

2001—2010 年生物地球化学研究进展与展望

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摘要: 阐述了 21 世纪第一个十年生物地球化学领域的重要研究进展和未来可能的重点发展方向。在近代陆-海系统碳循环的库和通量上已经取得了重要进展, 并发现了一些参与氮、硫循环新的微生物功能群。阐述了显生宙生物大灭绝期间碳循环异常的特点及其可能的原因, 但对氮、硫循环的了解比较薄弱。地球早期的碳、硫循环与生命起源、大气和海洋水化学条件的关系已经取得重要认识。生物地球化学过程可以通过生态毒理, 以及大气成分和海洋水化学条件的改变影响生命系统。微生物地球化学功能的微区、原位、痕量示踪等技术得到快速发展。未来将加强地质历史时期碳、氮、硫循环的定量分析以及空间变化的研究, 各种元素循环之间的相互关系及其界面过程、极端环境的生物地球化学过程将进一步受到重视。生命科学领域重要技术的引入将提升生物地球化学过程的研究。

关键词: 元素循环; 全球变化; 古海洋; 地质微生物; 生命起源; 生物大灭绝

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An Overview on Biogeochemistry During the Decade of 2001 to 2010

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Abstract: The significant achievements and future research orientation of biogeochemistry during the decade of 2001 to 2010 are briefly reviewed. Some carbon pools and related flux have been quantified in modern marine/ocean and land ecosystems. New microbial functional groups involved in sulfur and nitrogen cycles of modern ecosystems have been identified. The features and the possible causes of the abnormal carbon cycle occurring during the biotic crisis in Phanerozoic have been deciphered but the biogeochemical cycles of sulfur and nitrogen need more investigation. The relationship of carbon and sulfur cycles of the early Earth with life origins, atmospheric and oceanic chemistry conditions has been understood. Biogeochemical impacts on ecosystems via the chemical substances, climatic and oceanic changes are reviewed concerning both the modern and the ancient times. Some biogeochemical techniques including geotraces, metagenomics, micro-scale and in-situ analyses are particularly introduced in current biogeochemical studies. The quantification and spatial variations of the elemental cycles need further investigations in the future. The biogeochemical processes in some extreme environments and the various interfaces as well as the relationship among different elemental cycles demand more attentions. Introduction of new techniques in life science will further improve investigations of biogeochemical processes.

Key words: elemental cycles; global change; paleoceanography; geomicrobes; origin of life; biotic mass extinction

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生物地球化学在地球系统科学中具有重要地位,是研究地球表层系统的重要分支学科之一,在全球气候变化、生态环境演变及生态系统类群演替中均具有关键作用。2011 年,我们在《2011~2020 年我国学科发展战略研究报告》中简述了本学科的一些主要进展。2012 年,我们阐述了一些地质微生物功能群通过碳、氮、硫等元素的生物地球化学循环对地球环境的作用^[1]。在这里,我们将重点从近代海-陆系统的元素生物地球化学循环、重大地质突变期的生物地球化学循环异常、极端环境的生物地球化学过程、生物地球化学过程对生命系统的影响,以及生物地球化学研究的新技术新方法等方面概括最近十年本学科所取得的重要进展。

1 近代海-陆系统的元素生物地球化学循环

碳、氮、硫等生源要素的迁移转化过程是生物地球化学研究的核心内容。近代环境的元素地球化学循环在碳循环的库(源、汇)和流(通量)上取得了突出的进展,在参与氮、硫等循环的微生物功能群方面也获得了系列重要的新认识。国际重要期刊《Global Biogeochemical cycles》主要刊登了海-陆系统的生物地球化学论文,其影响力在地球化学乃至地球科学领域均是很高的。

1.1 碳循环

联系复杂的海洋生物-物理化学过程的碳循环对海洋生态系统运转和全球气候变化有重要的影响。旨在研究全球变化的一些研究计划 JGOFS、SOLAS 以及 IMBER 的实施,极大促进了海洋碳循环生物地球化学研究的深入^[2~6]。海洋固碳主要是通过生物泵和溶解度泵来实现的^[6]。溶解度泵受控于表层海水温度及海水混合等因素。生物固碳主要受控于浮游植物的初级生产过程和初级生产力水平。同时,它还取决于生源颗粒物向真光层之外传输的海洋生物泵的强度和效率、输入的有机物质在海水次表层被再矿化为无机碳并部分被埋藏的过程,以及钙化浮游植物如颗石藻外壳 CaCO_3 的沉降增加海水表层稳态 CO_2 浓度,从而促进 CO_2 向大气的释放等过程^[4~6]。“微型生物碳泵”理论框架的提出反映了微生物对储碳的重要性^[7]。海洋碳源/汇是动态变化的,即同一海域碳源/汇的性质及强度宏观上会随气象要素、海况、海洋生态环境等的季节变化而变化。目前,由于受观察手段等的限制,所获得的海洋碳源/汇具有很大的不确定性^[3,5,6]。

海-气界面的碳迁移过程是海洋碳循环的重要

过程,因为不管是生物固碳(生物泵)还是溶解碳(溶解度泵),最终都体现在碳是从海水向大气释放(源),还是大气中的碳向海水中溶解(汇),即通过海-气界面的碳通量来体现。大洋的碳源汇过程在 1990~2000 年已获得了系统认识,所以,陆架边缘海的海-气界面碳通量就成了最近十年来海洋碳源汇过程的焦点^[3,5]。中国近海(包括渤海、黄海、东海和南海)在总体上是大气 CO_2 的汇,年吸收大约千万吨级碳^[5,6,8],但在南海部分海域^[9~11]以及部分浅海海域如胶州湾^[6,12]、长江口^[6,12~14]等是大气 CO_2 的源。中国近海海-气界面碳通量在整体上主要受控于表层海水的温度以及气象条件(主要是风),但在春季受控于浮游植物的初级生产过程^[6]。细菌在碳的生产过程中具有重要的作用^[15],东海春季和秋季平均细菌生产力相当于浮游植物初级生产力的 23%,其高值区与初级生产力和叶绿素 a 高值区一致。碳在东海陆架垂直转移主要依赖于 POC,在表层水体占总碳的 98% 以上,在底层占 68% 以上^[5]。

尽管近海碳的生物地球化学过程取得了重要进展,但近期的研究发现,深海碳循环和海底深部生物圈在某种程度是耦合的,海底及其洋壳生物圈也可以显著地影响海洋碳循环^[16]。这使海洋系统碳的生物地球化学过程变得异常复杂。传统上认为,深海中的溶解有机质(DOC)主要来自海洋表层的光合作用产物。McCarthy 等^[17]根据海底热液喷口处 DOC 的 $\delta^{13}\text{C}$ (比海水 $\delta^{13}\text{C}_{\text{DOC}}$ 偏负)和 $\delta^{14}\text{C}$ (比海水 $\delta^{14}\text{C}_{\text{DOC}}$ 明显偏老)特征,认为这些 DOC 来自洋壳中生存的化能自养微生物。它们利用洋壳流体中的溶解无机碳,并向深海释放 DOC。类似的过程也存在于海底水合物富集区^[18]。甲烷氧化菌在将 CH_4 氧化成 CO_2 的同时,向海水中释放了大量的 DOC,参与深海的碳循环。研究还发现, CH_4 厌氧氧化过程(AOM)紧密调节着海底 CH_4 的生物地球化学循环,缓解了 CH_4 向海水和大气中的释放^[20,21]。AOM 过程可以发生于热液喷口、冷泉和水合物界面以及正常海底沉积物中^[22],主要是由甲烷厌氧氧化古菌和硫酸盐还原细菌共同完成。由于尚未得到甲烷厌氧氧化古菌的纯培养,甲烷厌氧氧化的机制问题还存在争议^[23]。海底甲烷厌氧氧化古菌通常被分为 3 类(ANME-1, ANME-2 和 ANME-3),均具有特征的脂类标志物^[24,25]。

