

論文の内容の要旨

Revealing the biogeochemical cycles of the hypersaline environments
based on the organic geochemical approaches

(有機地球化学的手法による高塩環境の生物地球化学循環の解明)

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Hypersaline environments are among the most extreme environments on the Earth, imposing strong stresses on the biological systems. The selection pressure results in a unique microbial community dominated by specific halophilic microorganisms, which should associate modifications in the biogeochemical cycle. Importantly, a variety of hypersaline environments, in terms of the physical and chemical properties of the water, are formed in the modern Earth surface as well as in the past. Thus, the Earth surface system and inhabiting organisms have experienced a variety of hypersaline condition throughout the Earth's history. Despite such importance, our knowledge on the biogeochemistry of hypersaline environments is still fragmentary, and much less is known on its response during the past massive evaporation events.

The present work focused on the carbon and nitrogen cycles of two distinct hypersaline environments; the solar salterns as an example of modern shallow hypersaline environment, and the massive evaporation event in the late Miocene, the Messinian Salinity Crisis (MSC). The solar salterns is characterized by the formation of a highly productive microbial mat inhabited by diverse groups of microorganisms, which enable us to investigate the response of biological activities and biogeochemical cycle to increasing salinity. On the other hand, more than 1 million

km³ of salts were precipitated over the Mediterranean basin during the MSC between 5.97 and 5.33 Ma. Because there is no modern analogue of a comparable scale, investigation of this events should broaden our understanding of the biogeochemical cycle of hypersaline environments.

In the solar salterns, primary productivity and biomass of the benthic microbial mats were substantially higher than that of the water column. The isotopic fractionation factor during the uptake of carbon by phototrophs along the salinity gradient, calculated from $\delta^{13}\text{C}$ of chlorophyll *a* and β -carotene, indicated that primary productivity was suppressed as the salinity increased (Fig. 1a). Such modification of the biological activity resulted in large variation in $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in the brine (Fig. 1b). While active photosynthesis consuming $\text{CO}_2(\text{aq})$ in the carbonate and gypsum ponds (degree of evaporation: 2–10)

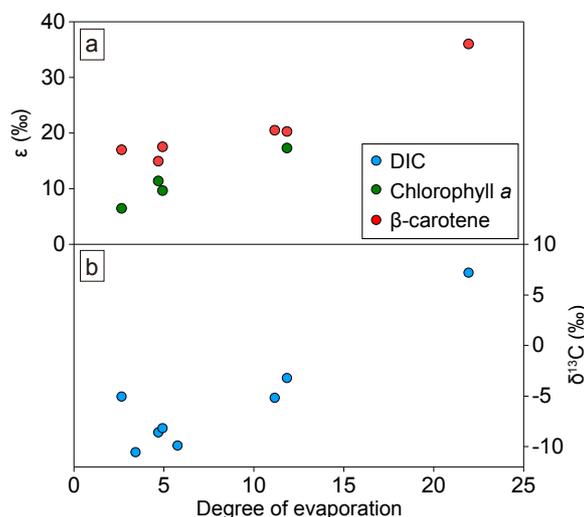


Fig. 1. Variations in (a) the fractionation factor ϵ calculated from $\delta^{13}\text{C}$ of chlorophyll *a* (green circles) and β -carotene (red circles), and (b) $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC, blue circles) along the salinity gradient.

induced dissolution of ^{13}C -depleted $\text{CO}_2(\text{gas})$ into the brine ($\delta^{13}\text{C}_{\text{DIC}} = -5.0\text{‰} - 10.6\text{‰}$), its suppression in the subsequent ponds resulted in the dominance of degassing of ^{13}C -depleted $\text{CO}_2(\text{aq})$ from the brine ($\delta^{13}\text{C}_{\text{DIC}} = 7.2\text{‰}$ in the halite pond).

By contrast, the depth profiles of $\delta^{15}\text{N}$ of nitrate, ammonium, and chloropigments in the microbial mats of the carbonate and gypsum ponds indicate that common processes control the nitrogen cycle in the hypersaline microbial mats across a wide salinity range. Ammonium accumulated in the anoxic layer of the mat as a result of anaerobic degradation of organic matter and suppression of nitrification, and was assimilated by purple sulfur bacteria and cyanobacteria as it diffused upwards through the mat. These processes efficiently recycled nitrogen within the mat, resulting in high primary productivity of this ecosystem (Fig. 2). Another important finding was that $\delta^{15}\text{N}$ of the surface brine ammonium became enriched in ^{15}N due to degassing of ^{15}N -

depleted dissolved ammonia induced by enhanced salinity ($\delta^{15}\text{N}_{\text{NH}_4^+} = 34.0\text{‰}$ in the halite pond). It is thus suggested that ^{15}N -enriched ammonium is a specific characteristic of an actively evaporating environment and that ammonium plays an important role in the nitrogen cycles of hypersaline environments.

