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国家重点研发计划课题
中期执行情况报告

项目名称：海洋生态系统储碳过程的多尺度调控及其对全球变化的响应

项目牵头单位：厦门大学

课题名称：海洋典型生态系统碳库变动与气候变化和海洋酸化的关联

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执行期限：2016 年 07 月 至 2021 年 06 月

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编报要求

一、内容说明

课题中期执行情况报告着重围绕课题任务书的内容，报告课题中期重要进展情况，具体包括课题的总体目标及考核指标实现程度，人员、资金等支撑条件落实情况，课题经费使用情况等，并报告中期执行过程中的重大事项及突出进展。

二、格式要求

文字简练；报告的密级一般与任务书规定的密级相同；报告文本统一用 A4 幅面纸，文字内容一律通过“国家科技管理信息系统公共服务平台”在线填报；报告文本第一次出现外文名称时要写清全称和缩写，再出现时可以使用缩写。

三、编制程序及时间要求

项目中期总结前，由课题承担单位组织课题参与单位编制课题中期执行情况报告，经课题负责人及课题牵头单位审核后，提交项目牵头单位。

目录

一、总体进展情况

1．课题中期总体进展情况

对照课题任务书的计划目标和各项主要指标要求，简要阐明课题中期进展情况，评述课题中期任务的实施进展状态。

课题按照任务书的研究计划执行，各项工作进展顺利，中期评估所要求达到的计划目标和各项指标均已经完成，具体如下：

任务书中标明的中期评估指标包括：1）建立有机碳来源辨识的方法；获取陆架区近 2000 年来温度和有机碳埋藏记录；2）获取珊瑚礁近 200 年来钙化率、温度和海水 pH 记录和 Mo 等生源要素同位素记录；3）发表论文 6-8 篇。具体的完成情况如下：

1）利用综合的有机地球化学指标，包括传统的碳氮含量、总有机碳的碳同位素（$\delta^{13}C_{org}$）和一些新型的分子标志化合物如甘油二烷基甘油四醚（glycerol dialkyl glycerol tetraethers：GDGTs）等来分辨近岸海域沉积物中埋藏有机碳的来源，并定量计算了台湾海峡和钦州湾等代表性近岸海域沉积物中陆源有机碳的贡献；课题还已经开始尝试更新的分子标志化合物如木质素的研究方法来更好量化估算陆源有机碳的贡献，在相关的分析技术方面已经取得一定进展；在南海北部陆架、粤西近岸海域和闽浙泥质区等多个近岸海域重建了近 2000 年来高分辨率的表层海水温度（sea surface temperature：SST）记录，探讨了不同区域 SST 变化的控制机制；重建了粤西近岸海域近 2000 年来高分辨率有机碳埋藏的记录，并定量区分了陆源有机碳和海洋有机碳的贡献，揭示了近 2000 年以来人类活动对近岸有机碳埋藏的影响；

2）系统测量了海南岛东部和西沙七连屿十多个近现代珊瑚的钙化率，了解相关海域近 200 年来珊瑚钙化率的变化及其对气候变化/海洋酸化的响应；重建了海南岛东部海域近 2000 年来重要特征时段年分辨率的 SST 和碳同位素组成的变化，探讨了珊瑚钙化（无机碳固定）对气候变化的响应；探讨了珊瑚 Mo 同位素对珊瑚生物活动变化的响应机制，为进一步重建珊瑚生物活动应对气候变化的响应提供新的研究手段；

3）目前已经发表标注项目资助的论文 9 篇（第一标注 8 篇，第二标注 1 篇），其中国际 SCI 论文 8 篇。

除了上述计划目标和指标外，任务书中设定的年度研究计划也均顺利完成，主要的研究工作如下：

1）海洋观测和采样航次：

2017 年 8 月 12 日--8 月 26 日参加了“2017 南海东北部及吕宋海峡共享航次”第三航段，历时 15 天。结合本课题需求，共完成 CTD 站位 14 个，在 6 个站位开展柱状沉积物取样，在其中 2 个站位获取了较长的沉积岩芯样品，为开展南海海盆沉积碳库变动与气候变化提供了良好载体；

2017 年 8 月 2 日--8 月 20 日课题独立组织了“2017 海南珊瑚礁野外考察采样”航次，历时 19 天。重点考察海南省琼海市青葛港到文昌市冯家湾等海域，并同时对课题自主研制的水下液压钻机进行海试。本航次共完成 31 根珊瑚岩芯的钻取，为研究珊瑚对气候变化和海洋酸化的响应规律提供了丰富素材。

2）实验室分析测试：课题对已经获取的研究样品全面展开实验室分析测试工作，获取了大量的元素和同位素地球化学数据。一些重要的分析测试工作包括：

年代学分析：完成了粤西近岸（YJ）和 S7A 和 8 站位沉积物岩芯的 ^{14}C 年代学测试，累计 ^{14}C 测试样品 30 个；对已采集的珊瑚岩芯开展 U-Th 年代学分析，累计完成测试样品 65 个，建立起约 50 个珊瑚岩芯的年代学框架；

生物标志化合物分析：对表层及岩芯沉积物样品开展了常规有机碳氮含量和同位素分析，以及包括长链烯酮、GDGT 等生物标志化合物分析，累计分析样品量超过 500 个；

沉积物综合地球化学分析：完成了粤西近岸岩芯（YJ）沉积物的粒度、环境磁学参数、矿物组成、主微量元素等综合地球化学同步分析，累计样品量 207 个。

课题总体上按照任务计划开展，各方面工作进展顺利，并达到了原先设计的研究目标。

2. 课题调整情况

如课题出现超前/迟滞等情况，请详细说明原因、措施及履行相关审批管理制度的情况。

课题按照任务计划开展，各方面工作进展顺利，不存在超前或者迟滞等情况，不需要进行调整。

二、取得的重要进展及成果

1. 课题中期重要进展及成果

简要介绍课题研究工作的重要进展、阶段性成果（一般不超过 3 项）及前景。

1.1 南海北部近海及珊瑚礁区中晚全新世 SST 变化

气候变化特别 SST 变化直接控制海洋生物活动，对海洋固碳及碳埋藏具有重要的影响，因而清楚研究海域 SST 的变化是探讨其碳循环演变的重要前提。与开放性大洋相比，近海海域和珊瑚礁的 SST 变化的影响因素更加复杂，如海陆界面相互作用和人类活动影响等，往往具有一些特殊的变化过程，很有可能影响到碳循环演变。

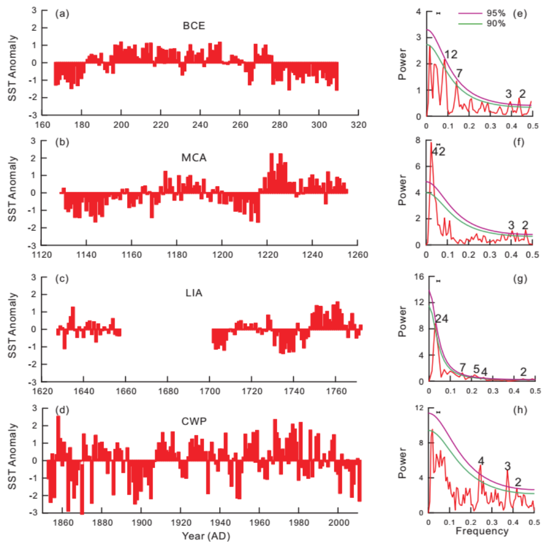


图 1 南海北部珊瑚礁中晚全新世特征时段 SST 变率

我们利用南海北部一系列的珊瑚岩芯，重建了近 2000 年以来重要特征时段年分辨率的温度、降雨演变记录，剖析热带海洋气候演变过程中人类活动的影响。结果显示，工业化革命以来的现代暖期温度和降雨和中世纪暖期相当，较小冰期及最近 2000 年的开始阶段要温暖但雨量稍少。现代暖期温度的变化频率加快、幅度有所加大，降雨的变率基本在正常的范围内，没有明显的异常波动（图 1）。因而工业化革命以来人类排放 CO_2 对热带海洋温度升高影响并不十分显著，对极端气候事件发生频率影响也不直接。（Deng et al., JGR-Oceans, 2017; Xiao et al., JAES, 2017）

通过对我国边缘海系列沉积物岩芯开展长链烯酮 SST 记录重建，基本探明了近 2000 年来的相关近海海域 SST 变化规律。整体来说，边缘海海表温度变化受东亚夏/冬季风及洋流的影响而显示与全球/北半球温度变化一致或相反的特性。在广海区域（>500 米水深以外）海表温度与全球温度变化一致。而在黄海

暖流经过的区域海表温度显示与全球温度相反的特征，主要受冷期暖流增强的影响；而在长江口受冬季风控制的岸边流影响，海温变化与全球温度一致。在闽浙泥质区及香港水域，海温可能受夏季风混合作用导致的降温效应影响，呈现与全球温度变化相反的趋势（图 2）；而在珠江口以西区域，可能受到淡水输入抑制了夏季的混合作用，海温变化又与全球温度变化一致，并由于冬季风的放大作用，近 2000 年来的温度变化幅度比其它低纬度区域要大得多。（Kong et al., QI, 2017; Liu et al., EPSL, 2018）

