

学校编码: 10384

密级 _____

学号: 33320131151736

厦 门 大 学

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

吴 乔

指导教师姓名: 高树基 教授

专业名称: 环境科学

论文提交日期: 2016年4月

论文答辩时间: 2016年5月

2016年5月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为()课题(组)的研究成果,获得()课题()经费或实验室的资助,在()实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

() 1. 经厦门大学保密委员会审查核定的保密学位论文，于 年 月 日解密，解密后适用上述授权。

() 2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月 日

目录

摘要.....	I
Abstract	IV
缩略语表(Abbreviations).....	VII
第一章 绪论	1
1.1 海洋氮循环.....	1
1.1.1 海洋水体中的氮循环过程	2
1.1.2 浮游植物吸收 NO_3^- 和 NH_4^+	4
1.1.3 稳定同位素在海洋氮循环中的运用	5
1.2 南海环流与水团交换.....	7
1.2.1 南海环流与水体交换	9
1.2.2 北太平洋中层水和北赤道流.....	11
1.3 研究内容和目标.....	13
1.4 论文框架.....	14
第二章 研究区域与方法	15
2.1 研究区域介绍.....	15
2.2 样品测定方法.....	17
2.2.1 实验样品采集	17
2.2.2 营养盐组分分析	18
2.2.3 NO_3^- -氮氧同位素以及颗粒氮浓度分析	19
2.3 数据处理与质量控制.....	24
第三章 南海北部真光层氮的动力学过程	28
3.1 引言.....	28
3.2 材料与方法.....	30
3.2.1 南海北部站位概况和样品采集.....	30
3.2.2 营养盐组分分析	32

3.2.3 NO ₃ ⁻ 氮氧同位素分析以及颗粒物浓度	32
3.3 结果	33
3.3.1 真光层内部 NO ₃ ⁻ 浓度以及氮氧同位素特征	33
3.3.2 真光层内部颗粒氮和溶解有机氮特征	35
3.4 讨论	36
3.4.1 对真光层的 NO ₃ ⁻ 浓度和同位素产生影响的过程	36
3.4.2 大气添加氮源的通量计算	38
3.4.3 硝酸盐吸收的氮氧同位素分馏	42
3.5 结论	48
第四章 硝酸盐同位素示踪南海中深层水团	50
4.1 引言	50
4.2 材料与方法	52
4.2.1 南海站位概况和样品采集	52
4.3 结果	53
4.3.1 南海及西菲律宾海水文参数分布特征	53
4.3.2 南海及西菲律宾海营养盐浓度和氮氧同位素特征	56
4.3.3 北太平洋 26.5, 26.8 和 27.2 等密面上 NO ₃ ⁻ 的浓度分布	59
4.4 讨论	61
4.4.1 密度范围 26.5-26.8 的 SCS 和 WPS 之间中层水的交换	61
4.4.2 密度范围在 26.8-27.2 的 SCS 和 WPS 之间中层水的交换	64
4.4.2 SCS 深层水和 WPS 之间的交换	67
4.4 结论	68
第五章 总结与展望	71
5.1 主要结论	71
5.1.1 南海大气输入氮通量以及同位素分馏	71
5.1.2 南海中深层水团的 NO ₃ ⁻ 及 δ ¹⁵ N _{NO₃} 示踪	72
5.2 特色与创新	74
5.3 尚未解决的问题和展望	74

参考文献.....	75
附录 1 攻读硕士期间参加的研究课题和科考航次.....	89
附录 2 攻读硕士期间参加的学术会议.....	89

厦门大学博硕士论文摘要库

contents

Abstract(in Chinese)	I
Abstract	IV
Abbreviations	VII
Chapter 1 Introduction	1
1.1 Marine nitrogen cycle	1
1.1.1 Nitrogen cycle processes in the ocean.....	2
1.1.2 The assimilation of NO_3^- and NH_4^+ by phytoplankton.....	4
1.1.3 The application of stable isotope in nitrogen cycle.....	5
1.2 The circulation and water mass exchange of South China Sea.....	7
1.2.1 The circulation of South China Sea.....	9
1.2.2 NPIW and NEqIW.....	11
1.3 Objectives.....	13
1.4 Framework	14
Chapter 2 Study area and methodology	15
2.1 Introduction of study area	15
2.2 The method of samples' measurment	17
2.2.1 The collection of samples.....	17
2.2.2 Nutrients measurment.....	18
2.2.3 The measurment of isotope of NO_3^- and PN concentration.....	19
2.3 Data analysis and quality control.....	24
Chapter 3 The dynamic processes of nitrogen cycle of northern South China Sea	28
3.1 Introduction	28
3.2 Materials and methods	30
3.2.1 The introduction of stations and samples' collection	30
3.2.2 Nutrient analysis.....	32

