

LIPIDS AND NITROGEN ISOTOPIC FRACTIONATION OF MARINE CYANOBACTERIA

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Nitrogen, essential for life in all known forms, enters the open oceans primarily via the pathway of N₂-fixation and cyanobacteria are believed to play a crucial role in this process. The pelagic *Trichodesmium* spp., comprising non-heterocystous filamentous cyanobacteria, are considered to be of major importance in this respect, although recent investigations inferred that unicellular cyanobacteria may contribute significantly to the nitrogen budget as well (Montoya *et al.*, 2001). It is obvious that diazotrophic cyanobacteria play a decisive role in the present global nitrogen cycle and most likely did so in the past. Especially during Oceanic Anoxic Events (OAE), when the supply of deep-water nitrate was suppressed by the presence of a stratified water body, N₂-fixing cyanobacteria could be of major importance in providing a form of combined nitrogen to the ocean's surface waters (Kuypers *et al.*, 2004).

Current cyanobacterial biomarkers include mid-chain monomethylalkanes as well as di- and trimethylalkanes (Gelpi *et al.*, 1970) and 2-methylhopanoids (Summons *et al.*, 1999). However, these molecular markers are not selective for N₂-fixing cyanobacteria and hence cannot be used to trace the role of these diazotrophs in ancient environments. Bulk nitrogen isotopes have been used as a proxy for diazotrophy as N₂-fixation is believed to show only modest discrimination against inorganic ¹⁵N and produces organic matter that is slightly depleted in ¹⁵N relative to atmospheric nitrogen. However, this assumption is based on relatively few culture studies.

We investigated the lipid composition and ¹⁵N fractionation pattern of 33 cyanobacterial cultures grown under varying conditions. Preliminary results indicate that cyanobacterial strains utilizing atmospheric dinitrogen gas exhibit bulk $\delta^{15}\text{N}$ values in the range of -1 to -2‰. Cyanobacteria that used nitrate ($\delta^{15}\text{N} \approx 4.8\text{‰}$) as a source of nitrogen expressed $\delta^{15}\text{N}$ values ranging between +1 and -5‰ and thus displayed considerable fractionation effects during nitrate uptake by up to 9‰. A phylogenetic cluster comprising members of the genera *Synechococcus*, which utilized nitrate to sustain growth, showed $\delta^{15}\text{N}$ values similar as those observed for N₂-fixing cyanobacteria. This suggests that the

interpretation of $\delta^{15}\text{N}$ values has to be done with caution. In addition to the measurement of bulk organic nitrogen isotopes a set of cyanobacteria will be investigated for their $\delta^{15}\text{N}$ fractionation patterns in N-containing biomarkers such as chlorophylls and phycobilins. The same cyanobacteria will be further analysed with regard to their bulk organic carbon isotopes and fractionation effects occurring during synthesis of biomarker lipids.

Initial screening of cyanobacterial lipids by GC-MS showed that normal and branched alkanes as well as mono- and polyunsaturated alkenes in the range of C_{17} to C_{19} dominate the hydrocarbon fraction in some of the investigated cyanobacteria. Phytol was the major constituent of the alcohol fraction whilst α -tocopherol, octacosanol and diplopterol were found only in several cyanobacteria species. Interestingly, all nitrate-utilizing cyanobacteria contained an unusual distribution of, tentatively identified, long chain isoprenoidal alcohols. These compounds as well as the bacteriohopanepolyols found in cyanobacterial species will be further subjects of investigations.

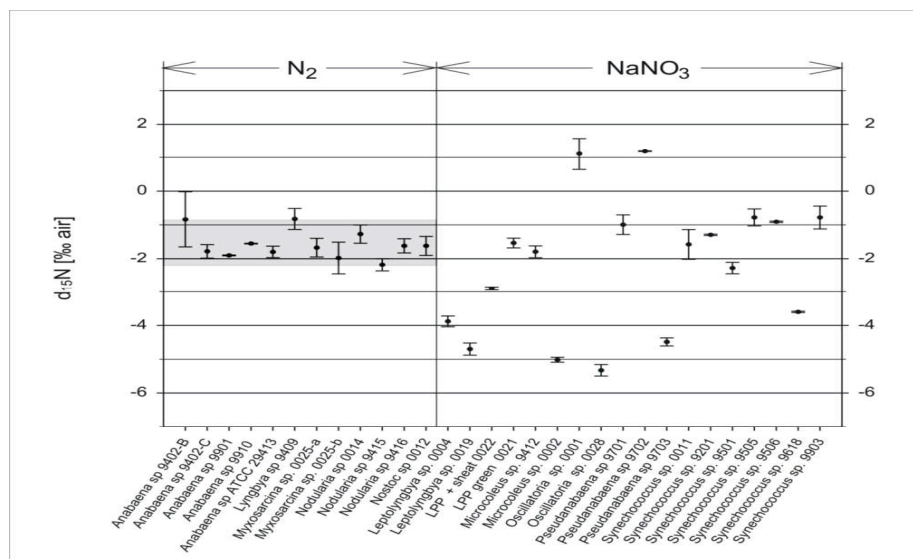


Figure 1. Scatter plot showing the N-isotopic composition of cell material of N_2 -fixing and non-diazotrophic cyanobacteria.

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