近二十年来,研究发现全球森林起到碳汇的作用,可固定碳 $(1.1 \pm 0.8) \times 10^{12} \text{ kg/a}$ ^[26],植树造林活动对增加碳汇和碳减排具有重要意义^[27]。中国

陆地系统固碳能力为 $(0.19 \sim 0.26) \times 10^{12} \text{ kg/a}$ [28], 虽比美国低, 但与欧洲的水平相当。研究显示, 陆地生态系统的碳循环受气候影响很大。北半球生态系统碳储量的变化受到秋季温度的影响 [29]。末次冰盛期结束时永久冻土区低活性碳库的消失是大气 CO_2 浓度上升的原因 [30], 而末次冰盛期以来北半球泥炭地释放 CH_4 与全球气候变化存在关联 [31, 32]。在酸性泥炭地, 人们证实了甲烷氧化细菌与泥炭藓存在互惠关系 [33]。甲烷氧化菌生活于泥炭藓的细胞中, 将 CH_4 氧化成 CO_2 , 供泥炭藓光合作用使用。这种互惠行为不仅存在于全球泥炭藓 [34], 也发生于西伯利亚苔原沉水生长的灰藓中 [35]。据估计, 泥炭藓利用来自 CH_4 氧化的碳可达光合作用固定总碳的 30% [34, 36], 从而减少了 CH_4 向大气释放。

1.2 氮循环

氮循环主要涉及固氮作用、硝化作用和反硝化作用 3 个过程。这些过程都由微生物参与完成, 因而氮循环的重要进展是新微生物功能群的不断发现。主要固氮微生物类群随环境的不同而不同。海洋中主要固氮细菌为蓝细菌 (*Trichodesmium*), 而在高纬度和深水等寡营养海区新发现的一些单细胞蓝细菌 (*Crocospaera watsonii*) 可能与 *Trichodesmium* 具有同等重要的固氮作用 [37, 38]。在 CH_4 厌氧氧化区域, 嗜甲烷古菌 ANME-2 被证明能够进行固氮作用而为硫酸盐还原细菌提供氮源, 且其 CH_4 氧化速率在固氮时不受影响, 但其生长速率减慢, 使 AOM 区域的碳-氮-硫循环建立起紧密的联系 [39]。

长期以来, 硝化作用过程被认为主要由硝化细菌单独完成。然而, 在现代土壤中, 氨氧化古菌的数量要明显高于氨氧化细菌 [40]。在包括海洋水柱及沉积物、湖泊、喀斯特洞穴在内的大部分地质环境中, 氨氧化古菌也都占有重要地位 [41, 42]。氨氧化古菌可能具有两种固碳机制, 包括 3-羟基丙酸/4-羟基丁酸循环和氧化型三羧酸循环 [23, 43]。它们可以通过吸收 HCO_3^- 或 CO_2 进行自养 [44, 45], 也可以通过吸收氨基酸等有机碳源进行混合营养生存 [46]。在氨浓度很低时, 氨氧化古菌比氨氧化细菌具有更强的耐受力, 这使得它在寡营养海区比其他浮游生物具有更强的竞争力 [47]。氨氧化古菌不断地从海洋和陆地环境中得以分离、并进行纯培养或富集, 为深入验证它的氨氧化功能、发现新的生理特征提供了可能性 [48~50]。氨氧化古菌的生物标志物为泉古菌醇, 其细胞膜主要由 GDGTs 化合物构成。这些化合物中五元环的相对数量与海水表面温度 (SST) 有

很好线性关系。基于此构建的海洋和湖泊古温度指标 TEX_{86} 已成为定量重建古温度的重要手段 [51~53]。氨氧化古菌 GDGTs 化合物与细菌支链 GDGTs 的相对比例能够指示因气候干旱而引起的土壤盐碱化, 已经被应用于青藏高原隆升导致的中新世亚洲内陆干旱化 [54]。可以看出, 包括氨氧化古菌在内的微生物 GDGTs 具有生物地球化学和古气候学研究的双重价值, 在重建古温度、识别干旱化事件方面取得了突出的进展, 开创了分子古气候学的一个新领域。

很长时间以来, 异养细菌参与的反硝化作用被认为是海洋中氮损失的主要原因。氨厌氧氧化细菌的发现开启了地质环境中氮损失的一个全新路径 [55], 它可将 NH_4^+ 和 NO_2^- 转化成 N_2 , 成为厌氧环境下氮损失的重要方式 [56]。氨厌氧氧化细菌属于浮霉菌门 (Planctomycetales), 为化能自养型细菌, 生长非常缓慢 [55], 可以利用乙酰辅酶-A 途径进行 CO_2 的固定 [57], 且能够合成“梯状”脂类 (ladderane) 以隔绝有毒中间产物 [58]。氨厌氧氧化细菌广泛分布于缺氧的海洋环境, 如黑海、阿拉伯海、哥斯达黎加海岸等 [59~61], 在湖泊水体 [62]、水稻田 [63] 甚至油田 [64] 中也能发现。

1.3 硫循环

硫循环常与铁循环相伴发生, 主要发生在微生物的风化作用过程。比较典型的例子是酸性矿排水区, 其 pH 通常为 2~3, 极端时可达 -3 [64]。金属矿和煤矿中的金属硫化物暴露于氧气和水后形成了酸性矿排水, 含有较高的金属离子 (如 Fe^{2+} , Cu^{2+})。在酸性矿排水中, 主要的微生物反应是铁氧化菌主导的亚铁离子氧化反应, 其次是硫酸盐还原过程 [65]。嗜酸铁氧化细菌主要为化能自养型, 种类比较单一 [66], 它可以通过调节矿物的形成来调控酸性环境硫和铁的生物地球化学循环 [67, 68]。微生物还可以通过海底玄武岩的风化作用而影响硫和铁的地球化学过程。铁氧化菌和锰氧化菌可以将玄武质玻璃作为唯一碳源生长, 释放的物质和能量供化能微生物群生长 [69], 使得海底玄武岩上的原核生物量比上覆海水高 3~4 个数量级 [70]。这些过程促进了碳、硫、铁等元素在海洋系统中的循环 [69, 71]。

最近十年来, 在地下水重要元素 (如 As) 的生物地球化学循环 [72, 73]、土壤系统碳的生物地球化学循环 [74]、冰冻区和耕作区的微生物作用和温室气体排放 [75, 76]、喀斯特石漠地区的生物地球化学 [77] 等也取得重要进展, 国际上在这些方面均有一些评述性总结, 这里不再一一阐述。

2 重大地质突变期的生物地球化学循环异常

地质历史时期元素生物地球化学循环的特征主要以同位素的形式保留在地质体中。这方面的研究集中在一些重大的地质突变期,如重大生物集群灭绝期、全球变暖和变冷时期、显生宙的大洋缺氧和前寒武纪的大氧化时期等。大量的研究表明,这些时期伴随着碳、氮、硫生物地球化学循环的重大变化,主要表现为碳同位素、硫同位素和氮同位素的显著波动(包括正漂移与负漂移)^[78~90]。这里重点总结显生宙数次生物集群灭绝时期的生物地球化学特征。与近代海-陆系统的研究相比,地质历史时期碳、氮、硫元素循环的库(源、汇)和流(通量)的研究极其薄弱。

