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评 述　　微生物海洋学专题

变化海洋中的甲烷气候临爆点潜力及生成悖论

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摘要　在世纪时间尺度上, 甲烷的全球增温潜势大约是二氧化碳的30倍. 甲烷排放被认为导致了地球史上多次全球气候变化事件的发生和大规模的物种灭绝现象. 因此, 研究甲烷生成过程对于理解全球气候变化至关重要. 长期以来一直认为, 海洋中可检测到的生源甲烷完全是由低氧和无氧环境中产甲烷古菌的厌氧代谢活动产生的. 但是, 有众多研究报道显示, 全球海洋范围内的许多含氧表面水体和近表水体中的甲烷是过饱和的, 由此造成向大气甲烷净排放. 含氧海水生成甲烷的现象被称为“海洋甲烷悖论”. 尽管该悖论仍未完全得到解决, 但是最近的研究已经提出了一些有关含氧海水中甲烷生成的科学假说. 文章将对甲烷在全球气候中的重要性的理解进行总结, 并分析含氧海水环境中甲烷生成的生物过程及其机理. 此外, 我们将初步探讨相关微生物代谢过程与气候及海洋环境的全球性变化之间的关系.

关键词　海洋甲烷悖论, 天然气水合物, 海洋颗粒物, 甲基膦酸酯, DSMP, 全球变暖, 海水缺氧, 海洋酸化

1　引言

全球变暖主要是由人为温室气体排放的急剧增加而引起的, 正在显著地改变着地球的气候和环境. 2013年5月, 据夏威夷莫纳罗亚观测台测量, 日均大气二氧化碳(CO_2)浓度在人类历史上首次超过400ppm (1ppm=1mg/L)(Showstack, 2013). 大气CO_2这一浓度水平可能是地球历史上过去的340万年、1500万年甚或是3400万年以来的最高值(Beerling和Royer, 2011; Bijma等, 2013; Brigham-Grette等, 2013). 古新世-始新世极热事件(PETM)时期的碳释放率约为1.1Pg C a^{-1}, 可能是过去6600万年以来地史中的最高天然碳释放率(Zeebe等, 2016), 但是, 当前人为碳释放率(约10Pg C a^{-1})几乎是PETM碳释放率的10倍. 人为产生的过量CO_2及其排放主要是由化石燃料的燃烧、森林砍伐和水泥生产造成的, 这些因素已被确定为全球气候变化的罪魁祸首(Bijma等, 2013). 目前有大量关于人为CO_2引起气候变化及环境影响的研究, 然而, 除CO_2以外, 其他温室气体如甲烷(CH_4)和一氧化二氮(N_2O)也会造成全球变暖(Dickinson和Cicerone, 1986; Ra-

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vishankara等, 2009; Dlugokencky等, 2011; Montzka等, 2011; Carpenter等, 2012). 在过去的几个世纪, CH_4与N_2O的排放量也急剧增加, 这主要是由人类活动造成的(Forster等, 2007; Bakker等, 2014). 尽管有一天我们有可能做到对人为CO_2排放量的控制, 但其他温室气体的全球变暖效应仍然会导致全球持续升温(Solomon等, 2010; Montzka等, 2011). 任何全球变化减缓的成功策略都有必要同时考虑所有主要的温室气体.

CH_4是仅次于CO_2的最具威胁性的温室气体, 相对于前工业时代, 当前CH_4全球总辐射强迫增加贡献率接近20%(Wuebbles和Hayhoe, 2002; Montzka等, 2011; Kirschke等, 2013). 虽然大气中CH_4浓度(约1.83ppm)远低于CO_2浓度(约400ppm), 但人为造成的CH_4辐射强迫约为人为造成的CO_2辐射强迫的1/4~1/3(Etminan等, 2016; Ruppel和Kessler, 2017). 由于过度人为排放, 大气中的CH_4浓度每年以约2%的速度递增(Rasmussen和Khalil, 1981). 当前, 大气中的CH_4浓度至少是过去80万年以来的最高水平, 自工业革命以来已经增加了2.5倍, 并且主要由人类活动造成(Wuebbles和Hayhoe, 2002; Loulergue等, 2008; Dlugokencky等, 2011). 相比之下, 同期大气中CO_2浓度的增加值不足50%. 因此, 有研究强调, CH_4在全球气候变暖过程中发挥了重要作用(Ruppel和Kessler, 2017), CH_4与全球变暖之间的正反馈循环对此提供了进一步佐证(MacDougall和Knutti, 2016). 全球CH_4排放量估计约为500~600Tg a^{-1}(Conrad, 2009; Ghosh等, 2015; Tsuruta等, 2017). 在全球变暖的影响下, 预计CH_4的自然和人为排放量将会继续增加(Montzka等, 2011; Hamdan和Wickland, 2016), 这反过来将对全球温度的上升产生更大的影响.

