New insights from bacterial biomarkers into the oxic/anoxic transition of the Holocene Black Sea

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The recent Black Sea is an analogue of euxinic oceans in Earth history. However, many aspects of the transition from a well mixed oxygenated lake to the contemporary marine setting with permanently anoxic deep waters before 7600 years are still unclear. In a comprehensive study of a Black Sea sediment core we analysed concentrations and distributions of bacteriohopanepolyols (BHPs), biomarkers produced by various bacterial groups in different zones of the water column.

Our results show that sedimentary BHP distributions mainly reflect euphotic zone primary production throughout the core, although BHP production was demonstrated to be also high in the chemocline at about 100m water depth [1]. The lack of BHP-signals from the oxic/anoxic transition zone of the water column is most likely due to the absence of transport mechanisms for organic matter in deeper waters (e.g. zooplanktonic fecal pellet express). Consequently, our data demonstrate that sedimentary biomarkers do not necessarily reflect the presence of a chemocline, in particular if it is located below the euphotic zone.

Moreover, we found highest total concentrations of BHPs at the transition between the oxygenated, lacustrine (Unit 3) and the brackish, euxinic stage (Unit 2) about 7600 years BP [2]. However, amounts of sedimentary BHPs already increased in the upper Unit 3. This was most likely caused by enhanced euphotic zone bacterioplanktonic palaeo-productivity brought about by ingressions of Mediterranean Sea waters at the end of Unit 3 (~9500 years BP). Thus, our data indicate that paleoproductivity was already enhanced before the onset of permanent anoxia in deep waters improved the preservation of organic matter at 7600 years BP (marked by an extreme increase in total organic carbon from about 1 to 9% [2]).

[1] Wakeham *et al*. (2007) *Org. Geochem.* **38**, 2070-2097.
[2] Blumenberg *et al*. (2009) *GCA* **73**, 750-766.

The molecular analysis of organic matter preserved in stalagmites

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Stalagmites are valuable archives of environmental change as they can be precisely dated, and contain multiple proxy records within a single context. Most stalagmite studies focus on stable isotope analysis of the stalagmite calcite, and with the exception of luminescence analysis, organic geochemical proxies have largely been neglected. However, the analysis of organic matter has much to offer stalagmite research, as it has the potential to provide much more detailed information about the overlying vegetation regime and soil conditions, and by extension, their response to climate. By combining organic and inorganic proxies, a truly integrated signal of past climatic changes and the related response of terrestrial ecosystems can be recovered from a single, well-dated, setting.

Four techniques are currently available to analyse the organic matter preserved in stalagmites at a molecular level. The best established approach is organic matter luminescence which provides a rapid and non-destructive technique for assessing dissolved organic matter quantity and quality. However, to obtain detailed identification and quantification of the organic components, invasive extraction techniques are required. The analysis of lipid biomarkers has been shown to provide signals relating to both the overlying vegetation and prevailing climate, although questions remain about potential mixing of the signal, and the degree to which individual compound proxies are globally applicable. Lipid biomarkers can also be used in compound specific isotope analysis, where the carbon isotopic composition of individual molecules is determined. This has particular relevance to stalagmite research, as it provides a complementary record to conventional isotopic analysis of the stalagmite calcite, allowing the different inorganic and organic components to identified, and thus different controls on the record to be ascertained. The last currently available technique is the analysis of larger aromatic organic molecules such as lignin phenols. These can provide detailed information on both vegetation regime and the degradation state of the organic material, the latter being an important issue in understanding the transport process and lags for organic matter between the soil and the stalagmite. The compounds can be recovered as part of a sequential extraction process with lipid biomarkers allowing us to take a holistic view of the organic matter preserved and maximise the environmental information recovered.