During the first stage of the MSC between 5.97 and 5.60 Ma, up to 16–17 cycles of gypsum–shale couplets deposited in the marginal sub-basins across the Mediterranean. I investigated the shale layers of the

Vena del Gesso Basin (Northern Apennines, Italy), which were deposited under density-stratified condition formed due to continental water inflow over gypsum-precipitating brine during the humid climate phase of the ~21 kyr precessional cycle. While the similar shifts in $\delta^{13}\text{C}$ values of total organic carbon and the porphyrins derived from chlorophyll *c* suggest the predominance of eukaryotic algae, $\delta^{15}\text{N}$ of the porphyrins ranging from -6.5‰ to -5.4‰ indicate that the phototrophs assimilated nitrogen supplied by diazotrophic cyanobacteria (Fig. 3). These observations indicate that the diazotrophic–diatom associations may have been of particular importance, considering their adaptation to stratified oligotrophic condition and rapid export production. Such condition probably resulted from conversion of ammonium into N_2 through nitrification–denitrification coupling near the pycnocline, inducing nitrogen-depletion in the surface photic zone. Active N_2 -fixation at the surface balanced the loss of nitrogen by denitrification, establishing dynamic equilibrium of the biologically-available nitrogen like in the modern oceans.

Another investigation on the freshwater–brine stratification is based on the analysis of the shale layers of the halite–shale couplets deposited annually during the peak of the MSC (5.60–5.55 Ma) in the Caltanissetta Basin (Sicily, Italy). Geoporphyrins purified from this shale layer was extremely enriched in ^{15}N ($\delta^{15}\text{N} = 17.2\text{‰}$), which is interpreted to reflect phototrophic

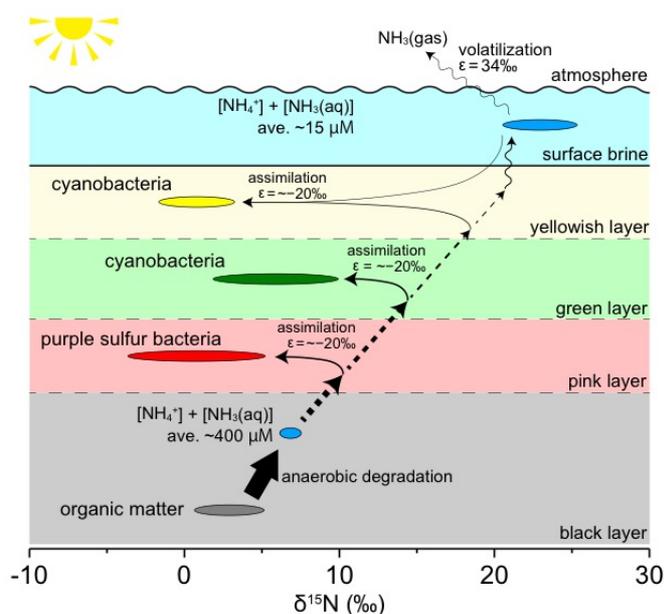


Fig. 2. Proposed nitrogen cycle for the carbonate and the gypsum ponds in the Trapani solar salterns. Ammonium produced by anaerobic degradation of organic matter is assimilated by purple sulfur bacteria and cyanobacteria.

assimilation of ^{15}N -enriched subsurface ammonium produced due to degassing of dissolved ammonia during the arid season. Such contrasting result compared to the freshwater–brine stratification during the first stage of the MSC can be attributed to thin freshwater layer with shallow pycnocline under the light-abundant condition, resulting in predominance of the phototrophic assimilation of subsurface ammonium over the nitrification–denitrification coupling. These results imply that the evaporation–precipitation balance in the Mediterranean Sea during the MSC has the potential to shift the mode of nitrogen cycle (nitrification–denitrification– N_2 -fixation coupling vs. phototrophic assimilation) through changing the depth of the chemocline.

Finally, based on the insights obtained in this work and in previous studies, the evolution of biogeochemical cycle throughout the MSC is discussed. The cyclical formation of different types of density stratification (i.e., thick freshwater–brine, thin freshwater–brine, brine–brine), which are produced in response to climatic condition changing at various timescales, may result in substantial shifts in the mode of the carbon and nitrogen cycles, and potentially influence the atmospheric CO_2 level and hence the global climate system.

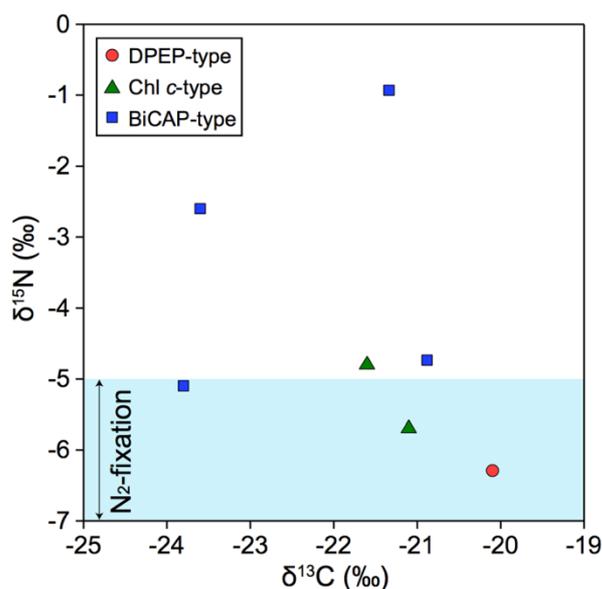


Fig. 3. Cross plots of the carbon and nitrogen isotopic compositions of the alkylporphyrins purified from the shales in the Vena del Gesso Basin. The DPEP-type (deoxophylloerythroetioporphyrin) is shown in red circles, the Chl *c*-type (chlorophyll *c*) in green triangles, and the BiCAP-type (bicycloalkano-porphyrin) in blue squares.