在调节大气化学方面, CH_4也发挥了非常重要的作用. 在对流层中, CH_4被羟基自由基(OH•)氧化, 这一过程造成了臭氧污染(Montzka等, 2011; Prather和Holmes, 2017). CH_4的氧化还有助于平流层水蒸气(H_2O)的积累, 这也是导致全球变暖的一种温室气体(Isaksen等, 2011). 除了在大气中生成CH_4汇之外, 羟基自由基在其他对流层温室气体(如氢氟碳化合物和氢氯氟烃)的破坏方面也发挥着主要作用(Montzka等, 2011). 此外, 羟基自由基能够氧化对流层中含有的二氧化硫(SO_2), 形成对全球气候具有一定降温作用的硫酸盐气溶胶(Montzka等, 2011). 因此, 通过延长大气CH_4的寿命和改变对流层中其他温室气体的动态, 日益增强的CH_4对羟基自由基的消耗有可能对全球变暖起到正反馈作用(Isaksen等, 2011; Montzka等, 2011). CO_2是CH_4氧化的终产物, CH_4由此还会提高大气中CO_2的浓度(Isaksen等, 2011). 此外, 即使CH_4的人为排放可以终止, 且它的大气寿命只有9年左右, CH_4也可能通过热膨胀对持续发生的海平面上升产生辐射强迫诱导的长期(>200年)重要影响(Zickfeld等, 2017; Sonnemann和Grygalashvyly, 2014). 总体而言, CH_4可能会在未来的地球气候和环境系统中发挥越来越重要的作用.

以100年期计, CH_4的全球增温潜势(GWP)是CO_2的20多倍. 然而, 为了在不久的将来(几十年内)能够对全球变暖进行及早控制, 以20年期计的CH_4全球增温潜势则更值得考虑, 其是CO_2的70多倍(Wuebbles和Hayhoe, 2002; Karthikeyan等, 2015). 虽然在短时间内找到解决方案极具挑战, 但为了避免跨出警戒线并错失良机, 我们仍需迅速及早地采取行动, 以避免全球变化带来的危险(Hansen等, 2007; MacCracken, 2008). 有人提出, 当前的人类活动所引起的全球变暖可能是不可逆转的, 如果我们不能迅速果断地采取行动在不久的将来阻止气候变化, 就有可能引发多米诺骨牌效应, 导致地球永久失去平衡和宜居状态(Frondel等, 2002; Solomon等, 2009; Hansen等, 2013; Schleuning等, 2016). 由于大气中CH_4的稳态寿命远远短于CO_2的稳态寿命, 因此减少CH_4(以及其他短寿命温室气体)的排放应该能够有效、快速地缓解气候变化(Montzka等, 2011; Karol等, 2013). 移除大气中的CH_4和其他短寿命温室气体比移除CO_2可以更快地减少辐射强迫(Zickfeld等, 2017). 虽然现已查实多种自然和人为的甲烷排放源(图1), 但对其中一些的形成机制及对大气CH_4的贡献尚未得到明确解答, 海洋中的尤其如此(Kirschke等, 2013; Hamdan和Wickland, 2016). 这一情况影响了对CH_4引起的全球变暖效应的机理性和综合性的预测及其在减缓气候变化中的应用.

2 海洋通常是大气甲烷的净排放源

一般而言, 海洋可净吸收人为产生的CO_2. 据估计, 自工业革命以来大约40%的人为排放CO_2被海洋所吸收(Sabine等, 2004; McKinley等, 2016; DeVries等, 2017). 然而, 海洋通常被认为是大气CH_4的源, 尽管多

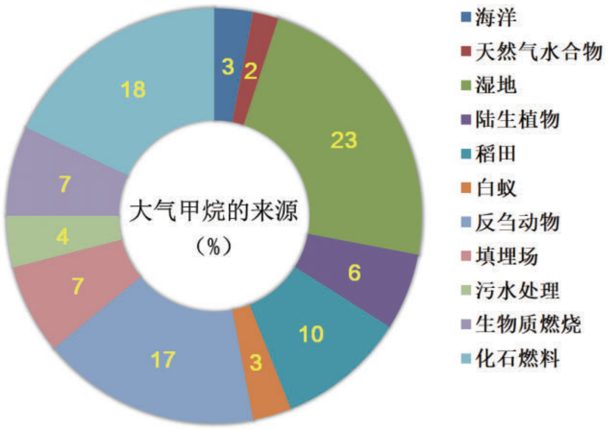

图 1　全球甲烷排放源概况

数据来自Conrad(2009)和Aronson等(2013)

种估算表明其贡献率并不高(Bange等, 1994; Matthews, 1994; Krüger等, 2005; Carpenter等, 2012). 海洋至大气的CH_4排放率估计约为1.3~13Tg a^{-1}(Ruppel和Kessler, 2017). 然而, 如此大的估值范围表明, 由于缺乏足够的采样覆盖率和全球海洋的长时间序列测量值, 估算中包含很多不确定性, 并且它们无法捕捉到海洋CH_4排放的时空动态(Bange, 2006; Fischer等, 2013; Hamdan和Wickland, 2016). 海-气CH_4通量随着海洋环境的改变而发生较大幅度的变化, 而且控制CH_4通量大幅度时空变化的机制尚未完全得到解析(Bates等, 1996; Ortiz-Llorente和Alvarez-Cobelas, 2012; Wilson等, 2017). 在区域和全球范围内缺乏具有足够时间和空间频率及分辨率的长期测量阻碍了全球海洋CH_4数据的整合, 从而无法对全球海洋的CH_4排放量进行准确的估算.

