Porphyrins reveal modes of nitrogen cycle controlled by chemocline depth under density-stratified condition during the Messinian Salinity Crisis

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From 5.97 to 5.33 Ma, the Mediterranean Sea experienced a massive evaporation event, known as the Messinian Salinity Crisis (MSC). Here, we investigated the biogeochemical cycle during the formation of water column stratification between freshwater and brine, which is periodically formed during the MSC. We sampled two shale beds of gypsum–shale alternation deposited in phase with the 21 kyr precessional cycle (Vena del Gesso, Northern Apennines, Italy), and a shale bed of halite–shale alternation deposited annually (Realmonte salt mine, Sicily, Italy). In both types of alternating layers, the shale beds were deposited under density-stratified condition, formed due to freshwater inflow during humid climate phases.

The chemical species and the carbon and nitrogen isotopic compositions of porphyrins, degradation products of chlorophylls, exhibit a common pattern in the two shale beds of gypsum–shale alternation, indicating the predominance of particular phototrophic community. These porphyrins show $\delta^{15}N$ values (−7.6‰ to −4.7‰) indicating that N_2-fixation was the dominant process supplying nitrogen for phototrophs under nitrate-depleted surface environment, formed primarily due to denitrification in the chemocline. On the other hand, the $\delta^{13}C$ values of porphyrins derived from chlorophyll *c* show approximately 5‰ difference between the two shales, probably reflecting the chemocline depth controlled by the amount of freshwater discharge.

By contrast, the porphyrins purified from a shale bed of halite–shale alternation exhibit substantially higher $\delta^{15}N$ value (17.2‰). We interpret this to reflect the supply of ^{15}N-enriched ammonium from the subsurface hypersaline water to the photic zone, due to the shallower chemocline depth. We suggest that the chemocline depth, fluctuating in response to changes in regional evaporation–precipitation balance, have the potential to shift the mode of nitrogen cycle during the MSC (nitrification–denitrification–N_2-fixation coupling vs. phototrophic assimilation of ammonium).

Keywords: the Messinian Salinity Crisis, nitrogen cycle, porphyrins, nitrogen isotopic composition

