TESTING THE RELIABILITY OF GDGT-BASED PROXIES AT THE ADVENT OF THE MESSINIAN SALINITY CRISIS

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The Messinian Salinity Crisis (MSC) is one of the most severe, but short-timed crises in recent Earth history. During the Messinian, the Mediterranean Sea was transformed into one of the largest salt basins on Earth, resulting in the deposition of a huge volume of evaporites. The water column conditions became progressively harsher and lethal for most marine organisms. As a consequence, the MSC rock record is scarce or locally even barren of microfossils and paleoenvironmental reconstructions are consequently difficult. Samples from a marginal Messinian basin in northwestern Italy (Piedmont) revealed a well preserved archaeal lipid assemblage, including various glycerol dibiphytanyl glycerol tetraethers (GDGTs) and diphytanyl glycerol diethers (DGDs). We test GDGT-based proxies (e.g. GDGT ratios, TEX_{86}) for deciphering the paleoenvironmental conditions and sea surface temperature (SST) before and at the advent of the MSC.

In great contrast to other marginal shallow basins, the studied section does not contain evaporites, but is composed of clays and marls alternating with carbonates (Dela Pierre et al., 2011). Archaeal GDGTs and DGDs are the most abundant lipids (30% of all lipids) before and after the MSC onset. In the pre-MSC samples, GDGTs with distributions typical of marine Thaumarchaeota prevail. The TEX_{86} was applied to calculate the sea surface temperature (SST); in detail, the $TEX86_L$ and the $TEX86_H$, recently calibrated for low and high SSTs, were both applied and yielded average SSTs of ~24ºC in pre-MSC samples. Such temperatures are consistent with SST cooling observed in the late Miocene (Herbert et al., 2016) and with modern average Mediterranean SSTs. Due to the lack of other paleotemperature proxies, the validity of the TEX_{86} for this section was verified by $\delta^{13}C$ values of ether-cleaved, GDGTs. During the pre-MSC, all TEX_{86}-relevant biphytanes showed a uniform isotopic signature (av. −21‰ PDB), agreeing with planktic Thaumarchaea. Similar $\delta^{13}C_{GDGT}$ and $\delta^{13}C_{biphytane}$ values are reported for modern and ancient sediments (Schouten et al., 2013; Pearson et al., 2016). Just above the MSC onset, the content of GDGTs (mainly caldarchaeol and crenarchaeol) and the DGDs archaeol and extended archaeol increased significantly. The latter are characteristic lipids sourced by halophilic Euryarchaeota and are especially found in salts (Teixidor et al., 1993), but also in Messinian carbonates (Birgel et al., 2014). The first appearance of extended archaeol in the MSC deposits points to a diversification of the archaeal community, most likely represented by the proliferation of halophilic Euryarchaeota. Further clues on an archaeal diversification are provided by the simultaneous shift of the caldarchaeol/crenarchaeol ratio from values of 1 up to values > 13, as well as a strong isotopic divergence of the caldarchaeol-derived acyclic biphytane (as low as −30‰ PDB) and the crenarchaeol-derived tricyclic biphytane (as high as −16‰ PDB). Nevertheless, ether-cleaved biphytanes derived from GDGTs-1 to -4 still mirror the higher $\delta^{13}C$ values of the crenarchaeol-derived tricyclic biphytane, pointing to the same thaumarchaeal source as found in the pre-MSC sediments. $\delta^{13}C$-depleted acyclic biphytane (caldarchaeol-derived) is most likely derived from unknown Euryarchaeota, since they are known to produce caldarchaeol as sole GDGT (e.g. Schouten et al., 2013).

Even though conditions were apparently more extreme during the MSC, most GDGTs were still sourced by planktic Thaumarchaeota, recording a positive carbon isotope excursion above the MSC onset. Since planktic Thaumarchaeota fix carbon by assimilation of inorganic carbon (DIC) and the respective fractionation factors are known for some cultured planktic Thaumarchaeota (Könneke et al., 2012), the $\delta^{13}C$ values of crenarchaeol can be used to calculate the paleo-$\delta^{13}C_{DIC}$ for the Messinian waters, resulting in $\delta^{13}C_{DIC}$ values in the pre-MSC deposits similar to modern values ($\delta^{13}C_{DIC}$: ~0‰). In the uppermost MSC samples of this section, they showed a positive carbon isotope excursion (+4‰). Interestingly, the shift in the caldarchaeol and crenarchaeol carbon isotopes is also reflected by a divergence of the SSTs calculated from the $TEX86_L$ and $TEX86_H$, ranging between 9°C and 25°C, respectively. Such high $\Delta TEX86_{L-H}$ values have been reported from shallow water settings of modern and ancient basins and they are positively correlated with low GDGT 2/3 ratios (Taylor et al., 2013). Analogously, above the MSC onset, the simultaneous increase of the $\Delta TEX86_{L-H}$ values and the decreasing GDGT 2/3 ratio values (<2) suggest a shallowing of the basins. The detailed information derived from archaeal membrane lipids can be used to obtain better insight into a dramatically changing environment, especially, at times when no constraints from body fossils are available.

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