与海洋相比, 全球湿地是CH_4排放更大的源(Bridgham等, 2013). 最近一项研究报告显示, 从2000~2007年, 全球范围内的湿地平均CH_4排放量为(177.2±49.7)Tg CH_4 a^{-1}(Zhang等, 2017). 作为陆-海界面, 沿海湿地也对近岸海水的CH_4释放产生了巨大影响. 由于大量有机物质和营养盐经陆地、河流与人类活动输入, 沿海湿地发生着剧烈的微生物活动, 这其中就包括CH_4的生成(Vizza等, 2017; Xiao L等, 2017). 虽然沿海湿地(指退潮时水深不超过6m的海水区域)(Navid, 1989)仅占全球海洋系统的一小部分, 但其产生的CH_4可能构成了邻近河口和近岸海域CH_4排放的主要来源(Wang等, 2016).

在海洋中, 许多河口和近岸水域是CH_4的排放热点环境, 这通常是由强烈的陆源和沉积物源输入以及低氧和缺氧条件下原位微生物的产甲烷作用引起的(Zhang等, 2004, 2008; Bange, 2006; Zhou等, 2009; Borges等, 2016; Upstill-Goddard和Barnes, 2016; Farías等, 2017; Sela-Adler等, 2017; Tseng等, 2017). 除了直接输送陆源CH_4外, 河流径流通常含有高浓度的有机物和营养盐, 会刺激河口与沿海微生物群落中多种生物生产和呼吸活动, 并产生局部和(或)季节性的缺氧甚至是无氧条件(Naqvi等, 2010; Dang和Jiao, 2014). 此外, 河口与近岸水体中通常含有高浓度的悬浮颗粒物, 可能在颗粒物内部存在缺氧和无氧微环境, 有利于厌氧微生物的代谢过程(Brooks等, 1981; Wright等, 2012; Dang和Jiao, 2014; Dang和Lovell, 2016). 海水中的缺氧环境和微环境有助于厌氧产甲烷古菌的产甲烷作用及CH_4的海-气释放(Offre等, 2013; Wen等, 2017). 尽管河口与近岸海域仅占全球海洋的一小部分, 但它们的CH_4排放量可能占海洋CH_4总排放量的75%左右(Bange等, 1994; Reeburgh, 2007).

沿岸上升流能够将底层水CH_4带到表层水, 直接导致CH_4的释放(Bange等, 1998; Capelle和Tortell, 2016; Chronopoulou等, 2017). 此外, 上升流过程增富真光层水体营养盐和有机物, 刺激水体有机物生物生产过程及微生物群落呼吸作用, 产生海水CH_4厌氧生成作用所需的缺氧和无氧环境(Sansone等, 2001; Wright等, 2012; Bakun, 2017; Shepherd等, 2017). 因此, 边缘海上升流区缺氧和无氧水层或多或少是CH_4生成和释放环境. 气候变化可能加剧沿海上升流, 特别是在高纬度地区(Sydeman等, 2014; Wang等, 2015), 这种变化可能会严重影响近海生态系统的结构和功能, 包括增强的CH_4和N_2O等温室气体的生成及向大气排放.

沉积物是海水CH_4的主要来源(Orcutt等, 2013; Chronopoulou等, 2017; Tseng等, 2017; Xiao K Q等, 2017). 沉积物中的缺氧条件促进了诸如产甲烷等厌氧微生物代谢作用(Ferry和Lessner, 2008; Sela-Adler等, 2017). 边缘海沉积物接纳大量的有机物, 有助于微生物源CH_4的生成(Wen等, 2017). 世界海洋许多边缘海沉积环境都含有甲烷水合物(也称为天然气水合物), 因其亚稳态特性及对变暖高度敏感, 天然气水合物向大气净排放CH_4(Conrad, 2009). 虽然从海洋天然气水

合物排放到大气的CH_4的估算量目前很小(约6Tg a^{-1}, 范围2~9Tg a^{-1})(Ruppel和Kessler, 2017), 但天然气水合物有可能在相对较短时间内释放出大量的CH_4气体, 因此其可能构成未来全球气候变化的临爆点(Archer等, 2009; Carpenter等, 2012).