3.2.3 The isotope of NO_3^- and PN concentration	32
3.3 Results	33
3.3.1 The characters of NO_3^- concentration and isotopes in the euphotic zone ..	33
3.3.2 The characters of PON and DON concentration in the euphotic zone.....	35
3.4 discussion	36
3.4.1 The processes that can influence NO_3^- concentration and isotopes in the euphotic zone.....	36
3.4.2 The estimation of atmospheric N depositon flux	38
3.4.3 The fractionation effect of NO_3^- assimilation.....	42
3.5 Conclusion.....	48
Chapter 4 Trace the intermediate and deep water of South China with nitrogen isotope	50
4.1 Introduction	50
4.2 Materials and methods	52
4.2.1 The introduction of stations and samples' collection	52
4.3 Results	53
4.3.1 The introduction of hydrology of SCS	53
4.3.2 The distribution of nutrient and isotope of NO_3^- in SCS and WPS.....	56
4.3.3 The distribution of NO_3^- concentration in north Pacific at potential density anolomy of 26.5, 26.8 and 27.2	59
4.4 Discussion.....	61
4.4.1 The water mass exchange of the potential density anolomy range of 26.5-26.8 between SCS and WPS	61
4.4.2 The water mass exchange of the potential density anolomy range of 26.8-27.2 between SCS and WPS	64
4.4.2 The deep water exchange between SCS and WPS	67
4.4 Conculsion.....	68
Chapter 5 Summary and prospect	71

5.1 Major conclusion.....	71
5.1.1 The N deposition flux and fractionation effect in SCS	71
5.1.2 Water masses exchange of intermediate and deep SCS	72
5.2 Innovations	74
5.3 Unknown and prospect.....	74
References	75
Appendix 1 Projects and cruises	89
Appendix 2 Conferences	89

厦门大学博硕士学位论文摘要库

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 $\delta^{15}\text{N}_{\text{NO}_3}$ 季节性变化较小， NO_3^- 的 $\delta^{15}\text{N}_{\text{NO}_3}$ 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 $31.9 - 199.6 \text{ mmol N m}^{-2} \text{ year}^{-1}$ ，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 $\delta^{18}\text{O}_{\text{NO}_3} - \delta^{15}\text{N}_{\text{NO}_3}$ 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 $\delta^{18}\text{O}_{\text{NO}_3} : \delta^{15}\text{N}_{\text{NO}_3}$ 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

厦门大学博硕士学位论文摘要库

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 NO₃⁻ 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 NO₃⁻ 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 $\delta^{15}\text{N}_{\text{NO}_3}$ were insignificant in

the northern SCS. The $\delta^{15}\text{N}_{\text{NO}_3}$ 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 $31.9 - 199.6 \text{ mmol N m}^{-2} \text{ year}^{-1}$. 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, $\delta^{18}\text{O}_{\text{NO}_3} - \delta^{15}\text{N}_{\text{NO}_3}$ 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 $\delta^{18}\text{O}_{\text{NO}_3}$ against $\delta^{15}\text{N}_{\text{NO}_3}$ 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 ($10^6 \text{ m}^3 \text{ s}^{-1}$) 流量为 $10^6 \text{ m}^3 \text{ s}^{-1}$
- 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
- $\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{15}\text{N}$ of NO_3^- 硝酸盐的 $\delta^{15}\text{N}$
- $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{18}\text{O}$ of NO_3^- 硝酸盐的 $\delta^{18}\text{O}$
- 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, Soluble 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

Degree papers are in the “[Xiamen University Electronic Theses and Dissertations Database](#)”.

Fulltexts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.