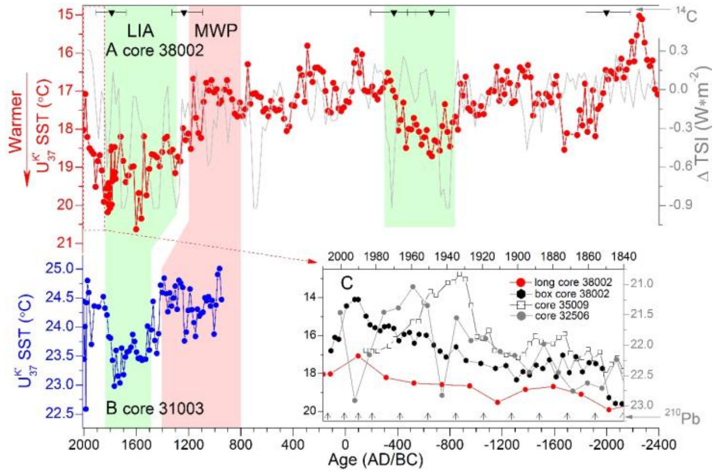


图 2 黄海暖流经过区域与海岸边相反的 SST 变化趋势

1.2 南海珊瑚钙化对气候和环境变化的响应

珊瑚礁是热带海洋独特的生态系统，具有极高的生产力和生物多样性，是热带海洋中非常重要的无机碳库。珊瑚的钙化是调控这个碳库变化的主要过程，因此了解钙化对气候环境变化的响应是了解热带海洋无机碳库变化特征与控制机制的关键。本课题重点针对珊瑚钙化过程中利用的碳源和钙化率的变化特征开展研究，重点解读其对气候环境演变的响应，获得了以下重要认识：

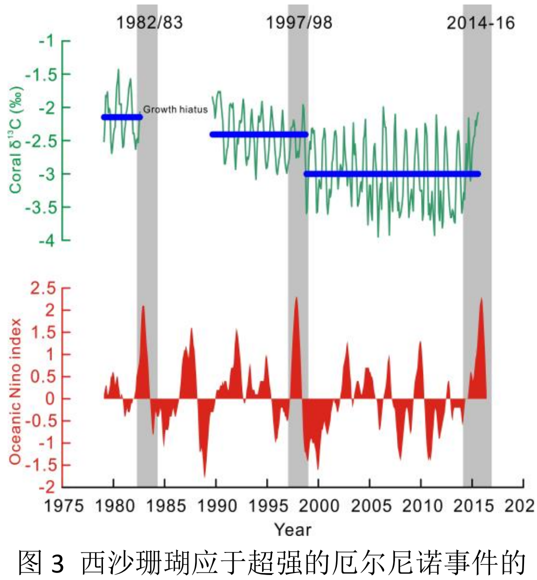


图 3 西沙珊瑚应于超强的厄尔尼诺事件的 $\delta^{13}C$ 的台阶式降低

珊瑚钙化所利用的碳，除一部分直接来源于海水中的溶解无机碳（dissolved inorganic carbon: DIC）,很大一部分来自珊瑚新陈代谢产生的碳，这一部分碳的利用体现在其 $\delta^{13}C$ 与影响珊瑚生物活动的要素如 SST 和太阳辐照量的对应关系上。我们的研究结果显示，在每经历一次超强厄尔尼诺事件后，珊瑚的 $\delta^{13}C$ 都出现一次明显的负偏（图 3），

意味着更多具较负 δ^{13}C 的新陈代谢碳被利用来进行钙化，可能反映超强厄尔尼诺期间的高温导致共生虫黄藻密度的降低引起虫黄藻对碳的利用效率的降低，或者与珊瑚自身为了适应极端环境变化而对虫黄藻种类的选择性利用有关。而将时间尺度放在最近 1000 年以来，可以看出工业化革命以前，珊瑚的 δ^{13}C 与太阳辐照量具有非常好的正相关关系，但在工业化革命以来，珊瑚的 δ^{13}C 与太阳辐照量呈现负相关关系（图 4），表明珊瑚固碳过程对不同来源碳的利用发生了明显的变化，意味着人类排放 CO_2 对表层海洋的碳循环产生了明显的影响。（Deng et al., Paleoceanography, 2017; Wang et al., Coral Reef, 2018）

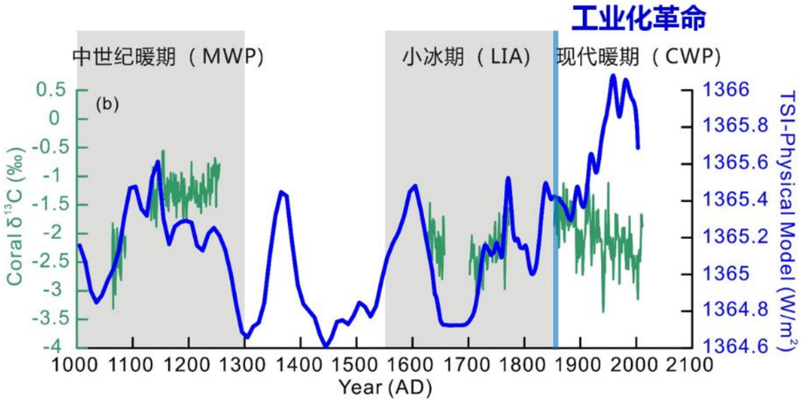


图 4 工业化革命前后珊瑚骨骼碳同位素和太阳辐照度的变化关系

珊瑚钙化发生在其息肉组织与钙质骨骼之间的半封闭钙化流体（Calcification Fluid：CF）中，珊瑚转化和利用无机碳的过程影响着钙化流体的 pH，从而控制着珊瑚的钙化能力。因此，厘清珊瑚钙化流体中碳酸盐系统的变化特征有助于我们认识珊瑚钙化对气候环境变化的响应机制。我们利用珊瑚 δ^{11}B 重建了过去 1000 年以来的珊瑚钙化流体中 pH_{cf} 的变化记录 （图 5）。结果显示，pH_{cf} 在工业化革命以前变化幅度不大；随着从中世纪暖期到小冰期，pH_{cf} 存在一个略微升高的趋势。对照同阶段 δ^{13}C 的变化，尽管太阳辐射对珊瑚新陈代谢碳利用过程影响显著，但是钙化流体 pH_{cf} 的年际波动幅度和平均值并没有明显的改变，说明珊瑚自身具有一定

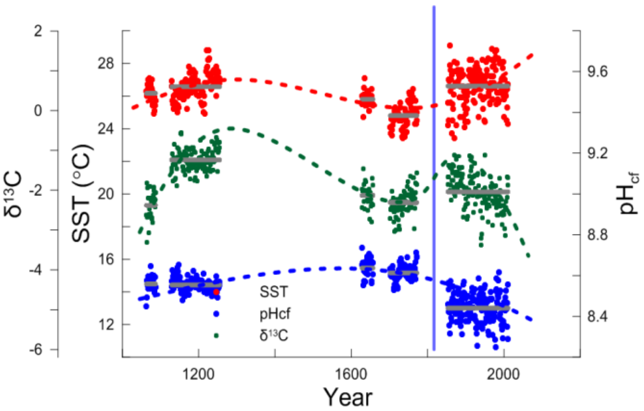
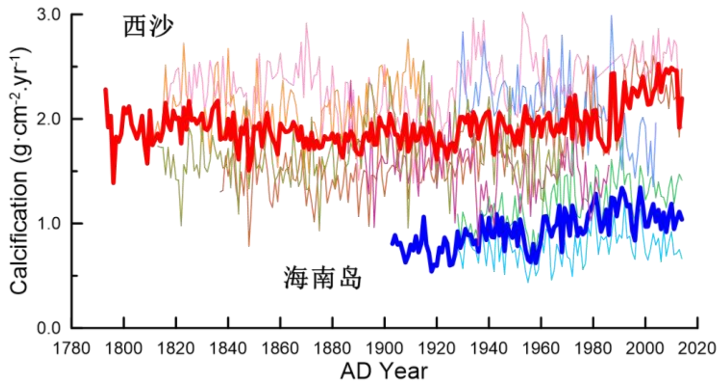


图 5 南海北部珊瑚钙化流体 pHcf 变化情况

的调节能力来维持一个相对稳定的钙化环境。但是，工业化革命以后珊瑚钙化流体的 pH_{cf} 明显降低，可能说明随着海洋酸化进程加剧，珊瑚钙化流体 pH_{cf} 也随之降低，意味着海洋吸收大量人类排放的 CO_2 后已经对钙质生物的生存产生了威胁。

除了碳利用的方式外，气候环境的影响还直接体现在珊瑚钙化率的变化上。虽然珊瑚自身生物活动会导致单个个体的钙化率有所波动，但通过一定数量的统计可以反映区域的珊瑚钙化率情况。我们通过测量计算海南岛东部和西沙七连屿的多个近现代珊瑚的钙化率，发现西沙的珊瑚钙化率系统高于海南岛东部，但均显示出在过去 200 年存在一个逐渐增加的趋势（图 6a）。这种增加趋势可能与过去 200 年来这些海域 SST 持续升高有关。工业化革命以来大气 CO_2 增加引起的海洋酸化并没有导致该区珊瑚钙化率的显著降低，或者其酸化的效应被该区珊瑚较旺盛的生长所掩盖。而海南岛东部的近现代珊瑚钙化率则明显低于中全新世暖期（图 6b）,再次说明中晚全新世以来温度是控制珊瑚钙化的主要因素，大气 CO_2 或者海洋酸化的影响的显著性还没有显现。