2.1 碳循环异常

2.1.1 奥陶纪末期 晚奥陶世赫南特阶发生了早古生代温室时期的一次显著而短暂的冰期事件,导致了海平面的显著下降以及生物大灭绝^[91]。上世纪 90 年代的研究表明,这一时期的碳循环发生显著异常^[92~96]。后续生物地层工作的深入,特别是赫南特阶层型剖面的确立,促进了这时期碳循环的研究^[97]。在世界不同地区都发现了赫南特阶 $\delta^{13}\text{C}$ 的正漂移事件($\delta^{13}\text{C}_{\text{carb}}$ 和 $\delta^{13}\text{C}_{\text{org}}$),且表现出两幕式的特点^[85,86,98~100]。第一幕开始于赫南特阶底部之下,峰值位于 *Normalograptus extraordinarius* 笔石带的中下部,之后有一个小幅度的下降。第二幕的峰值位于 *N. persculptus* 带中下部^[98,99]。 $\delta^{13}\text{C}_{\text{carb}}$ 的变化趋势和正漂移幅度呈现很大的区域性变化,这可能主要受冰期海平面下降导致地层缺失的影响^[98],一些地区还可能受到后期成岩作用的影响^[98]。

$\delta^{13}\text{C}_{\text{org}}$ 的变化比 $\delta^{13}\text{C}_{\text{carb}}$ 复杂^[86,96,101]。虽然 $\delta^{13}\text{C}_{\text{org}}$ 在华南不同剖面之间的变化趋势基本一致(-30‰ ~ -27‰)^[84~86],但在其他地区则表现出很大的差异^[94,96,99,101,102]。 $\delta^{13}\text{C}_{\text{org}}$ 的变化幅度一般小于 $\delta^{13}\text{C}_{\text{carb}}$ 。Young 等^[102]将这种变化归结于 p_{CO_2} 的升高,然而这与海平面下降及正的碳同位素漂移存在矛盾。

对于赫南特期碳同位素比值正漂移的原因还存在一些争议。许多学者都认为是由于海平面下降导致碳酸盐岩风化通量增强造成的^[96,99],也有学者认为是有机碳埋藏分数的增加所导致^[98]。

2.1.2 晚泥盆世弗拉阶-法门阶之交 晚泥盆世弗拉阶-法门阶之交碳循环异常主要表现在两幕显著

的 $\delta^{13}\text{C}_{\text{carb}}$ 正异常,对应于两幕海洋缺氧事件(称为上、下 Kellwasser 事件)^[103]。最近十年来,发现突变期之后的 $\delta^{13}\text{C}_{\text{carb}}$ 要明显高于突变期之前的值^[79,104,105]。下 Kellwasser 事件在许多剖面上并不明显,可能只是一次较大区域性的事件。上 Kellwasser 事件具有全球性特征^[79,104], $\delta^{13}\text{C}_{\text{org}}$ 也呈现出显著的正漂移,幅度在 3‰ 左右^[104,106]。近来的许多研究表明, $\delta^{13}\text{C}_{\text{carb}}$ 在偏正过程中出现了许多快速的负漂移现象^[79,107,108]。对于这些负漂移,很多学者认为是成岩作用的结果,但也可能是甲烷水合物的大量释放所引起的^[108]。

碳同位素在不同水深(沉积环境)以及不同纬度的变化特征也逐渐受到重视。Izokh 等^[109]发现高纬地区 $\delta^{13}\text{C}_{\text{carb}}$ 的变化幅度(4.6‰)明显大于低纬地区(3‰),而 $\delta^{13}\text{C}_{\text{org}}$ 的变化幅度(1.5‰)小于低纬地区,赤道地区(华南地区) $\delta^{13}\text{C}_{\text{org}}$ 的变化幅度最大(4‰)。这可能与温度控制的水体 CO_2 浓度有关,但还需要更多数据的支持。碳同位素分馏($\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$)是碳循环的一个重要参数。对于这个突变期碳同位素分馏的变化特征目前还存在一定的争议。Joachimski 等^[110]认为由于当时高的 CO_2 浓度(大约是工业革命前的 7~9 倍),因此碳同位素分馏没有明显变化。Chen 等^[79]则认为有明显变化,进而说明当时 p_{CO_2} 是有明显变化的。

弗拉阶-法门阶之交碳同位素的正漂移被认为是由于有机碳埋藏分数的增加造成的^[106],而这又主要归因于初级生产力的升高^[111,112]。与上述奥陶纪末期 $\delta^{13}\text{C}_{\text{carb}}$ 正漂移所对应的冷事件类似^[86],弗拉阶-法门阶之交的两幕正漂移也对应于两次明显的降温事件(大约 5°C)^[110]。因而,正的 $\delta^{13}\text{C}_{\text{carb}}$ 变化可能与低温下异养微生物代谢活动明显降低有关^[113]。

2.1.3 二叠纪-三叠纪之交 二叠纪-三叠纪之交的碳循环异常早在上世纪 80 年代末就被提出^[114~118],其中以 Holser 等^[115]的工作较为突出,发现了两幕碳同位素负漂移事件,且在二叠纪-三叠纪界线层型剖面得到证实^[119]。然而,对于 $\delta^{13}\text{C}_{\text{carb}}$ 负漂移的幅度、原因及其与生物大灭绝之间的关系并不清楚。最近十年来,人们发现二叠纪-三叠纪之交的碳循环异常一直持续到整个早三叠世,主灭绝之后很长一段时间 $\delta^{13}\text{C}_{\text{carb}}$ 未能恢复到灭绝之前的背景值^[120,121],进一步证实了二叠纪-三叠纪之交幕式的碳循环异常^[88,119,122],且在陆相环境也存在类似的表现^[78]。大量的研究表明,二叠纪-三叠纪之交

$\delta^{13}\text{C}_{\text{carb}}$ 的最低值可能在 -1‰ 左右^[87,119,123], 早期所报道的非常负的值 (-6‰) 可能主要受到后期成岩作用的影响。随着高分辨率生物地层和事件地层的建立, 发现碳循环的异常要明显早于后生生物大灭绝^[87,117,123~125], 且就 $\delta^{13}\text{C}_{\text{carb}}$ 的负漂移幅度来说, 主灭绝之前的负漂移幅度比主灭绝之后的幅度还要大^[87,125]。更值得注意的是, 在紧随后生生物的主灭绝, $\delta^{13}\text{C}_{\text{carb}}$ 出现小幅度的正漂移或保持在较稳定的范围内^[87,89,123,125]。但这些来自浅水地区的结果是否受到地层缺失的影响还有待于确认。在 $\delta^{13}\text{C}_{\text{org}}$ 方面, 发现了微生物的组成能显著地影响 $\delta^{13}\text{C}_{\text{org}}$ ^[88,126,127]。由于受不同来源有机质的影响, 二叠纪-三叠纪之交的 $\delta^{13}\text{C}_{\text{org}}$ 在变化趋势和变化幅度方面都具有区域性^[87,128~131], 且在某些剖面上完全相反^[132]。

虽然目前对二叠纪-三叠纪之交碳循环异常的原因还没有达成共识, 但过去十年的研究取得了许多新的认识。基于全球碳循环模型和碳同位素的记录, 许多研究认为甲烷水合物的大量释放可能是 $\delta^{13}\text{C}_{\text{carb}}$ 大幅度负漂移的主要原因^[133, 134]。最近的古海洋化学研究也表明, 当时的古海洋化学条件可能有利于 CH_4 的释放^[88]。生物大灭绝引起海洋初级生产力的消失是导致 $\delta^{13}\text{C}_{\text{carb}}$ 显著负漂移另一重要原因^[135]。然而许多研究表明, 二叠纪-三叠纪之交的碳循环异常发生在海洋后生动物主灭绝之前且 $\delta^{13}\text{C}_{\text{carb}}$ 负漂移的幅度更大^[89,123,125]。

