

CHARACTERIZING BITUMENS AND KEROGENS FROM LAKE MAGADI CHERTS, PLEISTOCENE ANALOGS FOR ARCHEAN HYDROTHERMAL DEPOSITS

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The quest for molecular biosignatures from early life on Earth and potentially beyond (e.g., Mars) is one of the great challenges in modern organo-geochemical research. One key for the traceability of molecular fossils is their preservation over large geological time scales. At hydrothermal sites, potential habitats for early life, biomolecules have to face immediate thermal and chemical stress that may lead to rapid transformation and/or complete degradation. To assess this problem, we analyzed organic matter in cherts from a modern analog environment (Lake Magadi, Kenya) via microscopy, Raman spectroscopy, catalytic hydrolysis (HyPy), gas chromatography–mass spectrometry (GC–MS), and gas chromatography–combustion–isotope ratio mass spectrometry (GC–C–IRMS).

The bitumens enclosed in the Pleistocene cherts from Lake Magadi revealed an immature fraction, containing fatty acids (OEP29 around 0.4) and –alcohols (OEP29 around 0.2), as well as glycerol mono- and diethers ($\delta^{13}\text{C}$ between -11 and -22 ‰; Reinhardt et al., 2019). These compounds were mainly produced by halophilic archaea, thermophilic sulfate reducers and cyanobacteria. At the same time, medium-chain *n*-alkanes (OEP21 ca. 1.0) and hopanes (mean $\text{C}_{31} \text{ 22S}/(\text{S}+\text{R}) = 0.56$) appear together with few PAHs (MPI-1 around 0.75), indicating that parts of the bitumen were thermally altered. Potential sources of this particular fraction are hydrothermal petroleum formation in deeper parts of the Magadi basin and/or in-situ maturation at hydrothermal sites in the lake (Reinhardt et al., 2019).

The kerogens isolated from the Lake Magadi cherts also show variations in thermal maturities. Within individual samples, Raman-derived T_{max} values vary between 40 °C and 110 °C (Reinhardt et al., 2019). One kerogen even revealed an extreme spread of T_{max} values, ranging from 40 °C (immature) to 440 °C (highly mature, graphitic). The presence of mature populations of organic matter is furthermore reflected by hydrolysis (HyPy) products of the kerogens which contain abundant PAHs (MPI-1 < 1.70) and show OEP21 values of *n*-alkanes around 1. Nevertheless, intact archaeal isoprenoid hydrocarbons were also released by HyPy from some of the kerogens, indicating rapid sequestration of biomolecules into the macromolecular network parallel to hydrothermal alteration (Reinhardt et al., 2019).

Organic matter populations with conflicting thermal maturities that co-occur within individual samples have also been observed in some Archean hydrothermal deposits (e.g., Allwood et al., 2006; Glikson et al., 2008). These discrepancies may not exclusively reflect post-depositional overprint or contamination, but could be inherited from the original hydrothermal environment in some cases. Additionally, archaeal isoprenoid hydrocarbons in HyPy pyrolysates from Magadi chert kerogens indicate that biomolecules may survive early destruction in hydrothermal environments (Reinhardt et al., 2019). Our study therefore

underlines the importance of Archean hydrothermal cherts in the search for molecular fingerprints of early life.

References

- Allwood, A. C., Walter, M. R., Marshall, C. P., 2006. Raman spectroscopy reveals thermal palaeoenvironments of c.3.5 billion-year-old organic matter. *Vib. Spectrosc.*, 41, 190–197, 10.1016/j.vibspec.2006.02.006
- Glikson, M., Duck, L. J., Golding, S. D., Hofmann, A., Bolhar, R., Webb, R., Baiano, J. C. F., Sly, L. I., 2008. Microbial remains in some earliest Earth rocks: Comparison with a potential modern analogue. *Precambrian Res.*, 164, 187–200, 10.1016/j.precamres.2008.05.002
- Reinhardt, M., Goetz, W., Duda, J.-P., Heim, C., Reitner, J., Thiel, V., 2019. Organic signatures in Pleistocene cherts from Lake Magadi (Kenya), analogs for early Earth hydrothermal deposits. *Biogeosciences Discuss.*, in review, 10.5194/bg-2018-513