Nitrogen loss and carbon cycle feedbacks during past marine anoxia

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The marine nitrogen cycle is sensitive to changes in ocean oxygenation due to the redox dependence of key steps in the cycle. Changes in the marine nitrogen cycle during past ocean anoxia, such as expressed in bulk sediment nitrogen isotopes ($\delta^{15}N_{bulk}$) during the Cretaceous, have been characterized to be driven by intensified nitrogen loss leading to increased cyanobacterial nitrogen fixation. However, direct evidence is lacking for the importance of nitrogen loss and the identity of the microbes driving this process, in part due to poor biomarker preservation in deep geological time. Pliocene and Pleistocene sapropels deposited during anoxic events in the Mediterranean Sea allow the study of nitrogen cycle processes in a relatively recent analogue system. We used biomarkers, compound-specific carbon isotopes, and $\delta^{15}N_{bulk}$ to investigate the nature and impact of nitrogen loss processes during sapropel deposition. In the sapropels, we find bulk sediment $\delta^{15}N$ values that are too negative (-2.8‰ relative to air) to be explained by N_2 fixation alone, suggesting increased nitrogen losses through denitrification and/or anaerobic oxidation of ammonium (anammox). Accordingly, we find high concentrations of the lipid bacteriohopanetetrol isomer (BHT-II), previously proposed as a biomarker for anammox bacteria (*1*). The characteristic carbon isotopic signature of BHT-II in the sapropels supports its origin from anammox bacteria. BHT-II carbon isotope data allow the estimation of $\delta^{13}C$ of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in the anoxic deep water. Together with $\delta^{13}C_{DIC}$ values from lipids produced in the oxic zone, these data enable the reconstruction of water column $\delta^{13}C_{DIC}$ gradients. Changes in the $\delta^{13}C_{DIC}$ gradient indicate progressive depletion of bottom water $\delta^{13}C_{DIC}$. This depletion likely originates from a gradual intensification of carbon burial during the course of sapropel deposition and suggests the existence of feedback mechanisms between the cycles of carbon and nitrogen during marine anoxia.

1. D. Rush *et al.*, *Geochimica et Cosmochimica Acta*. **140**, 50–64 (2014).