2.1.4 三叠纪-侏罗纪之交 在全球许多剖面上, 三叠纪-侏罗纪之交 $\delta^{13}\text{C}_{\text{org}}$ 呈现出两幕显著的负漂移^[136,137], 并得到了植物叶片角质层和叶蜡正构烷烃的碳同位素组成的支持^[138,139]。 $\delta^{13}\text{C}_{\text{org}}$ 的第一幕负漂移发生在晚三叠世瑞替阶晚期, 与三叠纪末期的生物大灭绝相一致^[136,137,140~146]。第二幕负漂移发生在三叠纪-侏罗纪之交^[146,147]。旋回地层学资料表明第一次负漂移持续的时间非常短 ($10 \sim 20 \text{ ka}$)^[148]。植物叶蜡正构烷烃单体 $\delta^{13}\text{C}$ 的负漂移高达 8.5‰ , 由此估算大约有 $12,000 \text{ Gt CH}_4$ ($\delta^{13}\text{C}_{\text{CH}_4} = -60\text{‰}$) 释放到大气中, 主要是甲烷水合物的大量释放^[146]。估算表明, 古大气 p_{CO_2} 显著升高, 由 1000×10^{-6} 左右上升到 2700×10^{-6} 左右^[149~151]。目前, $\delta^{13}\text{C}_{\text{carb}}$ 的资料还很少^[141, 143, 144, 152]。与二叠纪-三叠纪重大转折期类似, 越来越多的资料表明, 三叠纪-侏罗纪之交的碳循环异常也可能持续了很长一段时间, 开始于晚三叠世诺利阶与瑞替阶之交, 并一直持续到早侏罗世 Hettangian 晚期, 经历了数个 $\delta^{13}\text{C}$ 的正、负漂移^[146, 147, 153]。

2.2 氮循环异常

如前所述, 氮循环过程往往与特定的环境和微生物有关。例如, 硝化作用需要 O_2 的参与, 在前寒武纪大气 O_2 含量增加之前, 该过程就未能发生^[154]。反硝化作用和氨的厌氧氧化作用在缺氧环境中进行, 同时将环境中生物可利用氮转换成惰性的 N_2 。因而, 氮循环是探讨古海洋的氧化还原条件和微生物组成的有效手段^[155,156]。然而地质历史时期, 尤其是白垩纪以前的时代, 氮循环的研究总体较为薄弱。

LaPorte 等^[101] 首次研究了奥陶纪末期赫南特阶的 $\delta^{15}\text{N}$, 发现 $\delta^{15}\text{N}$ 有小幅度的上升 (-1‰ 上升到 1‰), 并归因于温度下降导致水体含氧量增加, 进而抑制了反硝化作用和生物固氮作用。但这与现代冰期-间冰期的氮循环特征不一样^[157], 同时其他剖面的资料却表现出相反的特点^[101]。

二叠纪-三叠纪之交氮循环的研究开展得相对较多^[89,124,158~161]。一些海相剖面的氮同位素可能受陆源有机质的影响, 限制了氮循环的研究。Luo 等^[89] 研究了受陆源有机质影响较小的深水盆地中孤立碳酸盐台地上氮同位素的组成特征, 发现后生生物的主灭绝伴随着显著的 $\delta^{15}\text{N}_{\text{org}}$ 负漂移, 且这一漂移可以进行大范围的对比。主灭绝界线之上的 $\delta^{15}\text{N}_{\text{org}}$ 在 -1‰ 至 1‰ 之间波动, 与大气 $\delta^{15}\text{N}$ 类似, 说明微生物固氮作用是当时生物可利用氮的主要来源, 也反映了当时海洋中的生物可利用氮非常缺乏。这主要是由于海洋缺氧程度的加剧, 导致大量的生物可利用氮通过反硝化作用和氨的厌氧氧化作用转换成生物不可利用的 N_2 。在二叠纪-三叠纪之交的海洋化学背景下, 氮循环的异常可能会大大增加 N_2O 进入大气的通量, 从而引起全球性的升温事件^[89]。

Sephton 等^[153] 发现在晚三叠世的诺利阶-瑞替阶之交有一次明显的氮同位素负漂移。但后续详细的生物地层工作表明, 该异常事件可能跨越了三叠纪-侏罗纪界线, 只是氮循环的异常开始于该界线之下^[162]。值得指出的是, 在早侏罗世 Hettangian 的 $\delta^{15}\text{N}$ 正漂移伴随着 $\delta^{13}\text{C}_{\text{org}}$ 的显著负漂移^[153,163,164], 但原因还不清楚。Paris 等^[164] 的研究表明, $\delta^{15}\text{N}$ 的变化主要发生在 $\delta^{13}\text{C}_{\text{org}}$ 的第二幕负漂移过程, 而在 $\delta^{13}\text{C}_{\text{org}}$ 第一幕负漂移时没有明显的变化。

2.3 硫循环异常

硫循环携带了大量的环境和生物信息。在现代海洋, 很多有机质矿化都是通过硫酸盐还原作用进行的。该代谢发生于严格的无氧条件下, 且能够留

下很明显的同位素分馏印迹。硫酸盐还原过程的产物 H_2S , 是一种致命的有毒气体, 对后生生物的代谢影响很大。另外, 早期的硫循环与大气的组成也密切相关, 硫同位素的组成对研究早期大气的演化有重要的启示意义。这使得地质历史时期硫循环方面的研究比较多, 仅次于碳循环的工作^[165, 166]。碳酸盐岩晶格硫酸盐 (Carbonate Associated Sulfate, CAS) 可以记录古海水硫酸盐的硫同位素组成, 这进一步促进了地质历史时期硫循环的研究^[167~169]。

晚奥陶世赫南特阶的硫循环研究还非常薄弱。Yan 等^[84] 发现这一时期黄铁矿 $\delta^{34}\text{S}_{\text{py}}$ 有一个显著的正漂移过程, 与 $\delta^{13}\text{C}_{\text{org}}$ 的变化特征相似。Zhang 等^[85] 也发现了类似的变化特征, 但得到结果与 Yan 等^[84] 有很大的差异。 $\delta^{34}\text{S}_{\text{py}}$ 受许多因素的影响, 对于这些变化能否反映当时的硫循环异常还有争议^[84, 85]。

对于晚泥盆世弗拉阶-法门阶的硫循环, 早期的研究主要集中在黄铁矿的硫同位素组成上^[170, 171], 发现了 $\delta^{34}\text{S}_{\text{py}}$ 存在明显的正漂移, 并在后期的研究中得到证实, 但只出现在上 Kellwasser 层, 而在下 Kellwasser 层并没有明显的表现^[106]。然而, 对 CAS 硫同位素 ($\delta^{34}\text{S}_{\text{CAS}}$) 研究发现, 弗拉阶-法门阶之交的硫循环并未发生显著的异常, 并且可能存在于一个与 $\delta^{34}\text{S}_{\text{py}}$ 相反的变化特征^[172]。

近十年来, 大量的 $\delta^{34}\text{S}_{\text{CAS}}$ 资料表明, 从二叠纪海水极低 $\delta^{34}\text{S}$ 向三叠纪高 $\delta^{34}\text{S}$ 的转换发生在二叠纪-三叠纪之交, 且海水硫酸盐 $\delta^{34}\text{S}$ 在主灭绝界线处有一个明显的正漂移, 体现了当时海洋缺氧的加剧^[90, 173~178]。即使在二叠纪-三叠纪之交很短的时间段内, 高分辨率的 $\delta^{34}\text{S}_{\text{CAS}}$ 资料表明, 硫循环经历多次显著的波动。区域性大幅度波动的 $\delta^{34}\text{S}_{\text{CAS}}$ 表明, 当时海洋硫酸盐库的通量很小^[90]。结合无机碳同位素资料和碳-硫循环模型, Luo 等^[90] 认为当时海洋中硫酸盐的浓度低于现代海洋的 15%。这可能引起生物地球化学循环和环境的变化。硫同位素的结果也表明二叠纪-三叠纪之交缺氧程度加剧, 使得化变层上升至海洋浅水部位^[176]。与 $\delta^{34}\text{S}_{\text{CAS}}$ 不一样, 黄铁矿 $\delta^{34}\text{S}$ 的影响因素更多, 对环境的解释存在多解性^[179], 研究相对较少^[176, 180]。黄铁矿和 CAS 硫同位素的成对研究可能会加强。Shen 等^[181] 将多硫同位素引入二叠纪-三叠纪古海洋化学的研究, 认为在海洋后生生物主灭绝前发生过数次强烈的缺氧事件。