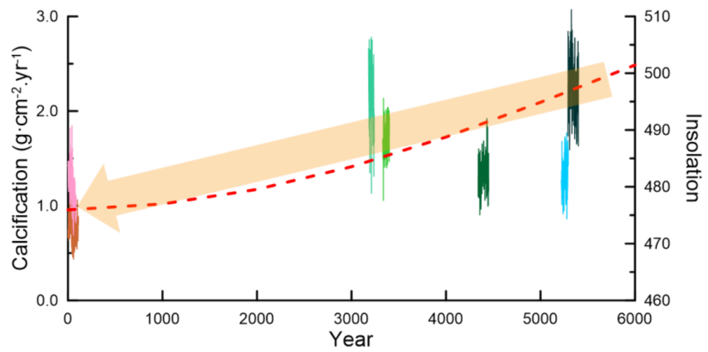


图 6 南海北部珊瑚钙化率的变化

a)近 200 年来的珊瑚钙化率变化；b)海南岛东部中晚全新世以来钙化率变化

1.3 南海北部近海有机碳来源辨识及近 2000 来有机碳埋藏变化

河口、海岸和陆架等近海海域是有机碳埋藏的重要场所，但这些海域中埋藏的有机碳相当一部分来自陆地，准确分辨陆源有机碳的贡献是了解这些海域碳循环特征的关键。传统的有机地球化学指标如有机碳氮含量和同位素，结合一些新型的生物标志化合物如 GDGT 等，是分辨有机碳来源的有效手段。

课题通过对系统采集的台湾海峡表层沉积物，开展包括总有机碳（TOC）及其稳定碳同位素（$\delta^{13}C_{org}$）、总氮（TN）和 GDGTs 等特征分子标志化合物-甘油二烷基甘油四醚的空间分布分析，发现 TOC 和 TN 含量在近岸沉积物中较高，向台湾海峡中部逐渐减少，其分布受台湾海峡水动力条件和沿岸上升流控制。计算出的 OC 堆积速率（AROC）为 1.9 - 47.2 g C/m^2/yr，与中国边缘海的其他区域相似。基于三端元模型计算的各类来源的 OC 贡献结果显示：海洋 OC 主要埋藏在上升流区域，陆地植被和土壤来源的 OC 主要埋藏在河口区（图 7）。总的来说，由于植被和海洋来源的易降解 OC 是台湾海峡埋藏 OC 的主要组成部分，台湾海峡在全球碳循环中是 CO_2 的汇。

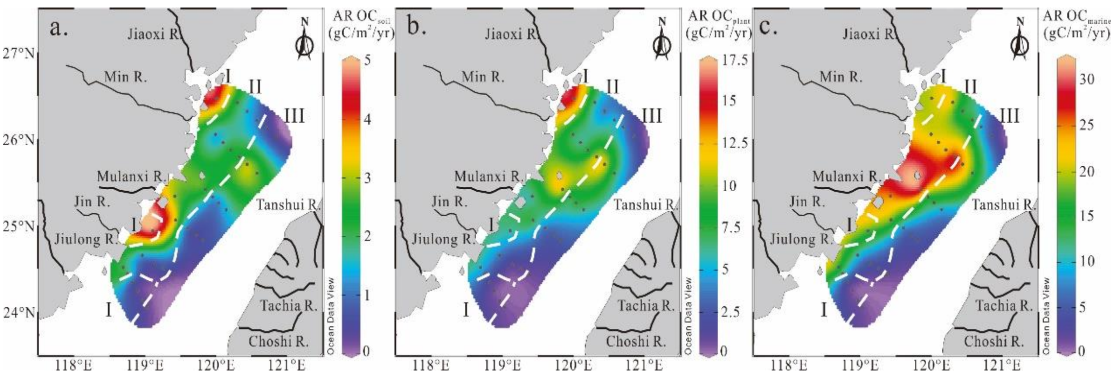


图 7. 台湾海峡表层沉积物中各组份堆积速率分布
a) 土壤有机碳；b) 植被有机碳 c) 海洋有机碳

课题同时在北部湾及邻近河流开展类似研究，发现陆源 OC 含量从茅尾海向钦州湾外湾、从河流到河口呈下降趋势；BIT（支链/类异戊二烯 GDGTs）指数也从茅尾海向钦州湾、从河流向河口湾逐渐减少，指示土壤有机质（OM）主要通过河流输送到北部湾，陆源 OC 主要分布在海岸及邻近区域（图 8）。

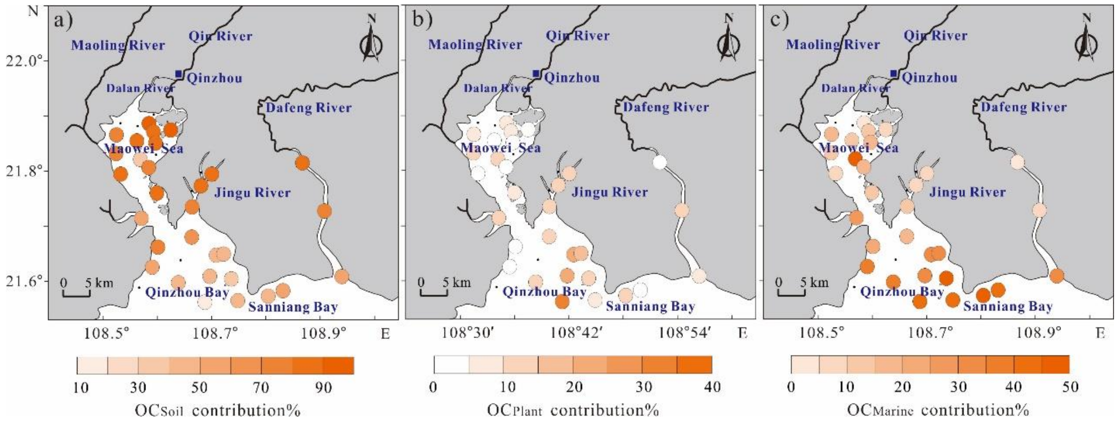


图8. 北部湾表层沉积物中基于三端元模型计算的各组份相对百分含量

a) OC_{soil}, b) OC_{plant} 和 c) OC_{marine}

茅尾海沿岸相对较高的 GDGT-0 / Crenarchaeol 比值和较高的 $\delta^{15}N$ 值指示由于人类活动的影响，向北部湾输送了大量的氮元素，可造成海水缺氧。此研究结果表明，在人类活动增强的背景下，需要采用多指标方法对河口地区沉积 OC 进行详细的源解析，以定量计算各类来源的 OC。

通过对粤西近岸沉积物岩芯（YJ Core）的综合分析，发现该区沉积物中海洋有机质的贡献为 10% ~ 47%，而陆源有机质的贡献为 53% ~ 90%。近 2000 年以来，陆源有机质整体上呈现下降的变化趋势，而海洋有机质则表现出上升的变化趋势。在 2000 cal a BP 至 1000 cal a BP 期间，有机碳埋藏速率处于相对较低的状态且未出现大的波动，而近 1000 年以来，有机碳埋藏速率显著提高（图 9）。进一步研究发现，近 1000 年以来有机碳埋藏的增加和陆源有机碳贡献的变化主要是日益增强的人类活动所致。（Huang et al., QSR, 2018）

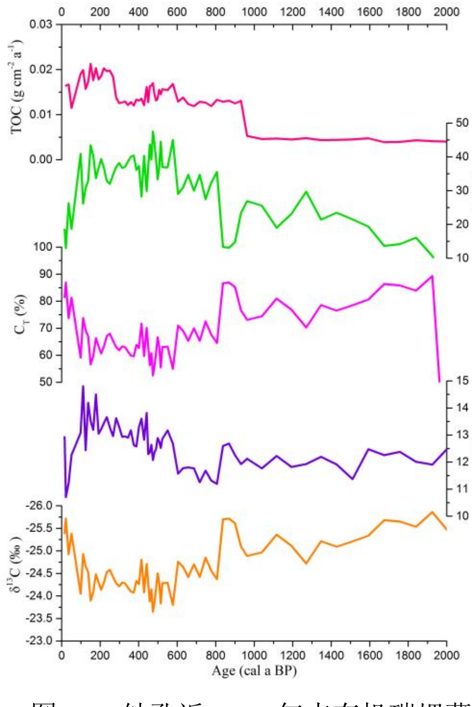


图 9. YJ 钻孔近 2000 年来有机碳埋藏

2. 预期社会经济效益

重点阐明对学科/行业产生的重要影响，对社会民生、生态环境、国家安全等的作用，以及研究成果的合作交流、转移转化和示范推广情况，人才、专利、技术标准战略在课题中的实施情况等。

课题的实施所获得的经济社会效益及相关指标主要包括学术研究、高等教育、科技人才培养与团队建设等几个方面。

在学术研究方面，围绕项目的总体研究目标，本课题聚焦我国代表性海域晚全新世以来固碳和碳埋藏的演变过程及其对全球变化和海洋酸化的响应等关键科学问题。课题研究开展以来，获取、整理、更新和发表了相关研究基础数据，同时利用传统的技术方法和本课题新建立的技术方法，对珊瑚钙化、近海海域有机碳来源辨识与埋藏演变过程，以及近海海域 SST 变化特征等方面均有了新的认识，为更系统阐述我国典型海洋生态系统固碳、储碳及其对全球变化响应的规律提供重要基础数据。课题研究成果主要是通过撰写、发表学术研究报告、论著、论文（期刊论文、学位论文和会议论文）和参加学术会议交流（口头报告和展板）等形式呈现。

在高等教育方面，由中国科学院广州地球化学研究所和香港大学深圳研究院共同承担课题。课题研究团队在教学和人才培养过程中，依托该项目为全球变化相关领域（海洋科学、环境地球化学）培养一批具有国际化视野和研究潜力的高质量毕业生。

在科技人才培养与团队建设方面， 课题骨干成员邓文峰 2017 年获得国家优秀青年科学基金资助，2018 年获得中国矿物岩石地球化学学会侯德封矿物岩石地球化学青年科学家奖，课题骨干成员叶丰晋升副研究员。参与课题研究的博士研究生陈雪霏、黄超和邹洁琼顺利通过答辩，获得博士学位，同时陈雪霏还获得了 2017 年中国科学院院长奖学金优秀奖。课题实施过程注重对青年科技人才的培养，通过广泛深入的国际合作与交流，为青年人才成长创造更有力的条件。

