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硕 士 学 位 论 文

硝酸盐同位素示踪南海上层氮动力学过程与中深层水团

Nitrate isotope constraint on N dynamics in the upper water column and water masses exchange in the intermediate and deep waters of the South China Sea

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目录

contents

摘要

氮是组成生命的重要元素。生物可利用氮限制了大部分海区的表层海洋生物生产力，成为调节全球气候的一个重要因子。几乎所有氮形态的转变，都有生物过程参与其中，显著影响着其他元素的循环过程，特别是碳和磷等，因此，氮循环在生物地球化学循环中扮演着重要的作用。此外，自工业革命以来人为活动对氮循环的影响日益加剧，至今人为活动向大洋排放的氮通量与生物固氮作用相当，因而受人为活动影响的氮循环过程也成为全球研究的热点。

边缘海作为连接大陆和大洋的媒介，受人为活动的影响相对开阔大洋更为强烈，是氮循环过程比较活跃的区域。南中国海作为世界最大的边缘海之一，其氮循环研究受到广泛的关注，但针对许多过程机制的研究还存在不足。本论文以南海作为主要研究区域，以硝酸盐 (NO_3^-)及其氮氧稳定同位素为主要手段，对于南海全水柱的硝氮同位素进行分析，开展(1)南海外源氮输入通量的评估；(2)构建分馏模型计算 NO_3^-吸收过程的同位素分馏大小及其影响因素；(3)并以 NO_3^-及其氮氧稳定同位素结合温度盐度保守参数，探讨南海与太平洋之间的水团交换。

大气氮沉降速率与河流输入受到人为影响，从十八世纪中叶以来显著增大，特别是边缘海地区。大气氮沉降、河流输入与生物固氮是上层海洋外源氮的主要来源，且同位素显著偏轻，异于海洋深层氮储库。本研究尝试应用南海次表层氮储库的氮同位素漂移量，通过南海三个不同区域 (陆架，海盆，吕宋海峡西南)高分辨率采样分析结合 SEATS 站不同年份三个季度的数据，反演外源氮对于南海次表层氮储库的贡献。发现南海北部 $\delta^{15}N_{NO3}$ 季节性变化较小，NO_3^-的 $\delta^{15}N_{NO3}$ 从深层往次表层逐渐减小，可能归因于外源较轻同位素氮源添加与矿化，假设南海北部的氮通量处于平衡状态，那么通过模型估算得到的外源活性氮输入通量约为 31.9 - 199.6 mmol N m^{-2} $year^{-1}$，等同于年均新生产力比例的 1.2 - 25.0 %。但是对于南海不同海盆的区域差异以及季节性和年纪尺度的时空变异研究还不够深入，通量和所支持的生产力数据还需要通过实际的采样观测和野外培养实验进一步佐证。

通过对南海北部三个站位高分辨率层位采样分析，我们均观察到 NO_3^-的$\delta^{18}O_{NO3}$ - $\delta^{15}N_{NO3}$从次表层往上均逐渐增大，显示真光层内部浮游植物吸收 NO_3^-的过程。并观察到浮游植物吸收 NO_3^-过程中 $\delta^{18}O_{NO3}$: $\delta^{15}N_{NO3}$的相对改变略大于1，可能是存在硝化作用的影响，但真光层内部的 NO_3^-循环过程仍然以浮游植物吸收占主导。运用不同条件下瑞利分馏模型对南海北部站位拟合的结果得到浮游植物的分馏系数约为 2.5 - 3.1 ‰。并对浮游植物吸收 NO_3^-的分馏系数进行评估，认为黑潮水通过吕宋海峡入侵南海对分馏系数能够产生一定影响。

NO_3^-是海洋中最大的固定氮储库，其虽为不保守参数，但是在中深层水生地化速率相对较小的条件下，可以被用来追溯水团流动和水体交换。本研究通过对南海和菲律宾海大量站位的调查，结合大洋环流及运用端元混合模型，探究南海和太平洋之间的水体交换。

南海的中层水的上部 (σ_θ 密度在 26.5 - 26.8 之间)和下部 (密度在 26.8 - 27.2 之间)通过吕宋海峡与菲律宾海进行水体交换。而菲律宾海中层水的上部主要源自于北太平洋中层水和北赤道流中层水两者的混合，并受到菲律宾海的次表层水体垂向混合的影响。南海中层水的上部，其不仅仅来自于菲律宾海中层水的上部通过吕宋海峡对南海的入侵，还因为南海内部强烈的涌升和垂向混合作用，使得其还受到次表层水和深层水两者的共同作用。

