

MOLECULAR STABLE CARBON ISOTOPE GEOCHEMISTRY OF ARCHAEAL LIPIDS ACROSS DIFFERENT MARINE ENVIRONMENTS AND GEOCHEMICAL ZONES

Q.Z. Zhu, M. Elvert, K.U. Hinrichs

MARUM Center for Marine Environmental Sciences, University of Bremen, Germany

Archaea play an important role in carbon cycling in ocean water and marine sediments. Their sedimentary membrane lipids are sensitive indicators of environmental change and have been widely used in paleo and biogeochemical studies (Schouten et al., 2002; Schubotz et al., 2011; Zhang et al., 2011). Specifically, intact polar lipids (IPLs) of archaea are presumed to represent living biomass and are taxonomically more informative than their fossil counterparts (Biddle et al., 2006; Lipp et al., 2008). In order to widen our understanding of the activity and carbon sources of archaea in marine sediments, we performed a systematic study targeting archaeal lipid abundance and corresponding stable carbon isotope composition ($\delta^{13}\text{C}$) combined with geochemical information in contrasting depositional regimes from the Mediterranean, Marmara and Black Seas. Specifically, we measured the $\delta^{13}\text{C}$ of biphytanes (BPs) derived from glycerol dialkyl glycerol tetraethers (GDGTs) in the apolar and polar fractions of total lipid extracts, representing fossil core lipids and IPLs, respectively, obtained from 40 sedimentary samples of the DARCLIFE project. The samples belong to different geochemical environments such as sulfate reduction, sulfate-methane transition zone (SMTZ) and methanogenesis.

Our preliminary results of 28 samples indicate that the average core $\delta^{13}\text{C-BP}_0$ value for GDGT-0 is slightly more negative by 0.8‰ relative to core $\delta^{13}\text{C-BP}_3$ derived from GDGT-5 across all marine environments and geochemical zones (Figure 1, A). This is consistent with a former study by (Pearson et al., 2016) which attributed this offset to the heterogeneous contribution of various archaeal sources to the sedimentary pool. In contrast, we observe a clear trend of $\delta^{13}\text{C-BP}_0$ derived from IPLs to be more negative by ~2‰ than that from core lipids which most pronounced in river-affected endmember samples (Figure 1, B), while the same difference in $\delta^{13}\text{C-BP}_3$ derived from IPLs and core lipids are indistinguishable (Figure 1, C). A large spread is, however, observed for the difference IPL-derived $\delta^{13}\text{C-BP}_0$ relative to $\delta^{13}\text{C}_{\text{TOC}}$ (Figure 1, D) which is resulting from variances in both parameters across the different environments. The top 25% of the data belong to samples deposited in the Black and Marmara Sea sediments during the lake phase time. However, the bottom 25% of the data are dominated by samples derived from the Eastern Mediterranean Sea associated with most positive $\delta^{13}\text{C}_{\text{TOC}}$ values.

The apparent isotopic offset between BP_0 derived from the IPL and core lipid pool is consistent with the in-situ activity and lipid production by sedimentary archaea. These archaea, producing IPLs with a GDGT-0 core structure, are likely heterotrophic and thus dominantly assimilate organic carbon. In contrast, the similarities of $\delta^{13}\text{C-BP}_3$ in IPLs and core lipids suggests that the alkyl moieties of intact crenarchaeol are not newly synthesized within the sediment; they either represent fossil IPL pools or are products of crenarchaeol recycling by sedimentary archaea (Takano et al., 2010). Further details and relationships among the different lipid pools and their molecular isotopic signatures across the various sedimentary regimes and geochemical zones will be discussed in the poster.