3 天然气水合物甲烷排放是气候变化潜在影响因素

在含有天然气水合物的沉积物中, CH_4的渗流量可能非常惊人(Boetius和Wenzhöfer, 2013; Rakowski等, 2015). 例如, 在活跃渗流区域, 海水中由海底上升的CH_4气泡可达400m高度(Dang等, 2010). 生物成因CH_4与热成因CH_4的生成过程都可以促进CH_4在海洋沉积物中的积累(Archer, 2007; Reeburgh, 2007; Hester和Brewer, 2009). 在合适的气体组成、低温和高压等条件下, 海洋沉积物中可形成甲烷水合物(Ruppel和Kessler, 2017). 据估计, 海洋天然气水合物中可能含有大量的CH_4, 全球范围内的总量为1700~4100000Gt C (Kvenvolden, 1988). 最新估算表明, 海洋甲烷水合物的存量可能处于最初估计值的低端, 约为1100~2000Gt C (Archer等, 2009; Boswell和Collett, 2011; Kretschmer等, 2015; Ruppel和Kessler, 2017). 由于沉积物天然气水合物的空间分布在海洋中极不均匀, 并且通常缺乏全球海洋的采样覆盖率, 因此要对天然气水合物资源进行准确估算并非易事(Marín-Moreno等, 2016), 而且对来源于全球分散的天然气水合物的CH_4排放通量进行估算也是相当困难的(Matthews, 1994).

尽管每年都会有大量的CH_4气体从海底天然气水合物中解离出来, 但是只有不定量(通常只是很小一部分)水合物CH_4实际上可能进入大气中. 按照一般估算, 水合物CH_4占大气CH_4总量的比例可能仅为2%左右(Matthews, 1994; Conrad, 2009; Hamdan和Wickland, 2016; Ruppel和Kessler, 2017). 厌氧与好氧型嗜甲烷微生物(包括细菌和古菌)消耗了沉积物和海水中大部分的游离CH_4, 可能因此大大降低了全球海洋向大气的甲烷释放通量(Krüger等, 2005; Reeburgh, 2007; Knittel和Boetius, 2009; DiSpirito等, 2016; James等, 2016). 很多嗜甲烷微生物携带固氮遗传潜力, 通过生物固氮促进CH_4代谢(Auman等, 2001; Dedysh等, 2004; Pernthaler等, 2008; Dang等, 2009; Dekas等, 2009; Khadem等, 2010; Fernández-Carrera等, 2016). 这种遗传和生化适应策略表明, 海洋嗜甲烷微生物可能与富含CH_4海洋环境在地球历史中完成共进化.

最近的研究表明, 水合物CH_4的排放对全球变暖存在高度不确定的影响(Biastoch等, 2011; Kretschmer等, 2015; Mestdagh等, 2017). 海底天然气水合物突然分解而导致的大量CH_4排放被认为是导致地球历史上某些历史事件中全球变暖的一个非常重要的因素, 这其中就包括PETM事件及马林诺“雪球”冰期的终结等(Dickens等, 1995, 1997; Kennett等, 2003; Maslin等, 2004; Svensen等, 2004; Kennedy等, 2008; Dickens, 2011). 大规模突发性海洋天然气水合物分解造成的灾难性CH_4排放也可能导致了大灭绝事件的发生(Katz等, 1999; Norris和Röhl, 1999; Hesselbo等, 2000). 尽管“可燃冰喷射假说”受到了质疑(Higgins和Schrag, 2006; Sowers, 2006; Gutjahr等, 2017), 但在数万年时间尺度上因海水持续升温造成的天然气水合物分解所排放出的CH_4可能仍然对地球气候产生重要的影响(Archer等, 2009), Leifer等(2006)的研究发现表明, 海底天然气水合物突然分解引发的大量CH_4气泡的释放, 即海底CH_4渗漏“井喷”式喷发, 可引起快速气候变化. 此外, 水合物分解释放出的CH_4在氧化过程中消耗了O_2并产生CO_2, 导致海洋缺氧和酸化(Biastoch等, 2011; Boudreau等, 2015).

天然气水合物的亚稳态特性表明其对温度和压力等变化敏感, 沉积环境的水合物可能受到海水升温等环境干扰而发生分解(Reagan和Moridis, 2007; Hunter等, 2013; Ruppel和Kessler, 2017). 据此推测, 随着全球和海洋温度的升高, 天然气水合物分解产生的CH_4排放可能会变得更剧烈(Kvenvolden, 1988). 有证据表明, 全球变暖已造成了海洋内部温度的升高(Masuda等, 2010; Mora等, 2013; Levin和Le Bris, 2015). 模拟研究表明, 在持续全球变暖的影响下, 海洋天然气水合物中的CH_4排放量呈上升趋势, 在诸如北冰洋和边缘海浅水海域等敏感环境中尤为如此(Reagan和Moridis, 2007; Shakhova等, 2010; Isaksen等, 2011; Marín-Moreno等, 2013; Thatcher等, 2013; James等, 2016). 已有的观察和模型预测结果显示, 响应全球变暖, CH_4会从天然气水合物中被更多地释放到大气中(Archer, 2007; Thatcher等, 2013; Stranne等, 2017). 而且, 全球变化绝不是一个简单过程, 实际上涉及地球系统及其组