三、课题人员及经费投入使用情况

1．人员及经费投入情况

课题由中国科学院广州地球化学研究所和香港大学深圳研究院两家单位共同承担，共计人员投入固定工作人员 7 人，其中高级职称 6 人、中级职称 1 人。另外参加课题研究的博士研究生 6 人，硕士研究生 2 人。

课题共收到拨付专项经费 115.80 万元，全部按照项目任务书及科技部相关规定执行。课题实际支出 101.74 万元，占实际到位经费的 87.86%，其中中国科学院广州地球化学研究所共支出 87.21 万元，其中材料费 10.59 万元、测试化验加工费 18.24 万元、燃料动力费 1.5 万元、会议/差旅/国际合作交流费 20.24 万元、出版文献费 3.77 万元、劳务费 25.37 万元、间接费 7.50 万元；香港大学深圳研究院共支出 14.53 万元，其中材料费 9.73 万元、测试化验加工费 3.95 万元，间接费 0.85 万元。

2．课题经费拨付情况

按照项目预算书，课题牵头单位中国科学院广州地球化学研究所向课题参与单位香港大学深圳研究院拨付了经费 25.50 万元。

3．人员及经费实际调整情况

人员和经费未进行调整。

四、课题配套支撑条件情况

阐述各主要研究任务的配套支撑条件落实及调整变化情况。 如有调整变化，请说明调整变化对完成课题目标的影响和作用。

按照任务书规划，课题牵头单位中国科学院广州地球化学研究所向课题参与单位香港大学深圳研究院所拥有相关的技术平台全力支持课题的开展，包括：加速器质谱（ AMS）、多接收器等离子质谱（ MC-ICP-MS）、二次离子质谱（ SIMS）、气体稳定同位素质谱（ IRMS）、气相色谱仪（ GC）、高分辨气相色谱质谱联用仪（ GC-MS）、等离子体质谱（ ICP-MS）、等离子体

光谱（ ICP-AES）、 X-荧光光谱（ XRF）、元素分析仪，和多个同位素与有机前处理和化学分离工作的超净化学实验室等专业实验室，在课题的运行过程中，相关保障均得到了落实，为课题相关的研究开展提供了重要的技术支撑。

五、组织实施风险及应对情况

阐述课题在组织实施过程中，面对外部政策、组织管理、研发变化和知识产权等方面的风险以及应对措施。

课题的实施严格按照国家、科技部和依托单位的相关法律法规开展，在外部政策、组织管理和知识产权方面基本不存在什么风险。可能存在的问题已经在相关的研究协议中进行约定。

在研发方面，作为探索性的自然科学基础研究，本身就存在不确定性的风险。在某些研究方面如果出现和预期不符合的情况时，课题组成员会进行积极汇商，分析问题的可能原因，同时通过向相关专家组，适当调整研究内容。在本课题目前已经开展的研究中，尚未出现严重不符合的情况。

六、课题组织实施中的重大问题及建议

无

七、任务书中有特殊约定或其他需要说明的事项

无

附件材料：已发表论文的清单和首页

共发表论文 10 篇，SCI 收录 9 篇；其中第一标注 11 篇，第二标注 1 篇。

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AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Oceans

RESEARCH ARTICLE

10.1002/2016JC012066

Key Points:

- $\delta^{15}N$ (and $\delta^{18}O$) of NO_3^-, NH_4^+, and PN in the Pearl River Estuary were determined
- Different degrees of biological processing occurred between winter and summer
- Atmospheric NO_3^- input to the coastal PRE is significant during the winter season

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Isotope constraints on seasonal dynamics of dissolved and particulate N in the Pearl River Estuary, south China

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Abstract Isotope measurements were performed on dissolved NO_3^-, NH_4^+, and suspended particulate total N along a salinity gradient in the Pearl River Estuary (PRE) to investigate seasonal changes in main N sources and its biogeochemical processing under the influence of monsoon climate. Our data revealed that municipal sewage and remineralized soil organic N were the major sources of DIN (NO_3^- and/or NH_4^+) in freshwater during winter and summer, respectively, whereas phytoplankton biomass was a major component of PN in both seasons. In low-salinity waters (<2–3), nitrification was proved to be a significant NO_3^- source via NH_4^+ consumption, with N isotope effects of −15.3‰ in summer and −23.7‰ in winter for NH_4^+ oxidation. The contribution of nitrification to the total NO_3^- pool was smaller in summer than in winter, most likely due to freshwater dilution. At midsalinities (3–20), $\delta^{15}N$ values of PN were similar to those of NO_3^- and NH_4^+ in summer, reflecting a strong coupling between assimilation and remineralization. In winter, however, higher $\delta^{15}N_{NH4}$ but lower $\delta^{15}N_{NO3}$ than $\delta^{15}N_{PN}$ were observed, even though $\delta^{15}N_{PN}$ was similar between summer and winter. Intense sediment-water interaction and resuspension of sediments during winter appeared largely responsible for the decoupling. At high salinities, the greater enrichment in $\delta^{18}O_{NO3}$ than in $\delta^{15}N_{NO3}$ (up to 15.6‰) in winter suggests that atmospheric deposition may contribute to NO_3^- delivery during the dry season. Overall, these results show the importance of seasonal variability in physical forcing on biological N sources and its turnover processes in the highly dynamic river-dominated estuary.

1. Introduction

As a transition zone between land and ocean, estuaries are characterized by strong gradients in environmental and ecological parameters. The behavior of nitrogen (N), one of the major and often limiting nutrient for primary production, in such a zone is complex, due partially to dynamic interactions between physical, chemical, and biological processes that govern the fate of N [*Wankel et al.*, 2007; *Dähnke et al.*, 2008]. In addition, the time-varying and/or multiple N sources that are closely associated with human activities in recent decades make it more difficult to understand N behavior in an estuary.

Among many methods, stable nitrogen isotope ($\delta^{15}N$) of various pools of N, combined with the oxygen isotope of NO_3^- ($\delta^{18}O_{NO3}$), has been successfully used to reveal sources and biogeochemical processes of N, especially during the last decade due to significant progress on precise measurements of N and O isotope ratios in seawater [e.g., *Wankel et al.*, 2007; *Dähnke et al.*, 2008; *Chen et al.*, 2013; *Xue et al.*, 2014]. In general, various N sources can be differentiated by their distinct ranges of N and O isotopic values [*Kendall*, 1998, and references therein]. For example, domestic sewage and manure are more enriched in ^{15}N ($\delta^{15}N$: 10–20‰) than fertilizer and atmospheric deposition, and $\delta^{18}O$ values of atmospheric NO_3^- is generally very high (50–80‰) relative to those from other sources (<25‰). However, the applicability of this technique to N source determination in estuaries can be further complicated by biological processes, e.g., assimilation, nitrification, and denitrification, in which significant isotope fractionation may occur due to preferential uptake of lighter isotopes (^{14}N and ^{16}O) [e.g., *Kendall*, 1998; *Casciotti et al.*, 2003]. Thus, a better understanding of N cycling in a coastal marine ecosystem could be achieved by an integrated knowledge of distribution and variation of $\delta^{15}N$ (and $\delta^{18}O$) signatures of various N pools, including dissolved and particulate N.

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PAPER

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Matrix effects and mass bias caused by inorganic acids on boron isotope determination by multi-collector ICP-MS

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The influence of inorganic acids (HCl, HNO_3, and HF) on boron isotope measurement by using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has been investigated. The acid concentration is in the range of 0–0.2 M. Generally, acids can enhance B signal intensities and reduce isotopic mass bias compared to that of the same B concentration in a H_2O matrix. The signal enhancement in each acid matrix differs slightly, while B isotopic mass bias is significantly different among them, with the highest $^{11}B/^{10}B$ ratio in the HF matrix and the lowest in the HCl matrix. In HCl and HNO_3 matrices, boron isotopic mass bias reduces when the acid concentration goes up. However, such a scenario is not observed in the HF matrix. Furthermore, the $^{11}B/^{10}B$ ratio in the HF matrix is the same as that in the H_2O matrix within the studied acid concentration (up to 0.2 M). This implies that changes in mass bias and the B signal cannot be related to the same process in ICP-MS. We suggest that B signal enhancement in inorganic acids can mainly be attributed to Coulomb fission during aerosol transport towards plasma, while boron ion redistributions in the plasma caused by matrix element (*e.g.* Cl, N) ionization lead to changes in isotopic mass bias. As acids can cause considerable matrix effects and mass bias for boron, acidity match between samples and standard solutions is imperative for accurate and precise B isotope measurement by MC-ICP-MS.

Introduction

Light element boron (B) has two isotopes ^{11}B and ^{10}B, which make up approximately 80.1% and 19.9% of the total boron, respectively.[1] With a relatively large mass difference, boron isotopes experience large fractionations in nature.[2] Furthermore, the chemical and biological properties of boron make it a very promising element to study for its isotopic variations in many fields such as: (1) geochemical proxy for paleo-pH of the oceans;[3–5] (2) geochemical tracer for studying high- and low-temperature fluid-related processes;[6–8] (3) chemical weathering;[9–11] (4) tracer for anthropogenic pollution;[12,13] and (5) B behavior in higher plants.[14,15]

MC-ICP-MS has become the most common approach for boron isotope measurements in recent years,[16–25] for it is more rapid and convenient to be carried out, and possesses the ability to maintain better temporal stability. Based on this instrument, several chemical treatments have been developed for separating boron from complicated matrices (*e.g.* silicates, carbonates, and plants *etc.*).[16–25] For different chemical procedures, the final solutions involve different types of acids (*e.g.* HCl, HNO_3, or HF) or H_2O as the introduction medium for MC-ICP-MS measurements.[16–25] Introduction of inorganic acids into the isotope analyses affects the mass bias of boron in the MC-ICP-MS.[20,22,26] Measurements performed on B standard solutions with trace HCl result in ~5% reduction in mass bias.[20] Moreover, B isotopic mass bias reduces with increasing acid concentration, and this scenario is more serious for HCl than HNO_3.[22,26] Meanwhile, ^{11}B signal intensity in the HCl matrix tends to be slightly higher than that in the HNO_3 matrix.[22] Such acid effects imply that an appropriate introduction medium and acidity match between samples and standard solutions are of critical importance for accurate and precise boron isotope ratio measurements. The mechanism for this, however, is not well known yet.