菲律宾海中层水的下部不仅由北太平洋中层水和北赤道流中层水两者在菲律宾海的保守混合得到，还受到南海中层水的下部外流进入菲律宾海的影响。而这个密度范围的南海中层水的下部似乎主要源自于深层水的涌升和南海中层水的上部在垂向上的混合。但是这个密度范围吕宋海峡的经度断面上的水体交换北部以东向流出为主，而南部以西向入侵为主，因此我们认为菲律宾海中层水的下部依然是南海的一个重要水团来源。南海的深层水则主要来自于菲律宾海的深层水在 1500 m 左右至吕宋底海峡底部这个深度范围对南海的入侵，而菲律宾海的深层水相对于同等深度的南海水密度较大，入侵后翻越吕宋海峡开始下沉，使得南海海盆的深层水体性质相对均匀。本研究数据填补了西北太平洋 NO_3^-同位素数据空白，能够为建立全球海洋氮循环模型提供支撑。

综上所述，本研究发现 (1)南海次表层氮储库显著受到外源氮的影响；(2)

浮游植物的分馏系数约为 2.5 - 3.1 ‰，相对于其他海域偏低，可能与藻种或是黑潮水侧向输入有关；(3)通过 NO_3^-氮氧稳定同位素分析南海水团交换得到的结果显示，南海内部的 NO_3^-性质的分布受控于南海环流和垂向水体交换，以及与太平洋水体的交换，从化学示踪剂的角度，佐证了吕宋海峡的“三明治”结构模型。

关键词：南海；稳定氮同位素；外源活性氮输入；同位素分馏；水团交换

Abstract

Nitrogen is critical elements in organisms. Nitrogen is the limiting nutrient in most of the ocean regulating the biological pump, thus, the atmospheric pCO2. Almost all processes involving nitrogen transform are associated with bio-processes. Thus, nitrogen cycle also links to various elemental cycles, such as carbon and phosphorus, playing an important role in the marine biogeochemistry. Moreover, human activities significantly alter the nature nitrogen cycle since the Industrial Revolution. Anthropogenic nitrogen input to the earth system now equals the amount of biological nitrogen fixation. To project the future climate and ocean, understandings on nitrogen cycle under human influence becomes an urgent environmental issue.

Marginal seas bridging the continent and open oceans have received remarkable impact from human activities. The South China Sea (SCS), as one of the largest marginal sea in the world, has been paid a lot of attention on its biogeochemical processes; however, nitrogen processes remain unclear. This thesis focused on the SCS region by using the dual stable isotope of NO_3^- as major tools to investigate the nitrogen dynamics in whole water column of the SCS. The main goals are 1) to evaluate the external nitrogen input, 2) to examine the fractionation factor (ε) during NO_3^- uptake, and 3) to explore the water masses exchange between SCS and the western.

Bioavailable nitrogen from the atmospheric deposition, river input and bio-nitrogen fixation, has relatively lower isotope signal than the deep oceanic pool of nitrate, are three major external nitrogen sources to the surface ocean. In this study, we use the isotopic shift of nitrogen isotope of nitrate accumulated in the subsurface to estimate the relative contribution of external nitrogen to the subsurface nitrogen pool of SCS. Results showed that seasonal changes of $\delta^{15}N_{NO3}$ were insignificant in

the northern SCS. The $\delta^{15}N_{NO3}$ of nitrate decrease upward from the subsurface layer because of the addition from lighter nitrogen source and remineralization. Assuming that the nitrogen supply and remove are at a steady state in the northern SCS, we calculate the external nitrogen flux to be about 31.9 - 199.6 mmol N m^{-2} $year^{-1}$. That accounts for about 1.2 - 25.0 % of annual new production in annual basis. More studies are needed for validation.

On the other hand, in the euphotic layer, $\delta^{18}O_{NO3}$ - $\delta^{15}N_{NO3}$ increase as nitrate decreased upward from subsurface layer. Such pattern was attributed to the assimilation of NO_3^- by phytoplankton. The ratio of changes in $\delta^{18}O_{NO3}$ against $\delta^{15}N_{NO3}$ is slightly larger than 1, which indicates that assimilation of NO_3^- is the most important process to control the pattern of nitrate isotopes, and the nitrification in the euphotic zone may be effective. Rayleigh fractionation models (closed system and steady state) showed that the nitrogen fractionation factor of NO_3^- uptake is about 2.5 - 3.1 ‰, which is slightly lower than reported values for diatom. That the lower fractionation was attributable to the species of phytoplankton or/and the dilution effect caused by Kuroshio intrusion.

