变化海洋中的甲烷气候临爆点潜力及生成悖论

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收稿日期: 2018-09-24; 收修改稿日期: 2018-10-05; 接受日期: 2018-10-09; 网络版发表日期: 2018-10-30

国家重点研发计划项目(编号: 2016YFA0601303)、国家海洋局项目(编号: GASI-03-01-02-05)、国家自然科学基金项目(批准号: 41676122、91328209、91428308)和中国海洋石油总公司项目(编号: CNOOC-KJ125FZDXM00TJ001-2014和CNOOC-KJ125FZDXM00ZJ001-2014)资助

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、1500万年甚至是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-

中文引用格式: 党宏月, 李嘉. 2018. 变化海洋中的甲烷气候临爆点潜力及生成悖论. 中国科学: 地球科学, 48: 1551–1567, doi: 10.1360/N072018-00266

英文引用格式: Dang H, Li J. 2018. Climate tipping-point potential and paradoxical production of methane in a changing ocean. Science China Earth Sciences, 61: 1714–1729, <https://doi.org/10.1007/s11430-017-9265-y>

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($\text{OH}\cdot$)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Grygalashvily, 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 $1.3\sim 13\text{Tg a}^{-1}$ (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 $(177.2\pm 49.7)\text{Tg CH}_4 \text{ a}^{-1}$ (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; Farias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CH₄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CH₄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, CH₄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CH₄气泡可达400m高度(Dang等, 2010). 生物成因CH₄与热成因CH₄的生成过程都可以促进CH₄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CH₄, 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(Marin-Moreno等, 2016), 而且对来源于全球分散的天然气水合物的CH₄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CH₄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CH₄实际上可能进入大气中. 按照一般估算, 水合物CH₄占大气CH₄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CH₄, 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CH₄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CH₄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CH₄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CH₄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CH₄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Schrage, 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CH₄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CH₄气泡的释放, 即海底CH₄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CH₄在氧化过程中消耗了O₂并产生CO₂, 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CH₄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CH₄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; Marin-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, CH₄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(McNeill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(McNeill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; Handwerker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; Obzhirev, 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Zhao, 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 3.6 Tg a^{-1} (Lambert和Schmidt, 1993; Bange等, 1994), 而其他一些研究则表明实际通量(约 0.4 Tg 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 Methanotherithrix paradoxum), 其在土壤团聚颗粒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磷酸酯并生成副产物 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; Martinez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は甲基磷酸酯降解和 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磷酸酯(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磷酸酯等反应底物并产生 CH_4 (Hove-Jensen等, 2014). 参与甲基磷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.

尽管与甲基磷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. DSMP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DSMP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(Flórez-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DSMP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(Sydean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缓海洋中的硝化作用, 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.