Mineral acids are the most commonly used medium for introducing analytes into the ICP-MS. The type of acid and its concentration affect the analyte signal, which can be attributed to acids' effects on aerosol generation, analyte transport, or changes in excitation and ionization processes within the plasma.[27–33] For most elements, the presence of an acid matrix can lead to signal depression compared to the H_2O matrix.[27,28,34] However, using very low concentration acids could increase signals.[31] In contrast to acids' matrix effects, few studies focus on their influences on mass bias in MC-ICP-MS.[26,35] A study on Fe isotope measurement showed that HNO_3 is superior to HCl as it yielded smaller drifts of instrumental mass bias with time and better signal stability in MC-ICP-MS.[35] In addition, as

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AGU PUBLICATIONS

Paleoceanography

RESEARCH ARTICLE
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Key Points:
- Coral delta^{13}C and TSI have significant positive correlation and coupled variation over centennial scales during the MWP and LIA
- Coral delta^{13}C and TSI become decoupled during the CWP around A.D. 1900
- The decoupling of coral delta^{13}C and TSI over centennial scales was caused by the oceanic ^{13}C Suess effect

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Decoupling of coral skeletal δ^{13}C and solar irradiance over the past millennium caused by the oceanic Suess effect

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Abstract Many factors influence the seasonal changes in δ^{13}C levels in coral skeletons; consequently, the climatic and environmental significance of such changes is complicated and controversial. However, it is widely accepted that the secular declining trend of coral δ^{13}C over the past 200 years reflects the changes in the additional flux of anthropogenic CO_2 from the atmosphere into the surface oceans. Even so, the centennial-scale variations, and their significance, of coral δ^{13}C before the Industrial Revolution remain unclear. Based on an annually resolved coral δ^{13}C record from the northern South China Sea, the centennial-scale variations of coral δ^{13}C over the past millennium were studied. The coral δ^{13}C and total solar irradiance (TSI) have a significant positive Pearson correlation and coupled variation during the Medieval Warm Period and Little Ice Age, when natural forcing controlled the climate and environment. This covariation suggests that TSI controls coral δ^{13}C by affecting the photosynthetic activity of the endosymbiotic zooxanthellae over centennial timescales. However, there was a decoupling of the coral skeletal δ^{13}C and TSI during the Current Warm Period, the period in which the climate and environment became linked to anthropogenic factors. Instead, coral δ^{13}C levels have a significant Pearson correlation with both the atmospheric CO_2 concentration and δ^{13}C levels in atmospheric CO_2. The correlation between coral δ^{13}C and atmospheric CO_2 suggests that the oceanic ^{13}C Suess effect, caused by the addition of increasing amounts of anthropogenic $^{12}CO_2$ to the surface ocean, has led to the decoupling of coral δ^{13}C and TSI at the centennial scale.

1. Introduction

Scleractinian reef corals are one of the main archives of past climatic and environmental information in the tropical oceans, such as sea surface temperature (SST), sea surface salinity (SSS), and pH [*Felis and Pätzold*, 2003; *Pelejero et al.*, 2005; *Wei et al.*, 2009; *Lough*, 2010; *Liu et al.*, 2014]. However, compared with some other widely used geochemical proxies (such as Sr/Ca, Mg/Ca, and δ^{18}O), the use of coral δ^{13}C as a proxy for environmental and climatic change remains a matter for debate [*Fairbanks and Dodge*, 1979; *Swart*, 1983; *McConnaughey*, 1989, 2003; *Swart et al.*, 1996; *McConnaughey et al.*, 1997; *Grottoli*, 2002]. At the cellular scale, carbon precipitated in coral skeletons originates directly from dissolved inorganic carbon (DIC) in the extracellular calcifying fluid (ECF) that forms an interior pool beneath the calicoblastic layer of coral polyps where the calcification takes place [*Gattuso et al.*, 1999]. Inorganic carbon derived from metabolic respiration inside the coral polyps and external seawater may both contribute to the carbon in the ECF used for calcification, although the relative contribution from these two sources remains unknown [*Furla et al.*, 2000; *Al-Horani et al.*, 2003; *McConnaughey*, 2003]. Therefore, any biological or environmental factor that is able to influence the δ^{13}C levels preserved in these two sources of inorganic carbon input to the ECF would also affect δ^{13}C variations recorded in coral skeletons.

The climatic and environmental implications of seasonal variations in coral δ^{13}C levels are site specific. A number of studies have demonstrated that a wide range of different factors, such as light availability (cloud cover) and water depth [*Land et al.*, 1975; *Weber et al.*, 1976; *Fairbanks and Dodge*, 1979; *Swart et al.*, 1996; *Grottoli and Wellington*, 1999; *Heikoop et al.*, 2000; *Grottoli*, 2002; *Maier et al.*, 2003; *Rosenfeld et al.*, 2003], kinetic isotope fractionation [*McConnaughey*, 1989], the δ^{13}C of DIC in surrounding seawater [*Swart et al.*, 1996; *Watanabe et al.*, 2002; *Moyer and Grottoli*, 2011; *Deng et al.*, 2013a], feeding [*Grottoli*, 2002; *Reynaud et al.*, 2002], spawning [*Gagan et al.*, 1994, 1996], and bleaching [*Porter et al.*, 1989; *Leder et al.*, 1991; *Allison et al.*, 1996], plays important roles in the seasonal variations of coral skeletal δ^{13}C levels.

AGU PUBLICATIONS

JGR

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RESEARCH ARTICLE

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Key Points:

- The fresher/wetter LIA relative to the CWP in the western Pacific may have been caused by the retreat of the East Asian Summer Monsoon
- MCA was similar to CWP rather than much warmer than the latter in the western Pacific
- The drier/saltier MCA and CWP may be associated with the variation of the Pacific Walker Circulation

Supporting Information:

- Supporting Information S1
- Data Set S1

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A comparison of the climates of the Medieval Climate Anomaly, Little Ice Age, and Current Warm Period reconstructed using coral records from the northern South China Sea

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Abstract For the global oceans, the characteristics of high-resolution climate changes during the last millennium remain uncertain because of the limited availability of proxy data. This study reconstructs climate conditions using annually resolved coral records from the South China Sea (SCS) to provide new insights into climate change over the last millennium. The results indicate that the climate of the Medieval Climate Anomaly (MCA, AD 900–1300) was similar to that of the Current Warm Period (CWP, AD 1850-present), which contradicts previous studies. The similar warmth levels for the MCA and CWP have also been recorded in the Makassar Strait of Indonesia, which suggests that the MCA was not warmer than the CWP in the western Pacific and that this may not have been a globally uniform change. Hydrological conditions were drier/saltier during the MCA and similar to those of the CWP. The drier/saltier MCA and CWP in the western Pacific may be associated with the reduced precipitation caused by variations in the Pacific Walker Circulation. As for the Little Ice Age (LIA, AD 1550–1850), the results from this study, together with previous data from the Makassar Strait, indicate a cold and wet period compared with the CWP and the MCA in the western Pacific. The cold LIA period agrees with the timing of the Maunder sunspot minimum and is therefore associated with low solar activity. The fresher/wetter LIA in the western Pacific may have been caused by the synchronized retreat of both the East Asian Summer Monsoon and the Australian Monsoon.

1. Introduction

Global warming remains an ongoing concern for the climate change research community. To better understand the present-day climate conditions and the potential trends of future climate change, it is necessary to extend the temporal scale of investigation into the last millennium [*Jones et al*., 1998; *McGregor et al*., 2015]. The last millennium includes three distinct climate intervals: the Medieval Climate Anomaly (MCA, AD 900–1300) [*Lamb*, 1965; *Crowley and Lowery*, 2000], the Little Ice Age (LIA, AD 1550–1850) [*Robock*, 1979; *Bradley and Jones*, 1993], and the Current Warm Period (CWP, AD 1850–present) [*Wu et al*., 2012; *Fleury et al*., 2015]. The MCA and LIA are climate anomalies that were caused by natural forcing (e.g., solar variability and volcanic emissions), but the CWP is linked to anthropogenic factors (e.g., industrialization and land-use changes) [*Masson-Delmotte et al*., 2013].