三叠纪末的硫循环研究还仅仅处于起步阶段, 仅 Williford 等^[182] 做了一些初步的工作。研究结果

表明, 在侏罗纪 Hettangian 早期有一次明显的 $\delta^{34}\text{S}_{\text{py}}$ 正异常事件, 但是要晚于三叠纪末期的生物大灭绝事件。

除了以上这些重大生物灭绝期的生物地球化学循环异常外, 人们还对前寒武纪的大氧化事件^[183, 184]、白垩纪的大洋缺氧和极端温暖时期^[185, 186]、古近纪的古新世-始新世之交的极端暖期^[187, 188] 等开展了许多生物地球化学工作, 并取得了重要进展。

3 极端环境的生物地球化学过程

近十年来, 极端环境的生物地球化学过程取得了突出的进展。深部生物圈一些新的生物地球化学功能对研究生命起源和生物演化具有重要的启示。

3.1 近代极端环境

近十年来, 海底热液喷口生物地球化学研究取得了显著的进展, 主要体现在对热液喷口生物群代谢途径的新认识上。化能自养微生物是热液生物群中的主要生产者, 它们通过氧化或还原热液中的无机物来获取能量。在热液区可以形成黑烟囱, 热液中富含 CH_4 和 S (如 S_0 、 H_2S) 等, 生物具有较高的代谢和生理多样性, 如产 CH_4 、好氧与厌氧甲烷氧化、硝化、反硝化、硫酸盐还原等^[189]。从冲绳海槽热液口分离出一株嗜热细菌 (*Caldanaerobacter*) 能够厌氧氧化 CO ^[190]。非生物合成的具有较重碳同位素组成的短链烷烃, 可以供海底热液区的异养微生物利用^[191, 192]。这些短链有机物的碳来自地幔, 而不是海水中的 HCO_3^- ^[192]。

在海底热液区, 还能形成白烟囱 (碳酸盐烟囱), 如位于大西洋洋中脊侧翼的 Lost City 热液区。该区流体来自橄榄岩与海水的相互作用 (黑烟囱区是海水与洋壳中冷却的玄武岩的相互作用), 属于超基性流体, 重金属浓度低, pH 高 (9~11), 形成的碳酸盐烟囱高达 60 m^[193], 生长时间长达三万年^[194]。在该热液区, 橄榄岩的蛇纹石化过程释放 H_2 , 同时非生物合成 CH_4 (具有较高的 $\delta^{13}\text{C}$ 值^[193, 195])、甲酸根与乙酸根^[196]、 $\text{C}_1\sim\text{C}_4$ 烷烃^[192] 等。这些非生物成因的 CH_4 和有机物供养了多样性较高的特殊生物群落。在烟囱内部, 主要是耐高温的单种古菌 (Lost City *Methanosarcinales*) 厌氧氧化甲烷^[193]。在烟囱外壁, 主要是硫氧化和甲烷氧化细菌^[197]。新生的烟囱通常具有较少的微生物种群, 而生长超过千年的烟囱则提供了研究稀有种群动态演变的机会^[198]。在 Lost City 热液区, 因碳源有限, 产甲烷菌

醚类化合物的 $\delta^{13}\text{C}$ 值高达 3.6‰ ^[199]。

热液区嗜热微生物的发现不断挑战人们对生命最高耐受温度的认识。Kashefi 和 Lovley^[200] 报道了从东北太平洋 Juan de Fuca 地区黑烟卤中分离出的一株铁还原菌,可以在 121°C 下进行铁还原过程。Takai 等^[201] 分离出可以在 122°C (20 MPa) 下生长的产甲烷菌 *Methanopyrus kandleri* strain 116。该菌株在超高压下合成的 CH_4 富集重的碳同位素组成。在热泉中,氨氧化古菌(AOA)的研究则极大地拓展了人们对其生存温度上限的认识。de la Torre 等^[202] 培养的热泉嗜热古菌 *Candidatus Nitrosocaldus yellowstonii* 在 74°C 仍可进行氨的好氧化。古菌 *amoA* 基因分析显示,AOA 广泛分布于全球热泉环境,温度可高达 94°C ^[203]。这些研究支持氨氧化能力起源于嗜热泉古菌^[204]。

洋壳上部(包括沉积物和玄武岩层)是地球上容量最大的含水系统,被称为地下海洋^[205]。全球玄武质含水层成为深部生物圈的生命孵化器,分布着生理和种群非常复杂的微生物^[206]。海底深部生物圈的下限可达海底 1.6 km ^[207]。海底深部生物圈可能分布于洋脊两翼、透水的火山玄武岩上部几百米以及洋脊之上的硫化物矿床中^[208]。海底深部的代谢以硫酸盐还原、产甲烷和发酵为主^[209,210]。深部微生物可以利用残存的来自表层生物圈的有机质^[210,211],以异养古菌为主^[212]。在海底深部,某些微生物还可以利用乙酸根和 H_2 合成乙烷和丙烷,供异养生物利用^[213]。在洋壳中,可供生物利用的 H_2 丰富,硝酸盐还原菌、三价铁还原菌、硫酸盐还原菌和产甲烷菌都可以利用 H_2 。地下深部产 H_2 的途径包括有机质的分解和发酵,火山岩的蛇纹石化^[214,215] 及水的分解^[210,216]。实验室模拟还发现,原核生物可以促进矿物(如玄武岩,石英)产生 H_2 ^[217]。

与上部洋壳相似,大陆深部生物圈也主要是依赖 H_2 的微生物群。Stevens 等^[218] 在哥伦比亚河玄武岩组含水层中检测到了高浓度的溶解 H_2 以及自养产甲烷微生物。美国爱达荷州火成岩热液中也主要是利用 H_2 的产甲烷古菌群落^[219]。南非 Mpomeng 金矿地下 2825 m 深处以利用 H_2 的嗜热硫酸盐还原菌(*Fermitutes*)为主^[220]。传统上,人们认为地下深处的原油主要由好氧微生物完成降解,所需的 O_2 由地表水带入。实际上,地表水携带的 O_2 在浅层就被消耗尽,地下深处的油气藏内部是严格厌氧的环境,生物降解主要由厌氧微生物完成^[221,222],如产甲烷古菌可以降解原油,通过 CO_2 还原途径来

合成 CH_4 ^[223,224]。

3.2 早期地球环境

如同近代极端环境,早期地球环境的生命主要是以细菌和古菌为主的微生物。尽管古生物学家努力尝试寻找早期生命的化石记录^[225],但早期生命的研究在很大程度上仍受制于可靠的形态化石^[226],寻找早期生命的生物地球化学记录变得更为重要。然而在过去的十年中,这一领域的首要进展便是对早期提出的地球化学记录的证伪。首先,格陵兰岛艾苏阿太古代地层的碳同位素记录显示,生命可能在 $37\sim 39$ 亿年前就已经出现^[227,228]。但随后的研究表明,成岩作用或变质过程也可导致相似的碳同位素记录^[229,230]。因此这些经历了高级变质作用的碳同位素记录的生物成因假说受到了广泛的质疑。其次,Brocks 等^[231] 报道了来自澳大利亚皮尔巴拉克拉通(Pilbara Craton)的生物标志化合物,表明真核生物和产氧光合蓝细菌在 27 亿年前就已经出现。但这些古老的生物标志化合物后来证实是受到污染所致^[232]。