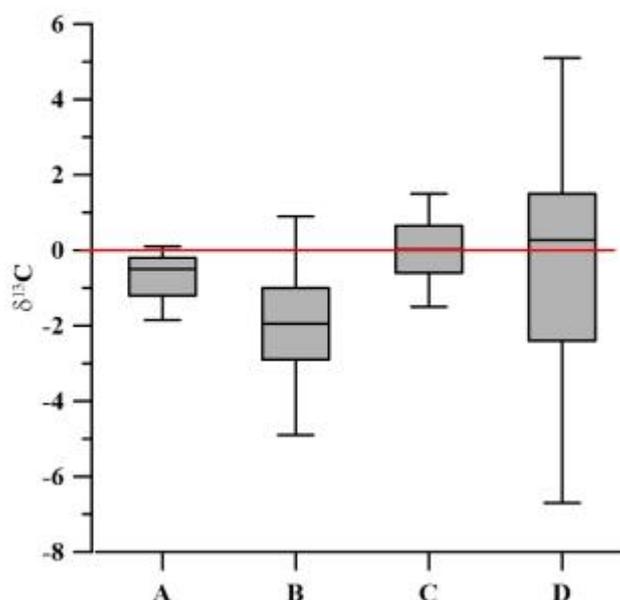


Figure 1 Differences in $\delta^{13}\text{C}$ of major biphytanes derived from core and intact GDGTs and relative to $\delta^{13}\text{C}_{\text{TOC}}$ of samples processed right now; A: $\Delta = \delta^{13}\text{C}_{\text{CoreBP0}} - \delta^{13}\text{C}_{\text{CoreBP3}}$ ($N=24$), B: $\Delta = \delta^{13}\text{C}_{\text{IPLBP0}} - \delta^{13}\text{C}_{\text{CoreBP0}}$ ($N=28$), C: $\Delta = \delta^{13}\text{C}_{\text{IPLBP3}} - \delta^{13}\text{C}_{\text{CoreBP3}}$ ($N=28$), D: $\Delta = \delta^{13}\text{C}_{\text{IPLBP0}} - \delta^{13}\text{C}_{\text{TOC}}$ ($N=28$).

References

- Biddle, J.F., Lipp, J.S., Lever, M.A., Lloyd, K.G., Sørensen, K.B., Anderson, R., Fredricks, H.F., Elvert, M., Kelly, T.J., Schrag, D.P., 2006. Heterotrophic Archaea dominate sedimentary subsurface ecosystems off Peru. *Proceedings of the National Academy of Sciences of the United States of America* 103, 3846-3851.
- Lipp, J.S., Morono, Y., Inagaki, F., Hinrichs, K.-U., 2008. Significant contribution of Archaea to extant biomass in marine subsurface sediments. *Nature* 454, 991-994.
- Pearson, A., Hurley, S.J., Walter, S.R.S., Kusch, S., Lichtin, S., Zhang, Y.G., 2016. Stable carbon isotope ratios of intact GDGTs indicate heterogeneous sources to marine sediments. *Geochimica et Cosmochimica Acta* 181, 18-35.
- Schouten, S., Hopmans, E.C., Schefuß, E., Damste, J.S.S., 2002. Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures?. *Earth and Planetary Science Letters* 204, 265-274.
- Schubotz, F., Lipp, J.S., Elvert, M., Hinrichs, K.-U., 2011. Stable carbon isotopic compositions of intact polar lipids reveal complex carbon flow patterns among hydrocarbon degrading microbial communities at the Chapopote asphalt volcano. *Geochimica et Cosmochimica Acta* 75, 4399-4415.
- Takano, Y., Chikaraishi, Y., Ogawa, N.O., Nomaki, H., Morono, Y., Inagaki, F., Kitazato, H., Hinrichs, K.-U., Ohkouchi, N., 2010. Sedimentary membrane lipids recycled by deep-sea benthic archaea. *Nature Geoscience* 3, 858-861.
- Zhang, Y.G., Zhang, C.L., Liu, X.-L., Li, L., Hinrichs, K.-U., Noakes, J.E., 2011. Methane Index: a tetraether archaeal lipid biomarker indicator for detecting the instability of marine gas hydrates. *Earth and Planetary Science Letters* 307, 525-534.