A comparison of the climatic and environmental changes that occurred during these three periods is essential if we are to develop a better understanding of past climate change and future global warming. However, instrumental observations cover only the last few decades, and this is clearly insufficient to examine changes that occurred many hundreds of years ago. Therefore, we must extend the historical records by using proxy data [*Mann*, 2002]. A large number of studies based on climate proxies, derived from archives such as coral, foraminifera, mollusks, stalagmites, sediments, tree rings, ice cores, and documentary records, have been used to successfully reconstruct the characteristics of climate change during the three periods defined above [*Jones et al*., 2009]. Even so, the full characteristics of the seasonal to annual climate during

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Full length article

Wet and cold climate conditions recorded by coral geochemical proxies during the beginning of the first millennium CE in the northern South China Sea

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A B S T R A C T

The past two millennia include some distinct climate intervals, such as the Medieval Warm Period (MWP) and the Little Ice Age (LIA), which were caused by natural forcing factors, as well as the Current Warm Period (CWP) that has been linked to anthropogenic factors. Therefore, this period has been of great interest to climate change researchers. However, most studies are based on terrestrial proxy records, historical documentary data, and simulation results, and the ocean and the tropical record are very limited. The Eastern Han, Three Kingdoms, and Western Jin periods (25–316 CE) cover the beginning first millennium CE in China, and were characterized by a cold climate and frequent wars and regime changes. This study used paired Sr/Ca and $\delta^{18}O$ series recovered from a fossil coral to reconstruct the sea surface water conditions during the late Eastern Han to Western Jin periods (167–309 CE) at Wenchang, eastern Hainan Island in the northern South China Sea (SCS), to investigate climate change at this time. The long-term sea surface temperature (SST) during the study interval was 25.1 °C, which is about 1.5 °C lower than that of the CWP (26.6 °C). Compared with the average value of 0.40‰ during the CWP, the long-term average seawater $\delta^{18}O$ (−0.06‰) was more negative. These results indicate that the climate conditions during the study period were cold and wet and comparable with those of the LIA. This colder climate may have been associated with the weaker summer solar irradiance. The wet conditions were caused by the reduced northward shift of the intertropical convergence zone/monsoon rainbelt associated with the retreat of the East Asian summer monsoon. Interannual and interdecadal climate variability may also have contributed to the variations in SST and seawater $\delta^{18}O$ recorded over the study period.

1. Introduction

Global warming has become the focus of increasing concern within the climate change research community over recent years. To better understand present-day climate conditions and the potential trend of future climate change, it is important to extend the temporal scale of investigation into the last two millennia (Taira, 1980; Fritz et al., 2000; Hu et al., 2001; Booth et al., 2006; Mann, 2007; Anderson et al., 2010; Tierney et al., 2010; Vuille et al., 2012; Consortium, 2013; Wurtzel et al., 2013; Denniston et al., 2015; Donnelly et al., 2015; H. Yan et al., 2015b). The importance of the last two millennia is that they include some distinct climate intervals. For example, climate anomalies such as the Medieval Warm Period (MWP, 900–1300 CE; Lamb, 1965; Crowley and Lowery, 2000; Bradley et al., 2003) and the Little Ice Age (LIA, 1550–1850 CE; Robock, 1979; Bradley and Jones, 1993; Matthews and Briffa, 2005) are believed to have been caused by natural forcing (e.g., solar variability and volcanic emissions). However, the Current Warm Period (CWP, 1850–present CE; Wu et al., 2012; Fleury et al., 2015) is a climate anomaly that has been linked with anthropogenic factors (e.g., industrialization and land-use changes).

In China, the problem of climate change over the past two millennia has been of longstanding interest to the paleoclimatic community (e.g., Gong and Hameed, 1991; Shi et al., 1999; Zheng et al., 2001; Yang et al., 2002, 2016; Ge et al., 2003, 2004, 2011; Holmes et al., 2009; Tan et al., 2011; Hao et al., 2012, 2016; Q. Ge et al., 2013; Q.S. Ge et al., 2013; H. Yan et al., 2015a; Q. Yan et al., 2015a, 2015b). However, almost all of these studies were based

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AGU PUBLICATIONS

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RESEARCH ARTICLE

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Key Points:

- Seasonal variations in POM $\delta^{13}C$ and $\delta^{15}N$ biogeochemistry were investigated
- Seasonal dynamics of POM are governed by climate variability and extreme events
- Effect of seasonal flooding on POM cycling is apparent at mid-salinities

Supporting Information:

- Supporting Information S1
- Table S1

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Seasonal dynamics of particulate organic matter and its response to flooding in the Pearl River Estuary, China, revealed by stable isotope (δ^{13}C and δ^{15}N) analyses

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Abstract Nine cruises were conducted on a seasonal basis from 2013 to 2015 to investigate the spatial distribution and seasonal variability of $\delta^{13}C$ and $\delta^{15}N$ in particulate organic matter (POM), and its response to flooding in the Pearl River Estuary (PRE), south China. Our study reveals highly variable isotope ratios between seasons in this subtropical estuary, following seasonal climatic and hydrological cycles. Wet seasons had more isotopically depleted $\delta^{13}C$ values, indicating the dominance of terrestrial and freshwater algae POM, whereas the contribution from marine phytoplankton (16%–59%) was higher during the dry seasons. In contrast, $\delta^{15}N$ exhibited a sharp increase (up to 17.6‰) at low salinities (0–5) during high flow seasons. This was consistent with high NO_3^- concentrations, reflecting phytoplankton and bacteria assimilation of $\delta^{15}N$ enriched-NO_3^- as well as notable isotope fractionation during microbial mineralization. There was little annual variability in $\delta^{13}C$ over the 2 year period; however, particulate nitrogen (PN) exhibited lower concentrations but more enriched isotope values in 2015 than in 2014. This can be best explained by temperature-modulated biological processing of particulate organic nitrogen, partially due to different biogeochemical responses during normal (2014) and strong El Niño (2015) years. After flooding in June 2015, terrestrial organic matter and freshwater phytoplankton were the major components of POM within the estuary and shelf areas, whereas marine phytoplankton was the dominant component in the adjacent coastal waters with mid-salinities ($10 < S < 20$), as revealed by a phytoplankton bloom (>10 μg L^{-1}) and $\delta^{13}C$-enriched but $\delta^{15}N$-depleted POM.

1. Introduction

Estuaries are important zones for the production, transformation and removal of organic matter, both in dissolved and particulate form [e.g., *Hedges et al.*, 1997; *Canuel and Hardison*, 2016]. Organic matter (OM) in estuaries is derived from autochthonous (in situ production) and allochthonous (e.g., terrestrial soils and urban sewage) sources. As compared to the dissolved organic matter (DOM), however, particulate organic matter (POM) is more bioavailable to organisms. Rivers export an estimated 0.14 Gt (10^{15} g) of particulate carbon and 0.02 Gt of particulate nitrogen (PN) to marine systems each year, of which 35% is in a labile form that is easily degraded by microbes [*Meybeck*, 1982; *Hedges et al.*, 1997; *Seitzinger et al.*, 2002]. Despite high OM loads, OM pools in the ocean have only minor terrestrial signatures based on measurements of carbon (C) isotopes and biomarkers (e.g., lignin phenols) [*Hedges et al.*, 1997]. Therefore, it is essential to understand the origin, distribution and fate of POM that sustains the high levels of biological activity in estuaries, and which has important implications for regional and global carbon and nitrogen (N) cycles.

It is difficult to determine the origin of POM in estuaries because POM is supplied from multiple sources that change over time, including riverine inputs (e.g., terrestrial soils, C3 and C4 land plants) and in situ production by phytoplankton and bacteria as well as local sources from urban runoff and sewage effluent. Moreover, POM usually exhibits nonconservative behavior due to a number of mechanisms, including strong internal biogeochemical processes (e.g., phytoplankton production and bacterial respiration) and complex sedimentary dynamics during estuarine mixing. Thus, elucidating the sources and turnover of POM in estuaries is a challenging but necessary step toward effective estuarine management.

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Northern South China Sea SST changes over the last two millennia and possible linkage with solar irradiance

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High-resolution surface temperature records over the last two millennia are crucial to understanding the forcing and response mechanism of Earth's climate. Here we report a bidecadal-resolution sea surface temperature (SST) record based on long-chain alkenones in a gravity sediment core retrieved from the northern South China Sea. SST values varied between 26.7 and 27.5 °C, with a total variability ~1 °C over the last 2000 years. The general SST variation pattern matches well with total solar irradiance (TSI) changes. Relatively warm period between 800 and 1400 AD and cool period 1400-1850 AD could be identified, in agreement with the commonly defined periods of Medieval Warm Period and Little Ice Age. Within chronological uncertainty, notable short cooling events at 640-670 AD, 1030-1080 AD, 1260-1280 AD and 1420-1450 AD, coincide with large volcanic eruption events. The general coincidence of SST changes with TSI and volcanic eruption events suggests strong impact of external forcing on sea surface conditions in the studied area. In addition to the direct TSI changes, volcanic eruptions might have induced oceanic and atmospheric circulation adjustments which might be responsible for the short cooling events as revealed in the alkenone-SST record.

1. Introduction

Earth's surface temperature changes over the last two millennia have been crucial to understanding current global warming issues, and reconstructed at regional, continental, and global scales using proxy data from various archives (Mann, 2007). Many of the high-resolution data have been used to produce a global array of climate as part of the “2k Network” in the IGBP Past Global Changes (PAGES) project (Ljungqvist et al., 2012; Mann, 2007, 2008; Mann and Jones, 2003; Neukom and Gergis, 2012; Neukom et al., 2014; PAGES 2k Consortium, 2013; PAGES Ocean2k Working Group, 2012), as well as in the 4th and 5th IPCC Assessment Report. Now some concepts, such as the Medieval Warm Period (WMP) and Little Ice Age (LIA), are widely accepted as the common climatic features over the last two millennia. However, comparisons among high-resolution temperature records derived from different proxies show distinctly spatial discrepancies, particularly between land and ocean, northern and southern hemispheres (PAGES 2k Consortium, 2013). Indeed, even the most prominent epochs during the last two millennia, the WMP and LIA, do not have specific definitions in terms of their time span, suggesting no global synchronous temperature patterns (Mann, 2007; PAGES 2k Consortium, 2013). Studies on those discrepancies would be helpful to deciphering climatic forcing-response processes, which however requires adequate coverage of high-resolution temperature reconstructions from various environment settings.