这些证伪工作并没有降低人们追踪早期生命的热情。在澳大利亚皮尔巴拉克拉通盆地,硫酸钡与硫化物的硫同位素分馏特征表明,硫酸盐还原菌及硫酸盐还原作用在 34.7 亿年前就已经出现^[233],这将前人的认识提前了大约 7.5 亿年^[234]。在澳大利亚哈莫斯利省(Hamersley Province),浅水与深水相干酪根碳同位素组成的差异清楚地表明,在 27 亿年前就出现深水缺氧生态系统和浅水需氧生态系统的共存,产氧光合作用也在此时广泛存在^[235]。同样在澳大利亚皮尔巴拉克拉通盆地,出现了具有明确生物成因的磁铁矿-醋酸铁-磷灰石矿物组合,证实了还原氧化铁的细菌在 24.8 亿年前就广泛存在^[236]。在阿曼,新发现的海绵动物标志化合物表明,最早的后生动物可能在新元古代大冰期就可能已经存在了^[237]。

4 生物地球化学过程对生态系统的影响

生源要素是海洋生物生长繁殖的物质基础,其水平与变异控制着海洋生物食物链的演替与变化趋势^[5,238~242]。因此,元素的生物地球化学循环在影响气候变化的同时,影响着生态系统的变化。人们已在生态毒理效应、生物危机、早期生命演化等方面取得了突出的进展。

4.1 生物地球化学过程与生态毒理效应

化学物质对生物的影响与毒性是海洋生物地球化学循环效应的重要体现,过量的化学物质会影响

海洋生物生长和繁殖。近年来,大量排入近海的氮、磷、重金属以及 POPs 物质已对海洋环境产生了重要影响^[5,243,244],其生物效应通过食物链传递使其危害更加显著^[245]。从分子生物学角度揭示这种影响是海洋生物地球化学过程关注点之一^[244,246],也是海洋生物地球化学与现代高端科学技术综合交叉的发展趋势。

近年来,近海海水氮持续增加,磷在降低或变化不大,氮磷比增加迅速,营养盐结构发生着根本性的变化^[5,243]。近海低氧区的规模及强度在增加,海水酸化效应有所体现,从而导致浮游植物和浮游动物群落结构及功能群随之变化。海水浮游植物的优势种由硅藻逐渐变为甲藻,受控于海水磷的浮游植物种类明显减少,胶质浮游动物大量出现,海洋生物明显出现小型化趋势,导致诸如赤潮、浒苔、水母以及海星这样生态灾害的频发和爆发,渔业资源受到沉重打击,近海生态系统变得愈来愈不稳定^[5,239~243]。

在渤海湾水体中,复合污染物主要有石油烃类有机污染物、重金属和过量无机氮等,导致渤海初级生产力总体下降、浮游植物群落结构重大变化、主要渔业资源平均营养级总体下降等。渤海湾近岸海域海水镉、汞、铅和石油烃复合污染对鱼类、甲壳类和双壳类的长期致死率分别为 29.7%、14.6% 和 12.9%,对种群增长率平均每年降低 6.4%、14.6% 和 12.9%^[5]。这种影响的生态毒理首先是通过复合污染物进入生物体内影响其生物酶活性,继而与其 DNA 形成加合物导致 DNA 损伤,最终改变其胚胎发育、幼体孵化、附着变态等生命史的关键阶段,导致海洋生物食物链变短、营养级降低,渔业资源小型化和低值化^[5,247~249]。

基于近海生态系统水平上的研究,对南海珊瑚礁生态系统提出了维持珊瑚礁生态系高生产力原因的新论点——“拟流网理论”^[5,6]。发现了珊瑚虫黄藻可“奢侈消费”营养盐的新规律,提出了南沙珊瑚礁生态系的高生产力主要是依靠其系统内部快速而高效的再生循环过程维持的,营养盐的原位快速再生是珊瑚礁营养盐的主要来源,化学物质的垂直转移主要靠生物过程来完成^[5,6]。发现了近海沉积物含有的氮、磷、硅的量虽然巨大,但仅有少部分可参与水体的生物地球化学循环,近海沉积物具有明显的生态学功能^[5,238,240,249]。

4.2 生物地球化学过程对生物危机的影响

显生宙的数次生物危机都伴随着强烈的 C、S 等元素的生物地球化学循环的异常,它们也记录了生物地球化学过程对生物危机的影响。碳循环的异

常往往与大气 CO₂ 和 CH₄ 含量的变化有关,而这些气体将影响古温度的变化,引起生物危机。在三叠纪-侏罗纪之交,负异常的碳同位素组成伴随着古大气 p_{CO_2} 的显著升高,由 1000×10^{-6} 左右上升到 2700×10^{-6} 左右^[149~151],并造成了生物钙化危机^[152,250]。基于全球碳循环模型和碳同位素记录,火山活动喷出的 CO₂ 和水合物释放的 CH₄ 可能是二叠纪-三叠纪之交 $\delta^{13}\text{C}_{\text{carb}}$ 大幅度负漂移的主要原因^[133,134],大量的 CO₂ 可能造成当时海洋钙质生物的选择性灭绝^[251]。而在奥陶纪末期和晚泥盆世弗拉阶-法门阶之交, $\delta^{13}\text{C}_{\text{carb}}$ 的正漂移对应了气候变冷事件^[86,104],这些 $\delta^{13}\text{C}_{\text{carb}}$ 的正漂移可能与低温下异养微生物代谢活动明显降低有关^[113],但是否造成动物危机还不清楚。

二叠纪-三叠纪之交的氮和硫同位素则反映了缺氧乃至硫化的海洋环境对生物的影响。当时海洋中的生物可利用氮非常缺乏,微生物不得不利用大气中的氮^[89]。硫同位素组成也表明,在二叠纪末期海洋后生生物主灭绝前和二叠纪-三叠纪之交,海洋的缺氧程度加剧,使得化变层上升至海洋浅水部位^[176,181]。这些结果表明了微生物地球化学过程对古海洋环境及生物危机的重要影响。

4.3 生物地球化学过程对早期生命演化的影响

前寒武纪也出现了一系列重大地质突变期,如太古代末期的大氧化时期、中元古代的硫化海洋时期和新元古代的雪球地球时期等。这些事件也伴随着显著的碳、氮、硫生物地球化学循环异常,对早期生命的起源和演化产生重要影响^[154,252~267]。

越来越多的研究表明,地球早期生命的起源与生物的演化与大气-海洋系统的氧化还原状态密切相关。近十年来,人们对早期地球大气与海洋氧化还原化学演化的研究取得了重要进展,并为重塑早期生命与早期地球环境的协同演化关系奠定了基础(图 1)。随着研究的深入,人们识别出在大约 18 亿年以前大气氧含量可能下降^[268],但基本上与前期的认识一致,即地球表层的大气演化主要经历了两次大的氧化阶段。第一次发生在早古元古代(24.5~23.2 亿年前),大气中的氧含量第一次超过目前大气氧含量水平的 0.001%^[257,269]。这次氧含量的增加很可能与产氧光合作用蓝细菌的出现有关^[270]。第二次氧化发生在晚新元古代(大约 8~5.42 亿年前),大气氧含量基本达到了现在的水平^[271,272]。这次大气氧含量的增加可能导致了多细胞动物的出现^[271,273]。