分的非线性变化和突发性变化(McNeall等, 2011). 这种复杂性表明, 特定外源强迫发生的微小变化可能导致气候巨大和(或)不可逆转的变化(McNeall等, 2011). 例如, 许多不同海洋环境中的海底沉积物CH_4渗流经常被发现是间歇性事件(Stranne等, 2017). 除全球变暖引起的海底温度上升造成的影响外, 海洋中还存在其他可能会影响沉积天然气水合物稳定性和CH_4排放的过程和因素. 当前的气候变化可能会改变海洋环流模式和某些洋流的强度, 例如, 墨西哥湾流中层水的温度变化可能会造成沿着其北美边缘海的宽阔流径内的海底天然气水合物快速失去稳定性(Phrampus和Hornbach, 2012). 如果海底火山和天然气水合物这两个地质特征恰好存在于同一地区, 那么海底火山喷发就可能会导致天然气水合物分解释放出大量CH_4气体(Svensen等, 2004), 因为地球上大多数(约80%)火山活动发生在海底环境中, 大大增加了该情形发生的可能性(Embley等, 2006). 大规模海底滑坡是一种主要的地质灾害, 可引发海盆尺度海啸、地震、火山、飓风和天然气水合物分解等会引发海底滑坡灾害(Masson等, 2006; Geissler等, 2016; Handwerger等, 2017), 反过来又会导致更大规模的天然气水合物分解活动, 并释放出CH_4. 地震还会直接导致海底产生裂隙及天然气水合物分解, 加剧CH_4渗漏(Tsunogai等, 2012; Fischer等, 2013; Obzhirov, 2013; Geersen等, 2016). 全球变暖可能会与上述一些海底地质灾害过程产生相互影响, 例如, 底层海水变暖可能会造成天然气水合物失去稳定性, 进而可能会引起海底滑坡的发生, 从而进一步引发水合物CH_4的释放. 这种情况可能会发生在北冰洋和其他一些浅海区域. 在格陵兰和南极, 可能还存在着另外一种机制. 在这里, 全球变暖导致冰盖萎缩, 并通过地壳均衡作用导致受影响的海底大陆坡升高. 静水压力的下降可能会破坏海底天然气水合物的稳定性, 从而导致大规模滑坡和天然气水合物分解事件的发生(Maslin等, 2010). 此外, 海上石油和天然气水合物的商业开发也可能会引发天然气水合物分解并释放出CH_4(Glasby, 2003; Zhang和Zhai, 2015; Fernández-Carrera等, 2016). 水合物CH_4释放对全球变暖产生的正反馈效应以及各种引发大规模“灾难性”天然气水合物CH_4释放可能性的存在, 合理地说明了学术界对海底天然气水合物对全球气候变化潜在重要影响的关注(Reagan和Moridis, 2008; Archer等, 2009; Carpenter等, 2012; Ruppel和Kessler, 2017).

4　海洋甲烷悖论及可能机制

许多微生物产生温室气体, 加剧全球变暖效应, 例如, 据估算, 产甲烷古菌占与人类活动有关的甲烷排放量的近60%(Jabłoński等, 2015). 曾经认为甲烷仅是由广古菌门(即甲烷杆菌纲、甲烷球菌纲、甲烷微菌纲、甲烷火菌纲)中的产甲烷古菌产生(Balch等, 1979; Garcia等, 2000; Liu和Whitman, 2008). 最近发现了一些广古菌门新的产甲烷古菌类群, 如Methanoflorentaceae科(隶属于甲烷微菌纲)、Methanocellales目和Methanomassiliicoccales目(分别隶属于甲烷微菌纲和热原体纲), 以及Methanofastidiosa纲和Methanonatronarchaeia纲(Sakai等, 2008; Iino等, 2013; Mondav等, 2014; Nobu等, 2016; Sorokin等, 2017). 另外, 近期还发现了非广古菌门的产甲烷古菌类群, 隶属于深古菌门(Bathyarchaeota)或韦斯特古菌门(Verstraetearchaeota)(Evans等, 2015; Vanwonterghem等, 2016).

在产甲烷古菌中现已确定了四种不同的产甲烷生化途径: (1) 采用H_2作为电子供体还原CO_2以生成CH_4的氢营养型产甲烷途径; (2) 采用醋酸盐作为反应底物进行甲烷歧化生成的乙酸发酵产甲烷途径; (3) 采用甲基化一碳化合物(如甲醇、甲胺和甲硫醇)为反应底物进行甲烷歧化生成的甲基营养型产甲烷途径; (4) 采用甲基化一碳化合物作为反应底物并以H_2和(或)甲酸盐作为电子供体生成甲烷的甲基还原产甲烷途径(Kallistova等, 2017). 辅酶M(CoM)和辅酶F_{420}是产甲烷古菌的核心辅因子, 甲基辅酶M还原酶是一种独特的关键酶复合物, 在CH_4生成的最后一步发挥作用(Balch等, 1979; Friedrich, 2005; Krishnakumar等, 2008; Purwantini等, 2014; Dziewit等, 2015; Greening等, 2016). 上述所有产甲烷古菌的共同生理特征是它们是厌氧微生物, 只能在诸如缺氧海洋沉积物和海水等缺氧环境中产甲烷(Valentine, 2011; Offre等, 2013; Welte和Deppenmeier, 2014). 传统的产甲烷过程中产生的代谢能是非常少的(Schink, 1997; Schäfer等, 1999), 在存有其他氧化剂和氧化代谢过程的环境中, 产甲烷古菌在群落中几乎很难成为成功的竞争者(Sela-Adler等, 2017; Wen等, 2017). 然而, 令人惊讶的是, 相对于大气的CH_4浓度, 全球海洋的很多表层和近表层含氧水体

