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Chapter 18

Nitrogen Isotope Fractionation and Its Significance in Biogeochemical Processes Occurring in Marine Environments

Eitaro WADA

Mitsubishi-Kasei Institute of Life Sciences, Minamiooya, Machida, Tokyo 194, Japan

ABSTRACT Natural abundance of ^{15}N in biogenic substances was investigated with special reference to marine plankton samples.

Simple model on the nitrogen isotope fractionation was developed for the processes of assimilation, fixation and denitrification.

The occurrence of nitrogen isotope fractionation was generally found out in the process of both ammonium and nitrate assimilation by marine diatoms and marine algal flagellates. In boreal areas the ^{15}N abundance for plankton is regulated by the nitrogen isotope fractionation during nitrate assimilation, while ^{15}N abundance for N_2-fixing blue-green algae showed characteristic low $\delta^{15}N$ values close to that of atmospheric nitrogen. Small isotope fractionation in the process of N_2-fixation is responsible for the latter fact. ^{15}N abundance provides three plankton groups according to the form of inorganic nitrogenous compounds used as nitrogen source for primary production.

Nitrogen isotope fractionation was studied during the decomposition of *Trichodesmium erythraeum*, *Chaeotoceros* sp. and *Calanus plumchrus* collected in the western North Pacific Ocean. It was found that $\delta^{15}N$ values for particulate matters were highly variable and closely correlated with the reproduction of bacterial

biomass and/or coagulation of dissolved organic nitrogen.

Significance of nitrogen isotope fractionation factor as a ecological parameter was figured out in marine environments along individual metabolic pathway involving N_2-fixation, assimilation, decomposition, and denitrification.

18.1 INTRODUCTION

Nitrogen is cycled in the ocean in a complex manner. Various kinds of biochemical processes are involved and the extent of nitrogen isotope fractionation varies depending upon the kinetic mode of individual metabolic reactions. Miyake and Wada (1967) were the first to report the $^{15}N/^{14}N$ ratios of nitrogenous compounds occurring in marine environments. $\delta^{15}N$ of marine biogenic nitrogen relative to atmospheric nitrogen is +7‰ on an average, and tends to increase along the food chain. ^{15}N abundance in pelagic plankton is apparently related to the form of inorganic nitrogen used for their growth (Wada and Hattori, 1976). Cline and Kaplan (1975) have shown that nitrate in the oxygen-depleted waters of the eastern tropical North Pacific Ocean is enriched with ^{15}N up to 18‰. Large isotope fractionation of nitrogen associated with denitrification was emphasized.

The nitrogen isotope fractionation by microorganisms have been investigated in laboratory experiments. Hoering and Ford (1960) showed that isotope fractionation of nitrogen hardly occurs in the molecular nitrogen fixation by *Azotobacter* spp. On the other hand, the fractionation factor up to 1.03 was obtained in denitrification and nitrate reduction to nitrite by *Pseudomonas*, *Bacillus* and *Alcaligenes* (Wellman et al., 1963; Cook et al., 1973), by an unidentified marine denitrifier (Miyake and Wada, 1971), and by *Serratia marinorubra* (Miyazaki, 1971). In order to explain the isotope effect in the chemical reductions of nitrate and hydroxylamine, Brown and Drury (1967) presented a two-atom model in which the cleavage of an N-O bond is rate-limiting. Rees (1973) developed a steady state kinetic model for sulphur isotope fractionation in bacterial sulfate reduction. A similar model was also applied to the nitrogen isotope fractionation in nitrate assimilation by marine diatoms (Wada and Hattori, 1978).

The present communication provide additional data on ^{15}N abundance in nitrogenous materials occurring in marine environments and on nitrogen isotope fractionation in decomposition of pelagic plankton, assimilation of