参考文献

- Angle J C, Morin T H, Solden L M, Narrowe A B, Smith G J, Borton M A, Rey-Sanchez C, Daly R A, Mirfenderesgi G, Hoyt D W, Riley W J, Miller C S, Bohrer G, Wrighton K C. 2017. Methanogenesis in oxygenated soils is a substantial fraction of wetland methane emissions. *Nat Commun*, 8: 1567
- Archer D. 2007. Methane hydrate stability and anthropogenic climate change. *Biogeosciences*, 4: 521–544
- Archer D, Buffett B, Brovkin V. 2009. Ocean methane hydrates as a slow tipping point in the global carbon cycle. *Proc Natl Acad Sci USA*, 106: 20596–20601
- Aronson E L, Allison S D, Helliker B R. 2013. Environmental impacts on the diversity of methane-cycling microbes and their resultant function. *Front Microbiol*, 4: 225
- Auman A J, Speake C C, Lidstrom M E. 2001. *nifH* sequences and nitrogen fixation in type I and type II methanotrophs. *Appl Environ Microbiol*, 67: 4009–4016
- Bakker D C E, Bange H W, Gruber N, Johannessen T, Upstill-Goddard R C, Borges A V, Delille B, Löscher C L, Naqvi S W A, Omar A M, Santana-Casiano J M. 2014. Air-sea interactions of natural long-lived greenhouse gases (CO_2 , N_2O , CH_4) in a changing climate. In: Liss P S, Johnson M T, eds. *Ocean-Atmosphere Interactions of Gases and Particles*. Heidelberg: Springer
- Bakun A. 2017. Climate change and ocean deoxygenation within intensified surface-driven upwelling circulations. *Phil Trans R Soc A*, 375: 20160327
- Balch W E, Fox G E, Magrum L J, Woese C R, Wolfe R S. 1979. Methanogens: Reevaluation of a unique biological group. *Microbiol Rev*, 43: 260–296
- Bange H W. 2006. Nitrous oxide and methane in European coastal waters. *Estuar Coast Shelf Sci*, 70: 361–374
- Bange H W, Bartell U H, Rapsomanikis S, Andreae M O. 1994. Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane. *Glob Biogeochem Cycle*, 8: 465–480
- Bange H W, Ramesh R, Rapsomanikis S, Andreae M O. 1998. Methane in surface waters of the Arabian Sea. *Geophys Res Lett*, 25: 3547–3550
- Bates T S, Kelly K C, Johnson J E, Gammon R H. 1996. A reevaluation of the open ocean source of methane to the atmosphere. *J Geophys Res*, 101: 6953–6961
- Beerling D J, Royer D L. 2011. Convergent Cenozoic CO_2 history. *Nat Geosci*, 4: 418–420

