

Oxygen-deficient niches on the northern European epicontinental shelf across the Toarcian carbon isotope excursion interval

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The worldwide recognition of the Toarcian carbon isotope excursion (T-CIE) in organic-rich sedimentary rocks has been linked to an oceanic anoxic event (OAE) that deoxygenated the world's deep oceans ~183 million years ago (Ma) [1]. The majority of independent redox proxies used to build this argument were mainly obtained from organic-rich T-CIE sedimentary rocks deposited in the northern European epicontinental shelf settings. However, increasing evidence has shown that European epicontinental sedimentary environments had limited connection with the open ocean [2], making these settings poor proxies for reconstructing the T-CIE ocean redox structure. To unveil the controversial oceanic redox structure during the T-CIE, this study presents integrated nitrogen isotope compositions of bulk rock and extracted kerogen (expressed as $\delta^{15}\text{N}_{\text{bulk}}$ and $\delta^{15}\text{N}_{\text{ker}}$, i.e., the per mil (‰) difference in $^{15}\text{N}/^{14}\text{N}$ ratio relative to air- N_2 standard) from the sedimentary succession of Dotternhausen, southwestern Germany, in combination with literature data from other recognized T-CIE profiles. Both $\delta^{15}\text{N}_{\text{bulk}}$ and $\delta^{15}\text{N}_{\text{ker}}$ values imply that the enhancement of N_2 fixation by cyanobacteria using molybdenum (Mo)-based nitrogenase enzyme played a critical role in keeping pace with bioavailable N loss following quantitative denitrification and/or anammox in a strongly redox-stratified marine setting. Such N isotope compositions are in contrast to the typical sedimentary $\delta^{15}\text{N}$ values (> 3 ‰) induced by partial water-column denitrification and/or anammox in oxygen minimum zones of the present-day ocean [3]. We propose the existence of local oxygen-deficient niches on the northern European epicontinental shelf in which dissolved N pool underwent extensive denitrification and/or anammox resulting in bioavailable N scarcity. Mo-based diazotrophy thus played a critical role in discriminating N isotope compositions among multiple hydrographically restricted T-CIE marginal basins.

[1] Jenkyns (1988), *American Journal of Science* 288, 101-151. [2] McArthur (2019), *Chemical Geology* 522, 71-83. [3] Stüeken et al. (2016), *Earth-Science Reviews* 160, 220-239.