The South China Sea (SCS) is an important pathway of water and heat exchange between the Pacific and Indian Ocean. Due to complicated basin topography and strong seasonality in the circulation pattern, knowledges of the water exchange through the Luzon Strait remain insufficient. Basing on physical observations, a sandwich structure had been revealed for the vertical profile of transport. However, the source waters and mixing pattern of the intermediate water, which dominates the exchange, remain unclear. By using the nitrogen isotopic composition, this paper aims to explore the mixing pattern and potential source waters of the intermediate layer in-and-out the Luzon Strait. This is the first report of N isotope of nitrate for intermediate and deep layers in the SCS and West Philippine Sea (WPS). By applying the end-member mixing model, we found that the upper intermediate water (UIW) with potential density anomaly (σ_θ) of 26.5-26.8 in the WPS was sourced from the

combination of North Pacific Intermediate Water (NPIW) and North Equatorial Intermediate Water (NEqIW), and is also influenced by the subsurface water of the WPS. The lower intermediate water (LIW, σ_θ of 26.8 - 27.2) of the WPS was sourced from the NPIW and NEqIW with the addition of the outflow from the SCS-LIW. The UIW of SCS mainly comes from the intrusion of the WPS-UIW; however, it was also influenced by the subsurface and deep water of SCS interior due to diapycal mixing. The LIW of SCS seems to be an internal mixing product of the SCS deep water and the UIW of SCS. The deep water of the SCS, showing a consistent physiochemical property, mainly comes from the intruded WPS deep water crossing the sill depth of Luzon Strait below 1500 m. Although uncertainties remain, NO_3^- stable isotope approach provides insightful information addition to physical properties.

In conclusion, we find that 1) external nitrogen has significant impact on the subsurface nitrate pool of the SCS; 2) the fractionation effect of NO_3^- assimilation is about 2.5 - 3.1 ‰ which is slightly lower than other regions, due to the different species of phytoplankton and/or the dilution effect by the horizontal intrusion of the surface Kuroshio Current; 3) basing on the stable isotopic compositions of NO_3^- the source waters and mixing pattern of the intermediate and deep water around the Luzon Strait were deciphered.

Key words: South China Sea; Stable nitrogen isotope; Extra bioavailable nitrogen input; Isotopic fractionation; Water masses exchange

缩略语表 (Abbreviations)

DO, Dissolved Oxygen 溶解氧

ON, Organic Nitrogen 有机氮

HNLC, High Nutrient Low Chlorophyll 高营养盐低叶绿素浓度

PN, Particulate Nitrogen 颗粒氮

Nr, Reactive Nitrogen 活性氮

SCS, South China Sea 南中国海

LS, Luzon Strait 吕宋海峡

Sv, Severdrup (10^6 m^3 s^{-1}) 流量为 10^6 m^3 s^{-1}

NPIW, North Pacific Intermediate Water 北太平洋中层水

NEqIW, North Equatorial Intermediate Water 北赤道流中层水

σ_θ, Potential Density Anomaly 位势密度超量

σ_n, Neutral Density 中性密度

AAIW, Antarctic Intermediate Water 南极中层水

SATFZ, Subarctic-tropic Front Zone 亚极地热带锋区

MC, Mindanao Current 棉兰老流

$\delta^{15}N_{NO3}$, $\delta^{15}N$ of NO_3^- 硝酸盐的 $\delta^{15}N$

$\delta^{18}O_{NO3}$, $\delta^{18}O$ of NO_3^-硝酸盐的 $\delta^{18}O$

HDPE, High Density Polyethylene 高密度聚乙烯

RO, Reverse Osmotic Water 反渗透水

GF/F, Glass Microfiber F 玻璃纤维膜 F

SRP, Solube Reactive Phosphate 溶解活性磷

AA3, Auto-Analyzer III 营养盐流动分析仪

SPE, Solid Phase Extraction 固相萃取

FIA-LWCC, Flow Injection Analysis-Liquid Waveguide Capillary Cell 流动注射分析-液芯波导毛细管流通池