的CH_4却是过饱和的，这一令人费解的现象被称为“海洋甲烷悖论”(Reeburgh, 2007; Karl等, 2008). 大量证据表明，这些海域中的CH_4很可能是在原位水体中产生的，并构成了向大气的净排放(Lamontagne等，1971; Scranton和Brewer, 1977). 据估算，全球大洋排入大气的CH_4通量可能约为3.6Tg a^{-1}(Lambert和Schmidt, 1993; Bange等，1994), 而其他一些研究则表明实际通量(约0.4Tg a^{-1})可能低一个数量级(Bates等，1996; Rhee等，2009). 虽然开阔大洋向大气的CH_4释放通量估计值在不同的研究中差异很大，但是人们普遍认为大洋通常是向大气净排放CH_4的源, 同时, 有关该环境的甲烷生成机制目前尚不很清楚且一直处于激烈的争论中(Reeburgh, 2007; Karl等, 2008; Conrad, 2009; Rakowski等, 2015; Tseng等, 2017).

海洋颗粒物和浮游动物肠道内的缺氧微环境中可能存在活跃的产甲烷古菌，贡献于含氧水体原位的CH_4生成和积累(Oremland, 1979; Brooks等, 1981; Cynar和Yayanos, 1991; de Angelis和Lee, 1994; Karl和Tilbrook, 1994; Tilbrook和Karl, 1995; Marty等, 1997; Holmes等, 2000; Reeburgh, 2007; Sasakawa等, 2008; Ditchfield等, 2012; Dang和Lovell, 2016). 一些产甲烷古菌可能已经对各种不利和多变的环境形成了生理生态适应. 例如，一些产甲烷古菌可以在有氧条件下存活，并且在环境有利时恢复产CH_4活性(Zehnder和Wuhrmann, 1977; Jarrell, 1985; Sieburth等, 1993; Tholen等, 2007; Poehlein等, 2017). 由于日间浮游植物的产氧光合作用及夜间群落的耗氧性呼吸，海洋表层水可能会经历溶氧量的昼夜交替变化(Dang和Lovell, 2016). 在夜间，海洋颗粒物和生物膜内更易形成缺氧甚至是无氧微环境, 从而促进产甲烷作用. 而且，一些从环境中分离得到的产甲烷菌株携带多种粘附素类蛋白, 有利于定殖海洋颗粒物和其他基质物(如浮游动物的体表和/或消化道) (Dang和Lovell, 2016; Poehlein等, 2017). 最近，在含氧土壤中发现了一种新型的产甲烷古菌，暂定名为“悖论甲烷丝菌”(Candidatus Methanothrix paradoxum), 其在土壤团聚颗粒物缺氧微环境中可进行乙酸发酵产甲烷(Angle等，2017). 该古菌代谢新颖性在于其在低乙酸盐条件下具有强代谢底物竞争和获得能力，在有氧环境中具备其他产甲烷古菌所不具备的生理生态优势. 在含氧的永久冰土、淡水、湿地、河口和海洋环境中，发现普遍存在与悖论甲烷丝菌16S rRNA基因序列高度相似的古菌序列(Angle等, 2017), 且其中的一些序列来自于与海洋雪有关的原核生物群落(Vojvoda等, 2014). 该特定产甲烷古菌的发现表明，缺氧微环境假说可以有效解释“海洋甲烷悖论”, 至少对于某些海洋水体来说是如此.

无颗粒物的含氧海水中也有CH_4生成(Bogard等, 2014), 并且某些研究发现, 浮游动物对含氧水体CH_4的生成贡献很小(Schmale等, 2018). 为了获得磷, 包括蓝细菌在内的一些海洋细菌能够代谢甲基膦酸酯并生成副产物CH_4，这一发现进一步尝试性地解释了海洋甲烷悖论(Karl等, 2008; Dyhrman等, 2009; Beversdorf等, 2010; Martínez等，2013; Carini等，2014; del Valle和Karl, 2014; Repeta等，2016; Horsman和Zechel, 2017; Sosa等, 2017; Teikari等, 2018). 此外, 已有研究表明海雪颗粒物是甲基膦酸酯降解和CH_4生成的热点(del Valle和Karl，2014). 奇古菌门氨氧化古菌、蓝细菌和其他一些海洋微生物能够生成大量的甲基膦酸酯(Dyhrman等，2009; Metcalf等，2012; Van Mooy等, 2015; Dang和Chen, 2017). 除细菌之外, 还发现了一些古菌含有可以编译碳-磷裂解酶的基因, 其负责分解诸如甲基膦酸酯等反应底物并产生CH_4(Hove-Jensen等, 2014). 参与甲基膦酸酯生成和消耗的不同微生物(Dang等，2013), 特别是在磷酸盐匮乏的环境中, 可能会在全球海洋表层水中产生大量的CH_4，并对海-气甲烷净排放通量产生显著贡献.