The mostly used annually-resolved proxy data are from continental archives, such as tree rings (Anchukaitis et al., 2012; Liu et al., 2009; Wilson et al., 2016) and ice cores (Dahljensen et al., 1998; Kobashi et al., 2011). Marine archives like corals and giant clams could produce annual-resolution paleotemperatures, which are often too short in most cases, and therefore usually concatenated to produce longer temperature records at millennial scale

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雷艳，胡建芳，向荣，等.末次盛冰期以来南海北部神狐海域沉积有机质的组成特征及其古气候/环境意义[J]. 海洋学报，2017，39(11):75－84，doi:10.3969/j.issn.0253-4193.2017.11.007
Lei Yan，Hu Jianfang，Xiang Rong，et al. Composition of sedimentary organic matter in Shenhu，northern South China Sea since the Last Glacial Maximum and its implication for paleoclimate[J]. Haiyang Xuebao，2017，39(11):75－84，doi:10.3969/j.issn.0253-4193.2017.11.007

末次盛冰期以来南海北部神狐海域沉积有机质的组成特征及其古气候/环境意义

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摘要：通过对两根沉积柱 GHE27L 和 GHE24L 的总有机碳(TOC)、总氮(TN)、C/N 比值及稳定碳同位素($\delta^{13}C_{org}$)的分析，本文探讨了 21.1 ka BP 以来南海北部陆坡神狐海域沉积有机质的组成特征及可能的古气候/环境信息。沉积柱 GHE27L 的 TOC 含量、TN 含量、C/N 比值及 $\delta^{13}C_{org}$ 值分别为 0.53%～1.81%，0.07%～0.18%，8.2～16.0 和－23.6‰～－20.3‰。沉积柱 GHE24L 各参数则分布为 0.45%～1.65%，0.09%～0.24%，5.3～12.2 和－22.6‰～－20.4‰。沉积柱总体有机质的剖面变化显示，末次盛冰期以来南海北部沉积有机质具有海洋和陆地混合来源，但以海洋有机质来源为主。冰期陆源有机质对总有机质的相对贡献比全新世高。末次盛冰期南海北部气候相对干旱，C_4 植被发育。全新世夏季风增强、降雨增多。自 2.0 ka BP 以来，人类活动对南海北部海洋初级生产力产生一定的影响。

关键词：南海北部；末次盛冰期；稳定碳同位素；古气候
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1　引言

南海是西太平洋最大的边缘海，其宽阔平缓的陆架以及特殊的地理位置使南海在冰期旋回过程中对气候变化具有放大效应[1－3]。此外，南海的碳酸盐补偿深度(CCD)相对于其他边缘海更深[1]，且陆坡沉积物供应充足[2]，沉积速率高[4－5]，是研究高分辨率古环境、古气候变迁的理想场所。前人在南海已经做了大量的古海洋学研究工作，涉及的研究领域包括地球化学[2,6－7]、磁学[5,8]和矿物学[9－10]等，其中有机地球化学的研究内容主要是重建海洋表层水体温度(SST)[11－13]，而关于末次冰期以来南海北部陆坡沉积有机质的研究还不多[2,14]，不利于探讨该地区冰期/间冰期旋回有机碳(OC)埋藏的变化特征及影响因素。

本文以取自南海北部陆坡神狐海域的两根沉积

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REPORT

Super instrumental El Niño events recorded by a *Porites* coral from the South China Sea

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Abstract The 2–7-year periodicities recorded in fossil coral records have been widely used to identify paleo-El Niño events. However, the reliability of this approach in the South China Sea (SCS) has not been assessed in detail. Therefore, this paper presents monthly resolution geochemical records covering the period 1978–2015 obtained from a *Porites* coral recovered from the SCS to test the reliability of this method. The results suggest that the SCS coral reliably recorded local seawater conditions and the super El Niño events that occurred over the past 3 decades, but does not appear to have been sensitive enough to record all the other El Niños. In detail, the Sr/Ca series distinctly documents only the two super El Niños of 1997–1998 and 2014–2016 as obvious low values, but does not match the Oceanic Niño Index well. The super El Niño of 1982–1983 was identified by the growth hiatus caused by the coral bleaching and subsequent death of the coral. Three distinct stepwise variations occur in the $\delta^{13}C$ series that are coincident with the three super El Niños, which may be related to a substantial decline in endosymbiotic zooxanthellae density caused by the increase in temperature during an El Niño or the selective utilization of different zooxanthellaes that was required to survive in the extreme environment. The increase in rainfall and temperatures over the SCS during El Niños counteracts the effects on seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$) and salinity; consequently, coral $\Delta\delta^{18}O$ series can be used as a proxy for $\delta^{18}O_{sw}$ and salinity, but are not appropriate for identifying El Niño activity. The findings presented here suggest that the method to identify paleo-El Niño activity based on the 2–7-year periodicities preserved in the SCS coral records might not be reliable, because the SCS is on the edge of El Niño anomalies due to its great distance from the central equatorial Pacific and the imprints of weak and medium strength El Niño events may not be recorded by the corals there.

Keywords El Niño · Coral · Sr/Ca · $\delta^{18}O$ · $\delta^{13}C$ · South China Sea

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Introduction

The El Niño–Southern Oscillation (ENSO) is the largest and strongest source of interannual climate variability, with a major impact on temperature and precipitation in the tropical Pacific and even on global climatic patterns, and profound global ecological, social, and economic consequences (Cane 1986). Under the background of global warming, El Niño events have become more severe and

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Full length article

A geochemical record of the link between chemical weathering and the East Asian summer monsoon during the late Holocene preserved in lacustrine sediments from Poyang Lake, central China

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ABSTRACT

This paper presents relatively high-resolution geochemical records spanning the past 4000 cal yr BP obtained from the lacustrine sediments of Poyang Lake in central China. The variations in the intensity of the East Asian summer monsoon (EASM) are traced using the K/Na, Ti/Na, Al/K, kaolinite/illite and clay/feldspar ratios, together with the chemical index of alteration (CIA), as indicators of chemical weathering. During the last 4000 years, the proxy records of chemical weathering from Poyang Lake exhibit an overall enhanced trend, consistent with regional hydrological changes in previous independent records. Further comparisons and analyses demonstrate that regional moisture variations in central China is inversely correlated with the EASM intensity, with weak EASM generating high precipitation in central China. Our data reveal three intervals of dramatically dry climatic conditions (i.e., ca. 4000–3200 cal yr BP, ca. 2800–2400 cal yr BP, and ca. 500–200 cal yr BP). A period of weak chemical weathering, related to cold and dry climatic conditions, occurred during the Little Ice Age (LIA), whereas more intense chemical weathering, reflecting warm and humid climatic conditions, was recorded during the Medieval Warm Period (MWP). Besides, an intensification of chemical weathering in Poyang Lake during the late Holocene agrees well with strong ENSO activity, suggesting that moisture variations in central China may be predominantly driven by ENSO variability.

1. Introduction

The Asian monsoon system is an integral part of the global climatic system, and a deeper knowledge of it will contribute to a better understanding of global atmospheric circulation and climate change. Understanding the nature of the variability within the Asian monsoon during the Holocene is critical for our understanding of present climatic conditions and for predicting future climate change (Yao et al., 2015). The historical evolution of the East Asian summer monsoon (EASM) has been widely studied using various geological archives, including loess–paleosol sequences, marine and lacustrine sediments, peat deposits, and stalagmites (Wang et al., 2005; Wei et al., 2006; Cosford et al., 2008; Liu et al., 2013; Mu et al., 2016; Zhang et al., 2016a; Fan et al., 2017; Goldsmith et al., 2017; Li et al., 2017; Wu et al., 2017; Zhu et al., 2017). However, spatial patterns in the long-term variations in the Asian summer monsoon remain debated. For example, An et al. (2000) proposed a time-transgressive Holocene optimum in the East Asian monsoon region, with an apparent southward-retreating trend. However, evidences from the previous reviews (Zhao et al., 2009; Zhang et al., 2011) and stalagmite $\delta^{18}O$ records (Dykoski et al., 2005; Dong et al., 2010) suggested a broadly synchronous climatic history across the monsoon region. Nevertheless, an updated perspective of the EASM diachronity presented by Zhou et al. (2016) deemed that the onset of the Holocene optimum took place at different times in different regions of China, with a marked northward shift. Recently, Rao et al. (2016a,b) reported that the spatial pattern of humidity variation in East China exhibited the "− + −" mode during the early-Holocene and late-Holocene, but the "+ − +" mode during the mid-Holocene. Interestedly, results from modern observations demonstrated that summer precipitation exhibited spatial differences in the Asian monsoon region (Zhu, 1934; Zhu and Wang, 2002; Zhao and Zhou, 2006; Zhou et al., 2009; Zhao et al., 2010). Such spatial pattern is described colloquially as "flood in the south and drought in the north", or "drought in the south and flood in the north". In addition, based on the dataset of 740 surface stations for recent 54 years (1951–2004), Ding et al. (2008) suggested that the spatial pattern of the inter-decadal variability of summer precipitation in monsoonal China is mainly characterized by two meridional modes: the dipole pattern and the positive-negative-

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1367-9120/

附表 2

国家重点研发计划课题中期执行情况信息表

一、课题基本情况

<table>
<tr><td>课题名称</td><td colspan="3">海洋典型生态系统碳库变动与气候变化和海洋酸化的关联</td></tr>
<tr><td>课题编号</td><td colspan="3">2016YFA0601204</td></tr>
<tr><td>密级</td><td colspan="3">■公开 □秘密 □机密 □绝密</td></tr>
<tr><td>课题承担单位</td><td>中国科学院广州地球化学研</td><td>单位性质</td><td>事业型研究单位</td></tr>
<tr><td>课题负责人</td><td>韦刚健</td><td>参加单位数</td><td>2</td></tr>
<tr><td>课题类型</td><td colspan="3">■基础前沿 □重大共性关键技术 □应用示范 □其他</td></tr>
<tr><td>课题进展情况</td><td colspan="3">■按计划进行 □进度超前 □进度拖延 □进度停顿
□申请调整或撤消</td></tr>
<tr><td>与项目内其他课题/
应用单位/企业合作情况</td><td colspan="3">■信息交流 □技术咨询 □研发合作 □成果转化 □实现产业化</td></tr>
<tr><td>课题实施情况</td><td colspan="3">■达到预期指标 □超过预期指标 □未达到预期指标</td></tr>
</table>