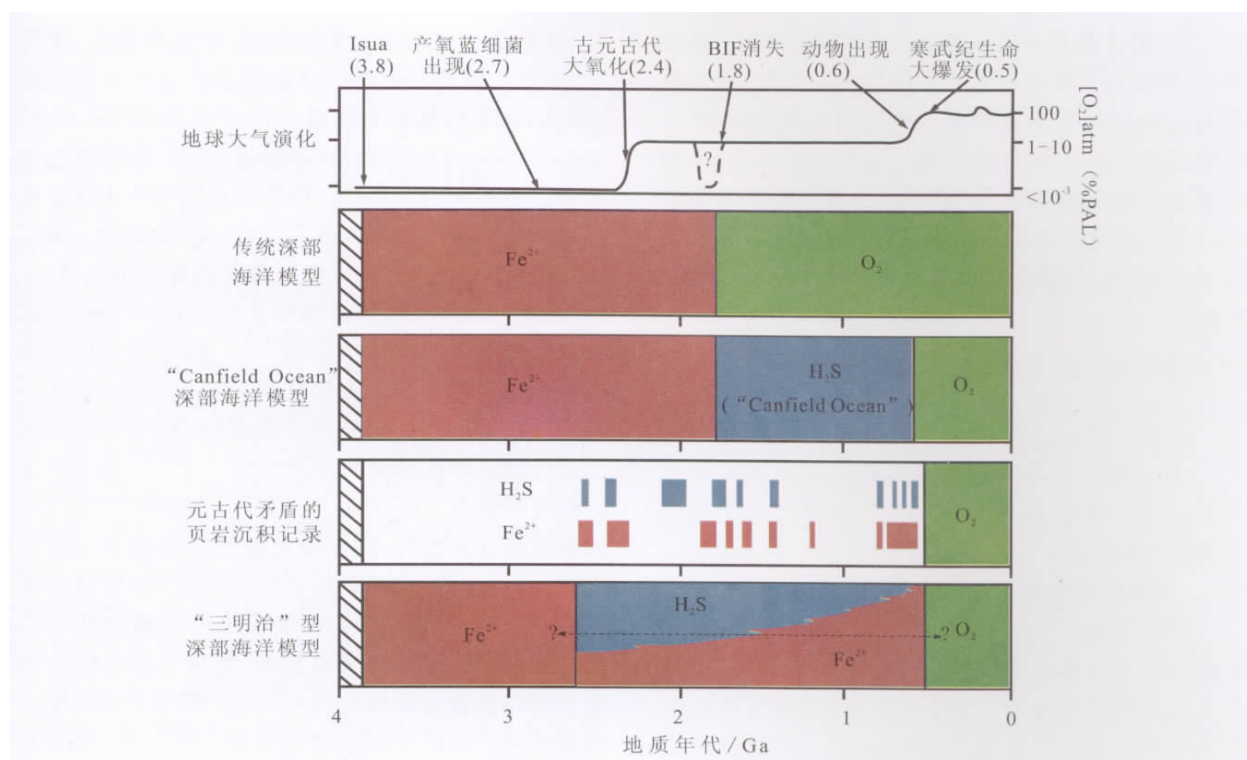


图1 早期生命与地球大气、深部海洋的协同演化(元古代矛盾的页岩沉积记录引自文献[287])。

Fig. 1 Co-evolution of life, atmosphere with deep oceans in the early time of the earth
(Conflicting Proterozoic shale records were from ref. [287])

然而,人们对早期地球深部海洋的化学演化存在很大的争议。传统的海洋化学模型认为,由于大气的逐步氧化,太古代和古元古代铁化的(即缺氧且含游离 Fe^{2+})深部海洋在大约 18 亿年前就已经彻底氧化^[274]。但是,Canfield^[275]基于全球硫化物与硫酸盐硫同位素演化模式则提出了完全不同的“Canfield 海洋”模型,认为早期地球深部海洋的缺氧至少持续到寒武纪初期(~540 Ma),太古代和古元古代铁化的深部海洋在 18 亿年前并未氧化,而是硫化(即缺氧且含游离 H_2S)。Canfield 等^[276]又根据新元古代铁组分数据进一步指出,这一硫化的深部海洋在大约 7 亿年以前又重新被铁化的深部海洋所取代,直至寒武纪初期深部海洋才被彻底氧化。古、中元古代铁组分化学^[277,278]、微量元素化学^[279]和生物标志化合物记录^[259]均支持这一模型。在此基础上,Anbar 和 Knoll^[280]提出了著名的生物无机桥假说(Bioinorganic bridge),认为中元古代广泛存在的缺氧硫化水体极大地限制了海洋生物固氮元素 Fe、Mo、Co 等的浓度,从而限制了海洋真核生物的演化。而来自 Fe-S-C 系统数据^[281~283]以及 Mo、Cr^[268,279,284]等微量元素的证据则表明,晚新元古代深部海洋的氧化(也即硫化的消退和海洋中生物固

氮元素浓度的增加)很可能是这一时期多细胞真核生物辐射与早期动物诞生的原因。

Canfield 海洋模型及其与早期生命之间的协同演化关系似乎比较完美。然而, Li 等^[264]根据华南新元古代南华盆地陡山沱组铁组分、硫同位素和微量元素在不同沉积相中的时空差异,提出了新的具有三维差异和动态的“三明治”型古海洋化学结构模型。该模型指出,在新元古代埃迪卡拉纪,在海洋表层氧化的水体之下、深部铁化水体之上,存在着一个由细菌硫酸盐还原作用和黄铁矿沉淀作用共同动态维持的从陆缘向远海楔状展布的硫化物带(即含游离 H_2S 的缺氧水域)。该模型可能适用于从晚太古代至寒武纪初期长达 22 亿年的前寒武纪海洋^[285~288]。由此,“三明治”型古海洋化学结构模型的提出构成了对目前占主导地位 Canfield 海洋模型的挑战,即地球的深部海洋可能从来就没有完全硫化过,其硫化部分可能仅局限于陆地边缘近海或局限盆地。这一模型解决了地球早期特别是新元古代多细胞真核生物辐射、早期动物诞生与地球化学记录的缺氧硫化之间的矛盾^[264],也解决了 Canfield 海洋模型与系统基因组学揭示的元古代生物酶增加使用 Fe、Mo、Co 等氧化还原敏感元素之间的矛

盾^[289]。更为重要的是,这个古海洋化学结构模型指出,中元古代硫化的海洋可能根本不存在,其对海洋 Fe、Mo、Co 等生物固氮元素浓度的限制完全与区域硫化楔的发展程度有关。这样,基于 Canfield 海洋模型建立起来的元古代海洋化学与真核生命之间的协同演化关系需要重新评估。这暗示着元古代真核生物(群)出现的时间可能比我们目前所了解到的更早。

5 生物地球化学研究的痕量、微区、原位技术

技术的发展不断推动着生物地球化学研究的突破,痕量、微区、原位一直是生物地球化学技术在不断努力的方向。

5.1 生物地球化学过程的痕量示踪技术

随着 GEOTRACES 的启动,生物地球化学过程的痕量示踪技术得到了前所未有的重视。尽管部分无机和同位素地球化学信号以及绝大部分有机地球化学古环境信息是经过沉降、水平运移和各种复杂的生物地球化学过程改造了的信号,但经过“校正”后,仍可用于揭示特定海域的海洋生物地球化学过程。这种“示踪技术”拓展和延伸了现代海洋生物地球化学的手段,近海生物地球化学过程以及生物系统功能群生活史在同位素水平、分子水平、超分子水平标志物信息的提取技术及示踪动力学成为近年来海洋生物地球化学发展的新热点^[239, 290~292]。

海水中痕量金属以及海洋中的 POPs 的变化可用于揭示海洋初级生产力水平、物质来源、海水污染程度等^[242, 244, 246~248, 290~292]。钼同位素可用于研究氧化还原环境。铁在一定程度上控制着海洋生物生产力的水平,因而铁同位素在表征生物生产力方面具有很大的潜力。但是,由于生物与非生物过程都可引起铁同位素的分馏,单独的铁同位素不能用来区分铁的生物过程和非生物过程^[5]。铜、锌同位素也是生物地球化学过程的示踪剂,但目前报道得不多^[5,6]。

5.2 微生物地球化学功能的宏基因组学

建立在传统微生物培养基基础上的研究方法无法满足当前地球科学对微生物研究发展的需要。宏基因组能够极大挖掘出环境微生物的代谢多样性及潜在的生物地球化学功能,通过高通量和高灵敏度的筛选和鉴定,使地质环境中绝大多数未培养微生物的地球化学过程在基因层次上得以确定^[293~296]。通过宏基因组技术,人们发现了广布海洋的 α -变形菌拥有与嗜盐古菌类似的合成细菌视紫质蛋白的基

