## 塩田バイオマット内の炭素・硫黄循環が高塩海水の化学組成に与える影響

Influences of carbon and sulfur cycle inside the hypersaline microbial mat on the chemical composition of overlying brine water

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Salinity is one of the most important environmental factors limiting the habitability of the marine organisms. As the seawater evaporates and the salinity increases, unique ecosystem is formed by specific organisms tolerable to substantial fluctuations in osmotic pressure, pH, and redox condition. In particular, microbial mat often formed in shallow hypersaline aquatic environment is known to be densely inhabited by microorganisms such as cyanobacteria, phototrophic and chemotrophic sulfur bacteria, sulfate reducing bacteria, methanogens, and others (e.g. Ollivier et al., 1994). Intensive studies have been made to reveal the biogeochemical processes of these microorganisms and their mutual interactions (e.g. Des Marais, 2003), but only few studies have focused on its effect on the chemical composition of the overlying brine water. In this study, we analyzed brine water collected from the modern saline pan in Trapani, Sicily, to understand the influence of the microbial activity on the overlying brine water with different salinity. Major ion concentrations, DIC (dissolved inorganic carbon) concentration, and its carbon isotopic composition ( $\delta^{13}C_{\text{DTC}}$ ) were measured on 9 brine water samples with different salinity (38-276). Although intensive carbon fixation by photosynthesis occurs in the ponds where microbial mat is formed (salinity 97-159), corresponding DIC concentration showed little decrease (1250-1000 µmol L <sup>-1</sup>). This may be because mineralization of the fixed carbon by sulfate reduction occurs in the mat, releasing DIC in the brine water (e.g. Des Marais, 2003). This interpretation is supported by the low  $\delta^{13}C_{\text{DTC}}$  value (~-10%), because sulfate reduction supplies relatively  $^{13}C$ -depleted DIC. Alternative explanation is the chemically enhanced atmospheric invasion of CO<sub>2</sub>, which can cause considerable depletion in  $\delta^{13}C_{nrc}$  (Baertschi, 1952; Lazar et al., 1992). By contrast, increase in the  $\delta^{13}C_{\text{DTC}}$  value (~7.2%) is observed in the ponds with higher salinity (>270) where no microbial mat is developing. This may be attributed to non-equilibrium escape of CO<sub>2</sub> due to higher salinity and lower pH (Stiller et al., 1985; Barkan et al., 2001). These results suggest that  $\delta^{13}C_{\text{DTC}}$  of hypersaline environment varies substantially due to both biological and physical processes. Despite the intense sulfate reduction taking place in the mat, variation in  $SO_4^{2-}$  concentration follows the ideal seawater evaporation path (Timofeeff et al., 2001). This may be because sulfide originating from the sulfate reduction is re-oxidized biotically by sulfur oxidizing bacteria or abiotically by the oxygen produced by cyanobacteria inhabiting the upper layer (e.g. Oren et al., 2009). Taken together, although DIC and  $SO_4^{2-}$  are utilized intensively by the microorganisms in the mat, their content in the brine water are relatively unchanged due to efficient recycling in the

mat.

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