尽管与甲基膦酸酯和颗粒物微环境相关的甲烷生成假说非常诱人且可能非常重要，但是科学家还提出了一些其他微生物过程假说来解释有氧海水中CH_4的生成. 在二甲基巯基丙酸内盐(DMSP)及其中间降解产物如二甲基硫(DMS)、甲硫醇(MeSH)和甲硫基丙酸甲酯(MMPA)的微生物代谢过程中可能也会产生CH_4 (Welsh, 2000; Damm等, 2008, 2010; Florez-Leiva等, 2013; Weller等, 2013; Zindler等, 2013). 某些产甲烷古菌可以合成甲硫醇：辅酶M甲基转移酶或其他底物特异辅酶M甲基转移酶, 利用甲基化硫化合物(如DMS、MeSH、MMPA等)作为反应底物生成CH_4(Tallant和Krzycki, 1997; Tallant等, 2001; Fu和Metcalf, 2015). 许多产甲烷古菌已经被分离纯化出来，并证明其可以利用甲基化硫化合物进行甲基营养型产甲烷作用(Kiene等, 1986; Oremland等, 1989; Finster等, 1992; van der Maarel和Hansen，1997; Lomans等，1999; Lyimo等,

2000; Cha等, 2013; Fu和Metcalf, 2015). 然而, 所有这些古菌菌株仅在缺氧条件下才能产生CH_4. 有关甲基化硫化合物利用型厌氧甲基营养型产甲烷古菌是否以及如何在海洋表层水含氧条件下应对氧胁迫这一问题, 目前还没有得到解决. 最近的比较基因组分析揭示了产甲烷古菌的耐氧性差异, 表明Ⅱ类产甲烷古菌可能比Ⅰ类产甲烷古菌更能适应微氧环境(Lyu和Lu, 2018). 此外, 有人指出, 某些需氧细菌可利用DSMP作为碳源, 并在有氧海水中产生CH_4作为代谢副产物(Damm等, 2010). 甲基化硫化合物相关的CH_4生成机制可能构成了海-气CH_4通量及海洋碳与硫循环中的重要途径. DMSP是一种丰富的浮游植物和珊瑚代谢物, 在保护生物体免受渗透压、氧化和高温压力等方面起到了重要作用(Bullock等, 2017). CH_4是强效温室气体(Bogard等, 2014), 而二甲基硫则是自然界中最重要的生源气候冷却气体(Carini, 2016). 浮游植物水华是全球近海海域所面临的世界性环境与生态问题(Dang和Jiao, 2014; Dang和Lovell, 2016; Dang和Chen, 2017). 随着人为影响的增强, 例如将过量的营养盐排放到海水中, 浮游植物水华的发生将更加频繁和广泛, 在河口和近岸海域尤甚(Jiao等, 2014). 这预示着, 边缘海浮游植物将生成更多的DMSP以应对海洋富营养化的趋势(Dang和Lovell, 2016). 在这种情况下, 我们可以合理假设, 海洋微生物将DMS转化为CH_4可能会进一步打破地球热平衡并加速和增强全球变暖效应(Florez-Leiva等, 2013).

除了关于有氧海水中甲烷生成悖论微生物过程和机制的上述三个主要假说外, 学术界还提出了其他一些假说. 陆生植物是CH_4的一个主要来源(Conrad, 2009). 最近发现, 海洋赫氏圆石藻(*Emiliania huxleyi*)可直接产CH_4, 且该过程无需产甲烷古菌和产甲烷细菌的参与(Lenhart等, 2016). 赫氏圆石藻在海洋中分布很广, 是海洋中丰度最高的钙化浮游植物, 且在海洋碳封存中发挥重要作用(Krumhardt等, 2017). 赫氏圆石藻在有氧表层海水中CH_4的生成及对海-气CH_4通量的贡献值得深入、系统的研究. Damm等(2015)最近提出了关于在硝酸盐胁迫的海洋环境中CH_4产生机制的另一假说. 细菌呼吸和细胞膜低通透性可能会产生和维持细胞内的厌氧条件, 有助于含氧海水中细菌细胞内的DMSP依赖型CH_4的生成(Damm等, 2015). 单细胞代谢模型分析进一步支持了这一观点(Damm等, 2015).

关于海洋甲烷悖论, 上述提出的含氧海水中的CH_4生成的大多数微生物过程和机制可能都是有效的. 它们可能在不同的环境和(或)生物条件下起作用. 然而, 目前仍不清楚造成这些差异的环境或生物决定因素究竟是什么. 它们各自对于海水CH_4收支和海-气CH_4排放的作用尚不清楚, 同时对于海洋磷和硫循环的定量影响也未可知. 这些不确定因素表明, 有关海洋微生物群落和全球变化的研究仍是挑战, 但同时也为未来的科学突破提供了机遇.