因,这种蛋白能够将光能转化为微生物自身能量^[297,298]。这类功能基因还存在于广泛分布海洋的 α -变形菌目甚至是浮游型广古菌热原体目(Thermoplasmatales),这极大拓展了我们对海洋微生物能量代谢的认识^[299~302]。群落宏基因组还了解译微生物间相互作用和协同进化开创了新的途径。通过宏基因组方法,人们发现噬菌体在感染蓝细菌(Prochlorococcus)时可以巧妙地利用其基因产生能量并合成复制所需的脱氧核苷酸^[303]。对酸性矿排水表面微生物膜的宏基因组研究则发现,当部分细菌分泌胞外物质形成生物膜保护群落时,部分其他细菌则进行固氮和铁氧化的协同合作^[304~306]。通过宏基因组测序重建出的代谢方式显示,与海洋蠕虫共生的细菌是自养型的,能够通过硫氧化和硫酸盐还原为蠕虫提供多种营养物质^[307]。宏基因组能够帮助我们发现特殊环境微生物未知的生物地球化学功能。通过微生物宏基因组技术,发现了在海洋最低含氧带存在微生物的硫循环路径,改写了该区域以氮循环为主导的生物地球化学模型^[156]。利用宏基因组方法,人们在最低含氧带观察到一类与深海蛤共生的微生物,它可能同时存在碳固定、硫氧化和呼吸硝酸盐等多种功能,能够适应于水柱中变化的氧化还原状况^[308]。这些不断被发现的微生物地球化学过程,将逐渐改写基于微生物培养建立起来的生物地球化学模型。

5.3 微生物地球化学功能的微区与原位分析

尽管微生物学和同位素地球化学都早已进入了单细胞和微区研究水平,但对微生物地球化学过程的研究在很长一段时间内都停留在“大样品量”的阶段。宏基因组技术只能对控制微生物地球化学功能的基因进行确定,而这些基因是否能表达出相应的性状却不得而知。纳米离子探针(Nano-SIMS)技术的出现,使得微生物地球化学过程的研究能够深入到单细胞和微区水平,为直接了解微生物生理和代谢过程提供了新的手段。通过同位素标定的底物对微生物代谢途径进行示踪,并结合荧光原位杂交以识别微生物细胞,纳米离子探针产生的 Cs^+ 离子束轰击到微生物细胞体或群落表面并溅射出二次离子被质谱检测,最终通过成像的方式将代谢了标定同位素的区域反映出来^[309]。这项技术早期主要用于海洋冷泉口甲烷厌氧氧化过程的研究,可以获取细胞或集合体纵截面不同位置的碳同位素比值,示踪 CH_4 在古菌和硫酸盐还原菌共生体中的代谢路径^[21]。用 SIMS 对南太平洋海底沉积物未培养古菌单细胞碳同位素的分析表明,这些底栖古菌主要

靠海底有机质进行异养代谢,而不是以 CH_4 作为主要碳源^[22]。结合同位素标定技术,通过单细胞的 Nano-SIMS 分析,发现了参与甲烷厌氧氧化的古菌能够利用 $^{15}\text{N}_2$ 进行固氮作用,为古菌和硫酸盐还原菌共生体提供氮源^[39]。对于环境体中生物量较少和不活跃的微生物,如厌氧光合细菌,也可以通过 Nano-SIMS 对其代谢和生理活动进行示踪^[310]。除碳和氮外, Nano-SIMS 还可用于研究磷、硫甚至是金属元素的微生物地球化学循环,为解译复杂微生物群落中微生物个体代谢和功能提供重要的手段。

结合成像技术,二次离子质谱还可以原位分析生物标志物在微生物体中的分布^[311]。利用 TOF-SIMS,人们在黑海微生物席中检测到原位的古菌标志物,包括 hydroxyarchaeol, dihydroxyarchaeol 和 GDGTs 等。前两个化合物主要分布在甲烷成因的 CaCO_3 周围,而 GDGTs 则主要出现在嗜甲烷古菌 ANME-1 的细胞膜脂中^[312, 313]。TOF-SIMS 同样可以应用于地质样品。例如,用离子束打开含油地层的流体包裹体后,人们从中检测到单个包裹体中的微生物甾类和藿类化合物^[314, 315]。可以预测,TOF-SIMS 技术的不断发展和应用将给生物地球化学研究带来一场革命,改变传统的有机分子提取、分离、衍生化,以及仪器测试的分析流程,对环境微生物标志物进行原位无损分析,获取其在样品表面的空间分布模式甚至相对含量,对深入理解环境微生物的地球化学过程、示踪生物标志物的母体和探索早期生命起源均具有重要的应用价值^[311]。Rasmussen 等^[232]就是通过先进的高精度原位纳米离子探针技术,不仅测定了代表原生有机质的干酪根的碳同位素组成,而且也测定了由干酪根热演化排烃过程中残留在岩石中的极微量的原始沥青的碳同位素组成,由此发现了可提取生物标志化合物的碳同位素组成与其母岩原始有机质的不一致^[231],从而证明可提取生物标志化合物是后来迁移进来的。

6 研究展望

过去十年,对全球变化过程探究的强烈需求驱动了现代海洋环境生物地球化学的飞速发展。未来 10~20 年,逐步趋于系统的海洋生物地球化学过程研究也必然会在全球变化和人类活动的双重压力下,在诠释海洋生态系统运行发展机制上发挥不可替代的作用,可望在海洋碳循环及与氮循环的耦合关系、海洋生物地球化学循环和海洋食物网的相互作用、海洋生物地球化学过程的生态系统响应与动

力学表征、陆架边缘海系统的营养盐动力学等关键科学问题上有重要突破。

在陆地上,系统研究典型陆地生态系统和典型区带(农田、矿区、地下水、河口、石漠区等)的生物地球化学过程,详细解剖不同物质在不同环境条件下的水-土-气-生物的生物地球化学界面过程(包括具体的动力学过程、机制、影响因素)及其通量变化,为阐述生物地球化学过程与全球气候环境变化提供依据。地下深部生物圈和地表极端环境生物地球化学的研究,将为探索生命起源、研究特殊基因提供服务。

对于重大地质突变期的生物地球化学研究,目前的工作还主要处于资料的积累阶段,C-N-S 生物地球化学循环的研究重点主要在纵向(时间)变化,而对其横向(空间)的变化特征还未进行深入的探讨。这些时期往往会在空间上出现巨大的环境分异,如海洋的分层及氧化还原梯度、低纬度地区与高纬度地区之间的温度梯度等。这些横向的环境变化对 C-N-S 的同位素记录有很大的影响,进而影响 C-N-S 生物地球化学循环的解译。因此,分析重大地质突变期 C-N-S 同位素的空间变化特征,挖掘其所隐含的古海洋、古大气环境分布特征,才能准确获得重大地质突变期的 C-N-S 生物地球化学循环特征,查明生物与环境的协同演化规律。此外,C-N-S 等各种关键元素的库和通量的定量研究也将会有较大的突破,一些金属元素(如钼、铁、钙、铜、锌等)同位素将更多地应用到生物地球化学的研究中。

在技术层面,微生物宏基因组技术在国外迅速发展并取得重要突破和进展,我国在这方面的研究仍显得较为薄弱。一个很重要的原因是,微生物学和地球科学在相当长的时间内交叉融合较少,微生物未放到地质环境背景下进行研究,更多的关注于微生物的生物学信息,而忽略了其在环境体中对物质和能量循环的作用。那些生物地球化学功能明确又能在地质体中留下指纹的地质微生物功能群将受到人们的广泛关注。技术的突破还将带动极端环境生物地球化学研究的重要突破。目前,国内学者也已经开始重视对环境微生物宏基因组的研究,并有望在土壤、陆地热泉、深海热液喷口、水稻田、泥炭地等环境的微生物宏基因组研究中做出贡献。

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