- Beman J M, Chow C E, King A L, Feng Y, Fuhrman J A, Andersson A, Bates N R, Popp B N, Hutchins D A. 2011. Global declines in oceanic nitrification rates as a consequence of ocean acidification. *Proc Natl Acad Sci USA*, 108: 208–213
- Beversdorf L J, White A E, Björkman K M, Letelier R M, Karl D M. 2010. Phosphonate metabolism by *Trichodesmium* IMS101 and the production of greenhouse gases. *Limnol Oceanogr*, 55: 1768–1778
- Biaostoch A, Treude T, Rüpke L H, Riebesell U, Roth C, Burwicz E B, Park W, Latif M, Böning C W, Madec G, Wallmann K. 2011. Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification. *Geophys Res Lett*, 38: L08602
- Bijma J, Pörtner H O, Yesson C, Rogers A D. 2013. Corrigendum to “Climate change and the oceans—What does the future hold?” *Mar Pollut Bull*, 76: 436
- Boetius A, Wenzhöfer F. 2013. Seafloor oxygen consumption fuelled by methane from cold seeps. *Nat Geosci*, 6: 725–734
- Bogard M J, del Giorgio P A, Boutet L, Chaves M C G, Prairie Y T, Merante A, Derry A M. 2014. Oxic water column methanogenesis as a major component of aquatic CH₄ fluxes. *Nat Commun*, 5: 5350
- Borges A V, Champenois W, Gypens N, Delille B, Harlay J. 2016. Massive marine methane emissions from near-shore shallow coastal areas. *Sci Rep*, 6: 27908
- Boswell R, Collett T S. 2011. Current perspectives on gas hydrate resources. *Energy Environ Sci*, 4: 1206–1215
- Boudreau B P, Luo Y, Meysman F J R, Middelburg J J, Dickens G R. 2015. Gas hydrate dissociation prolongs acidification of the Anthropocene oceans. *Geophys Res Lett*, 42: 9337–9344A
- Braeckman U, Van Colen C, Guilini K, Van Gansbeke D, Soetaert K, Vincx M, Vanaverbeke J. 2014. Empirical evidence reveals seasonally dependent reduction in nitrification in coastal sediments subjected to near future ocean acidification. *Plos One*, 9: e108153
- Bridgman S D, Cadillo-Quiroz H, Keller J K, Zhuang Q. 2013. Methane emissions from wetlands: Biogeochemical, microbial, and modeling perspectives from local to global scales. *Glob Change Biol*, 19: 1325–1346
- Brigham-Grette J, Melles M, Minyuk P, Andreev A, Tarasov P, DeConto R, Koenig S, Nowaczyk N, Wennrich V, Rosén P, Haltia E, Cook T, Gebhardt C, Meyer-Jacob C, Snyder J, Herzschuh U. 2013. Pliocene warmth, polar amplification, and stepped Pleistocene cooling recorded in NE Arctic Russia. *Science*, 340: 1421–1427
- Brooks J M, Reid D F, Bernard B B. 1981. Methane in the upper water column of the northwestern Gulf of Mexico. *J Geophys Res*, 86: 11029–11040
- Bullock H A, Luo H, Whitman W B. 2017. Evolution of dimethylsulfoniopropionate metabolism in marine phytoplankton and bacteria. *Front Microbiol*, 8: 637
- Capelle D W, Tortell P D. 2016. Factors controlling methane and nitrous-oxide variability in the southern British Columbia coastal upwelling system. *Mar Chem*, 179: 56–67
- Carini P. 2016. Microbial oxidation of DMS to DMSO: A biochemical surprise with geochemical implications. *Environ Microbiol*, 18: 2302–2304
- Carini P, White A E, Campbell E O, Giovannoni S J. 2014. Methane production by phosphate-starved SAR11 chemoheterotrophic marine bacteria. *Nat Commun*, 5: 4346
- Carpenter L J, Archer S D, Beale R. 2012. Ocean-atmosphere trace gas exchange. *Chem Soc Rev*, 41: 6473–6506
- Cha I T, Min U G, Kim S J, Yim K J, Roh S W, Rhee S K. 2013. *Methanomethylovorans uponensis* sp. nov., a methylotrophic methanogen isolated from wetland sediment. *Antonie van Leeuwenhoek*, 104: 1005–1012
- Chronopoulou P M, Shelley F, Pritchard W J, Maanoja S T, Trimmer M. 2017. Origin and fate of methane in the Eastern Tropical North Pacific oxygen minimum zone. *ISME J*, 11: 1386–1399
- Conrad R. 2009. The global methane cycle: Recent advances in understanding the microbial processes involved. *Environ Microbiol Rep*, 1: 285–292
- Cynar F J, Yayanos A A. 1991. Enrichment and characterization of a methanogenic bacterium from the oxic upper layer of the ocean. *Curr Microbiol*, 23: 89–96
- Damm E, Helmke E, Thoms S, Schauer U, Nöthig E, Bakker K, Kiene R P. 2010. Methane production in aerobic oligotrophic surface water in the central Arctic Ocean. *Biogeosciences*, 7: 1099–1108
- Damm E, Kiene R P, Schwarz J, Falck E, Dieckmann G. 2008. Methane cycling in Arctic shelf water and its relationship with phytoplankton biomass and DMSP. *Mar Chem*, 109: 45–59
- Damm E, Thoms S, Beszczynska-Möller A, Nöthig E M, Kattner G. 2015. Methane excess production in oxygen-rich polar water and a model of cellular conditions for this paradox. *Polar Sci*, 9: 327–334
- Dang H Y, Chen C T A. 2017. Ecological energetic perspectives on responses of nitrogen-transforming chemolithoautotrophic microbiota to changes in the marine environment. *Front Microbiol*, 8: 1246
- Dang H Y, Lovell C R. 2016. Microbial surface colonization and biofilm development in marine environments. *Microbiol Mol Biol Rev*, 80: 91–138
- Dang H Y, Luan X W, Chen R P, Zhang X X, Guo L Z, Klotz M G. 2010. Diversity, abundance and distribution of amoA-encoding archaea in deep-sea methane seep sediments of the Okhotsk Sea. *Fems Microbiol Ecol*, 72: 370–385
- Dang H Y, Luan X W, Zhao J Y, Li J. 2009. Diverse and novel *nifH* and *nifH*-like gene sequences in the deep-sea methane seep sediments of