二、课题中期经费及人员投入情况（经费单位：万元）

<table>
<tr><td colspan="4">总经费</td><td colspan="5">专项经费</td><td colspan="3">自筹经费</td></tr>
<tr><td colspan="2">预算数</td><td colspan="2">到位数</td><td>预算数</td><td>到位数</td><td colspan="2">是否按计划拨付课题承担单位</td><td>执行数</td><td>预算数</td><td>到位数</td><td>执行数</td></tr>
<tr><td colspan="2">386</td><td colspan="2">115.8</td><td>386</td><td>115.8</td><td colspan="2">是</td><td>101.74</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>总人数</td><td colspan="2">其中女性</td><td>高级职称</td><td>中级职称</td><td>初职称级</td><td>其他人员</td><td>博士</td><td>硕士</td><td>学士</td><td>其他学历</td><td>总人年</td></tr>
<tr><td>12</td><td colspan="2">3</td><td>6</td><td>2</td><td>0</td><td>0</td><td>7</td><td>1</td><td>4</td><td>0</td><td>11</td></tr>
<tr><td rowspan="2">人才情况</td><td colspan="2">院士</td><td>千人计划</td><td>万人计划</td><td>百人计划</td><td>长江学者</td><td>青年长江学者</td><td>杰青</td><td>优青</td><td colspan="2">海外引进人才数</td></tr>
<tr><td colspan="2">0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>1</td><td>1</td><td colspan="2">0</td></tr>
</table>

三、课题中期目标及考核指标完成情况

课题目标	成果名称	成果类型	考核指标				考核方式（方法）及评价手段	中期实际完成指标状态
			指标名称	立项时已有指标值/状态	中期指标值/状态	完成时指标值/状态		
通过选取南海北部陆架和海盆高沉积速率岩芯和持续生长超过200 年的造礁珊瑚岩芯，重建陆架、海盆近2000年以来，和珊瑚礁工业革命以来年分辨率的气候变化、海洋酸化进程和这些典型生态系统碳库变动过程，从历史记录中了解碳库变动与气候变化、海洋酸化之间的关联，揭示自然过程和人类活动的多重胁迫下（如全球变暖、海洋酸化）碳库变动的机制，为评估气候变化和海洋酸化对海洋储碳的影响提供理论依据。	3. 海洋生态系统碳库变动和气候变化与海洋酸化的关联	■新理论 □新原理 □新产品 □新技术 ■新方法 □关键部件 □数据库 □软件 □应用解决方案 □实验装置/系统 □临床指南/规范 □工程工艺 □标准 ■论文 □发明专利 □其他________	指标 3.1海洋生态系统碳库变动和气候变化与海洋酸化的关联。	沉积物碳埋藏研究方法较多，但缺少对碳来源的准确判别，而珊瑚礁碳库变动的量化研究还比较欠缺； 全球变化背景下碳库的变动已有相关研究，但对其关联性认识不足。	建立有机碳来源辨识的方法；获取陆架区近2000 年来温度和有机碳埋藏记录；获取珊瑚礁近 200 年来钙化率、温度和海水 pH 记录和Mo 等生源要素同位素记录； 发表论文 6-8篇	建立准确估算陆架、海盆和珊瑚礁碳库变动的方法，获得南海代表海域海洋酸化记录，提高对碳库变动和气候变化、海洋酸化之间内在关联的认识。 发表论文15-20篇。	论文 新方法	利用综合的有机地球化学指标辨识了台湾海峡与钦州湾等代表性近岸海域现代沉积物中埋藏有机碳的来源及陆源贡献；在南海北部陆架、粤西近岸海域与闽浙泥质区等重建了近 2000 年来高分辨率表层海水温度（SST）记录，探讨了不同区域 SST 变化的控制机制；重建了粤西近岸海域近2000 年来高分辨率有机碳埋藏的记录，定量区分了陆源和海洋有机碳的贡献，揭示了近 2000 年以来人类活动对近岸有机碳埋藏的影响； 系统测量了海南岛东部和西沙七连屿十多个近现代珊瑚的钙化率，了解相关海域近 200 年来珊瑚钙化率变化及其对气候变化/海洋酸化的响应；重建了海南岛东部海域近 2000 年来重要特征时段年分辨率的 SST 和碳同位素组成的变化，探讨了珊瑚钙化（无机碳固定）对气候变化的响应；探讨了珊瑚 Mo 同位素对珊瑚生物活动变化的响应机制； 已发表论文 10 篇（项目资助第一标注 9 篇，第二标注 1 篇），其中国际 SCI 论文 9 篇。

科技报告考核指标	序号	报告类型	数量	提交时间	公开类别及时限	是否按计划提交科技报告
	1	年度科技报告	2	2016-2017 年 12 月	延期 3 年公开	是
	2	中期科技报告	1	2018 年 7 月	延期 3 年公开	是

其他目标与考核指标完成情况	除课题中期计划目标和指标外，任务书中设定的年度研究计划也均顺利完成，主要的研究工作如下： 1） 海洋观测与采样航次 2016 年 7 月 13 日--7 月 26 日参加了项目组织实施的“台湾海峡夏季预研航次”第一航段，历时 14 天。本课题系统采集了台湾海峡表层沉积物 32 个，并在其中 2 个站位获取了沉积岩芯样品，以构建和校验代表性近岸海域有机地球化学指标与现代沉积物中埋藏有机碳来源和陆源贡献之间的关联。 2017 年 8 月 12 日--8 月 26 日参加了“2017 南海东北部及吕宋海峡共享航次”第三航段，历时 15 天。在 6 个站位开展柱状沉积物取样，在其中 2 个站位获取了较长的沉积岩芯样品，为进一步开展南海海盆近 2000 年来沉积碳库变动与气候变化、海洋酸化的关联提供了良好载体； 2017 年 8 月 2 日--8 月 20 日课题独立组织了“2017 海南珊瑚礁野外考察采样”航次，历时 19 天。重点考察海南省琼海市青葛港到文昌市冯家湾等海域，并同时对课题自主研制的水下液压钻机进行海试。本航次共完成 31 根珊瑚岩芯的钻取，为研究工业革命前后珊瑚礁碳库对气候变化和海洋酸化的响应规律提供了丰富素材。 2） 实验室分析测试 课题对已经获取的研究样品全面展开实验室分析测试工作，获取了大量的元素和同位素地球化学数据。一些重要的分析测试工作包括： **年代学分析**：完成了粤西近岸（YJ）和 S7A 和 8 站位沉积物岩芯的 14C 年代学测试，累计 ^{14}C 测试样品 30 个；对已采集的珊瑚岩芯开展 U-Th 年代学分析，累计完成测试样品 65 个，建立起约 50 个珊瑚岩芯的年代学框架； **生物标志化合物分析**：对表层及岩芯沉积物样品开展了常规有机碳氮含量和同位素分析，以及包括长链烯酮、GDGT 等生物标志化合物分析，累计分析样品量超过 500 个； **沉积物综合地球化学分析**：完成了粤西近岸岩芯（YJ）沉积物的粒度、环境磁学参数、矿物组成、主微量元素等综合地球化学同步分析，累计样品量 207 个。

四、课题中期实现经济社会效益情况

<table>
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<tr><td colspan="2">申请发明专利项数</td><td>0</td><td colspan="2">获得授权发明专利项数</td><td>0</td></tr>
<tr><td colspan="2">其中国外</td><td>0</td><td colspan="2">其中国外</td><td>0</td></tr>
<tr><td colspan="2">申请其他各类专利项数</td><td>0</td><td colspan="2">获得授权其他各类专利项数</td><td>0</td></tr>
<tr><td colspan="2">其中国外</td><td>0</td><td colspan="2">其中国外</td><td>0</td></tr>
<tr><td colspan="2">毕业研究生数</td><td>5</td><td colspan="2">发表科技论文数</td><td>10</td></tr>
<tr><td colspan="2">其中博士生</td><td>3</td><td colspan="2">其中 SCI、EI 收录数</td><td>9</td></tr>
<tr><td colspan="2">取得软件著作权数</td><td>0</td><td colspan="2">出版专著数</td><td>0</td></tr>
<tr><td colspan="2">取得的新理论、新原理数</td><td>0</td><td colspan="2">取得的新技术、新工艺、新方法数</td><td>0</td></tr>
<tr><td colspan="2">取得的新产品、新品种、新装置 数</td><td>0</td><td colspan="2">示范、推广面积数（亩）</td><td>0</td></tr>
<tr><td colspan="2">获得新药（医疗器械）证书数、临床批件数</td><td>0</td><td colspan="2">获得临床指南、规范数</td><td>0</td></tr>
<tr><td colspan="2">新建生产线数</td><td>0</td><td colspan="2">新建示范工程数</td><td>0</td></tr>
<tr><td colspan="2">培训农民数</td><td>0</td><td colspan="2">培训技术人员数</td><td>0</td></tr>
<tr><td colspan="2">获得国家级科技奖励数</td><td>0</td><td colspan="2">获得省部级科技奖励数</td><td>0</td></tr>
<tr><td>成果转让数（项）</td><td>0</td><td>成果创产值(万)</td><td>0</td><td>成果创税收(万)</td><td>0</td></tr>
<tr><td>成果转让收入(万)</td><td>0</td><td>成果创利润(万)</td><td>0</td><td>成果创出口额(万)</td><td>0</td></tr>
</table>