5　海洋甲烷研究的前景

温室气体引起的全球气候变化是非常复杂的过程, 存在复杂的相互作用机制和正反馈效应, 使得全球变暖难以得到缓解. CH_4作为强效温室气体在推动全球温度升高方面发挥着重要作用. 然而, 与CH_4这个最简单有机分子相关的生物地球化学循环中涉及的过程和机理的诸多特征仍未得到解决. 通过海洋沉积物天然气水合物分解所释放的CH_4是大气中CH_4的一个净源. 一些最近的研究表明, 以这种方式释放出的CH_4对生态和气候产生了意想不到的影响. 近来发现, 斯瓦尔巴特边缘海海底CH_4气泡上升产生的上升流将深水营养盐输送到了海洋表层水中, 从而增强了光合固定效应(Pohlman等, 2017). 最近的一项研究表明, 在近岸浅海海域, 渗流区可能普遍存在CH_4大量排放现象(Borges等, 2016). 虽然CH_4释放量不可避免地增大了, 但像斯瓦尔巴特海和其他类似的具有CH_4相关的地质和生态过程的海洋环境, 可能构成了温室气体净的汇, 从而对区域和全球气候产生了降温效应(Pohlman等, 2017).

人类已经从历史中汲取了很多教训, 其中之一便是现实世界通常比最初想象的更复杂. 关于全球变暖过程中的海源性CH_4存在着诸多不确定性和未知因素. 尽管如此, 我们对CH_4在海洋碳循环和全球气候变化中所起作用的认识已经在逐渐进化, 例如, 无论在有氧海水中甲烷生成悖论背后的过程和机理是什么, 似乎总有微生物活动的参与(Reeburgh, 2007). 微生物及它们代谢途径和环境适应策略的多样性是自然生态系统过程和功能复杂性的基础, 这其中就包括在有氧海洋环境中CH_4的产生.

在持续的全球和海洋环境变化的影响下, 某些微

生物过程可能会发生变化. 全球变暖可能对全球微生物产CH_4产生直接影响, 现已发现微生物产CH_4对温度变化的敏感性和反应程度比呼吸作用和光合作用更强烈(Yvon-Durocher等, 2014). 随着海洋温度升高, 有人认为海洋CH_4生成和排放的增加将超过CO_2(Yvon-Durocher等, 2014). 人类活动的增强和海洋变暖将加剧大多数河口、近岸海域及大洋氧最小带的缺氧情况(Gruber, 2011; Gilly等, 2013; Dang和Jiao, 2014; Dang和Lovell, 2016; Dang和Chen, 2017). 一些低氧水体可能会生成缺氧核心区, 从而促进微生物产CH_4. 在全球气候变化影响下, 某些海区内的上升流将得到加强(Sydeman等, 2014; Wang等, 2015), 这可能会生成缺氧甚至是无氧水体, 从而促进产甲烷作用(Bakun, 2017). 上升流的增强也会刺激浮游植物水华的形成(Kudela等, 2010), 通过增加DMSP的产量和提高海洋颗粒物的形成而提高CH_4的生成量(Damm等, 2008; Damm等, 2010; Florez-Leiva等, 2013; Weller等, 2013; Dang和Lovell, 2016). 此外, 海洋酸化作用的增强可以减低海洋中的硝化作用, 这是因为更多的环境氨会转化为铵, 进而降低海水和沉积物中氨氧化古菌和氨氧化细菌的氨氧化速率(Beman等, 2011; Braeckman等, 2014; Dang和Chen, 2017). 目前尚不清楚这如何影响氨氧化古菌(而非氨氧化细菌)甲基膦酸酯的生产及相关的CH_4的生产. 此外, 产甲烷微生物和甲烷氧化微生物控制着CH_4的产生和消耗, 从而控制其在海洋环境中的丰度和动态. 某些微量元素(如Co、Cu、Fe和Ni)是参与微生物甲烷生成和甲烷营养型过程的酶的重要辅助因子(Glass和Orphan, 2012; DiSpirito等, 2016; Paulo等, 2017; Semrau等, 2018), 这些微量元素在海洋中的生物可利用度可能在涉及CH_4生成和消耗的微生物活动中起重要作用. 另一方面, 重金属可能会通过酶毒化作用对产甲烷微生物和甲烷营养型微生物的代谢和生理活性产生负影响. 海洋变暖、酸化、缺氧、富营养化和污染都可能影响海洋环境中微量元素的生物可利用性, 并影响重金属的作用(Dang和Chen, 2017). 微生物活动与海洋无机元素和污染物之间的关联使得对未来气候和海洋环境变化的预测变得更加复杂和困难. 宏基因组学、宏转录组学和宏蛋白质组学等“组学”技术的进步为研究和理解海洋CH_4动态中的微生物及其过程和机理提供了契机(Lloyd, 2015). 将“组学”分析与原位通量测量相结合可以开发出更强大、更准确的生物地球化学模型, 从而更好地预测海洋CH_4行为及其对全球变化的影响.

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