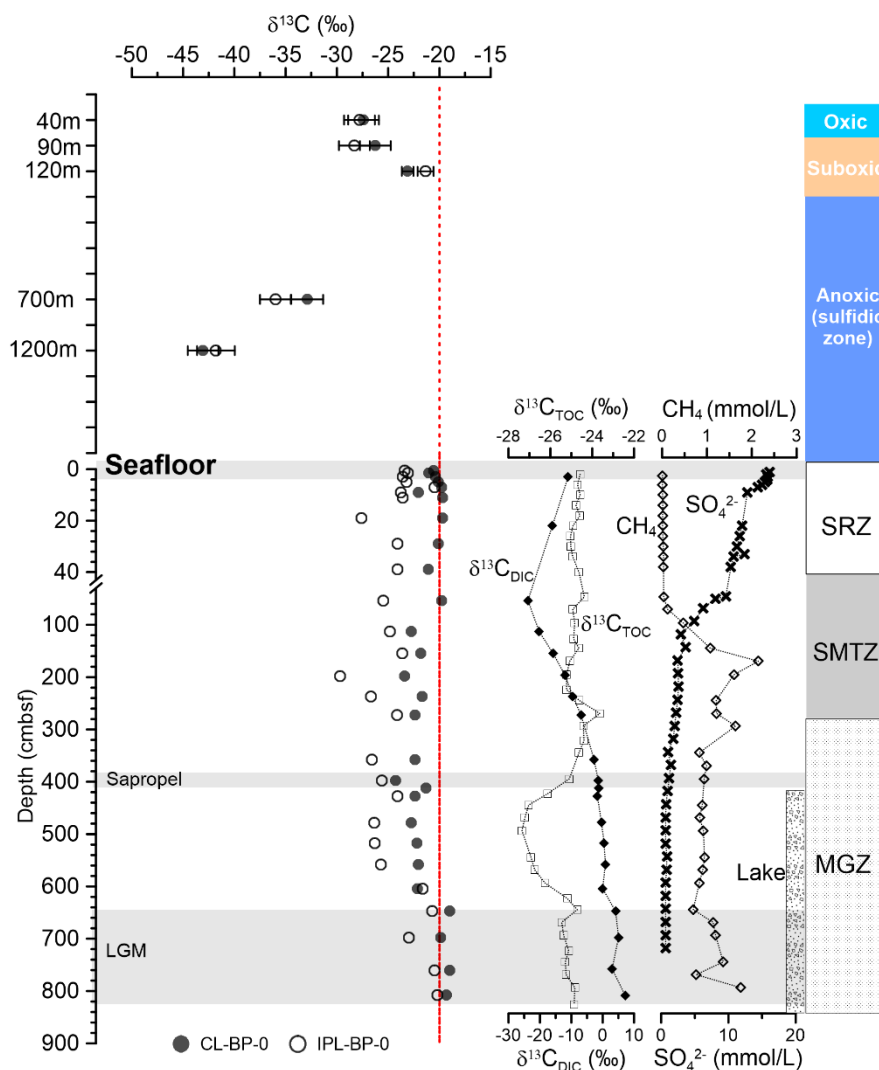


Figure 1. The carbon isotopic compositions of CL-BP-0 and IPL-BP-0 in the Black Sea water column and sediment. SRZ: sulfate reduction zone; SMTZ: sulfate-methane transition zone; MGZ: methanogenic zone; LGM: Last Glacial Maximum; Red dashed line is -20‰ line, indicating the average values of marine planktonic archaeal isoprenoid lipids.

References

- Lipp, J.S., Hinrichs, K.-U., 2009. Structural diversity and fate of intact polar lipids in marine sediments. *Geochimica et Cosmochimica Acta* 73, 6816-6833.
- Schouten, S., Hopmans, E.C., Damsté, J.S.S., 2013. The organic geochemistry of glycerol dialkyl glycerol tetraether lipids: a review. *Organic Geochemistry* 54, 19-61.