- the Okhotsk Sea. *Appl Environ Microbiol*, 75: 2238–2245
- Dang H Y, Zhou H X, Yang J Y, Ge H M, Jiao N Z, Luan X W, Zhang C L, Klotz M G. 2013. Thaumarchaeotal signature gene distribution in sediments of the northern South China Sea: An indicator of the metabolic intersection of the marine carbon, nitrogen, and phosphorus cycles? *Appl Environ Microbiol*, 79: 2137–2147
- Dang H, Jiao N. 2014. Perspectives on the microbial carbon pump with special reference to microbial respiration and ecosystem efficiency in large estuarine systems. *Biogeosciences*, 11: 3887–3898
- de Angelis M A, Lee C. 1994. Methane production during zooplankton grazing on marine phytoplankton. *Limnol Oceanogr*, 39: 1298–1308
- Dedysh S N, Ricke P, Liesack W. 2004. *NifH* and *NifD* phylogenies: An evolutionary basis for understanding nitrogen fixation capabilities of methanotrophic bacteria. *Microbiology*, 150: 1301–1313
- Dekas A E, Poretsky R S, Orphan V J. 2009. Deep-sea archaea fix and share nitrogen in methane-consuming microbial consortia. *Science*, 326: 422–426
- del Valle D, Karl D. 2014. Aerobic production of methane from dissolved water-column methylphosphonate and sinking particles in the North Pacific Subtropical Gyre. *Aquat Microb Ecol*, 73: 93–105
- DeVries T, Holzer M, Primeau F. 2017. Recent increase in oceanic carbon uptake driven by weaker upper-ocean overturning. *Nature*, 542: 215–218
- Dickens G R. 2011. Down the Rabbit Hole: Toward appropriate discussion of methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events. *Clim Past*, 7: 831–846
- Dickens G R, Castillo M M, Walker J C G. 1997. A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology*, 25: 259–262
- Dickens G R, O'Neil J R, Rea D K, Owen R M. 1995. Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography*, 10: 965–971
- Dickinson R E, Cicerone R J. 1986. Future global warming from atmospheric trace gases. *Nature*, 319: 109–115
- DiSpirito A A, Semrau J D, Murrell J C, Gallagher W H, Dennison C, Vuilleumier S. 2016. Methanobactin and the link between copper and bacterial methane oxidation. *Microbiol Mol Biol Rev*, 80: 387–409
- Ditchfield A, Wilson S, Hart M, Purdy K, Green D, Hatton A. 2012. Identification of putative methylotrophic and hydrogenotrophic methanogens within sedimenting material and copepod faecal pellets. *Aquat Microb Ecol*, 67: 151–160
- Dlugokencky E J, Nisbet E G, Fisher R, Lowry D. 2011. Global atmospheric methane: Budget, changes and dangers. *Philos Trans R Soc A-Math Phys Eng Sci*, 369: 2058–2072
- Dyhrman S T, Benitez-Nelson C R, Orchard E D, Haley S T, Pellechia P J. 2009. A microbial source of phosphonates in oligotrophic marine systems. *Nat Geosci*, 2: 696–699
- Dziewit L, Pyzik A, Romaniuk K, Sobczak A, Szczesny P, Lipinski L, Bartosik D, Drewniak L. 2015. Novel molecular markers for the detection of methanogens and phylogenetic analyses of methanogenic communities. *Front Microbiol*, 6: 694
- Embley R W, Chadwick W W, Baker E T, Butterfield D A, Resing J A, de Ronde C E J, Tunncliffe V, Lupton J E, Juniper S K, Rubin K H, Stern R J, Lebon G T, Nakamura K I, Merle S G, Hein J R, Wiens D A, Tamura Y. 2006. Long-term eruptive activity at a submarine arc volcano. *Nature*, 441: 494–497
- Etminan M, Myhre G, Highwood E J, Shine K P. 2016. Radiative forcing of carbon dioxide, methane, and nitrous oxide: A significant revision of the methane radiative forcing. *Geophys Res Lett*, 43: 12,614–12,623
- Evans P N, Parks D H, Chadwick G L, Robbins S J, Orphan V J, Golding S D, Tyson G W. 2015. Methane metabolism in the archaeal phylum Bathyarchaeota revealed by genome-centric metagenomics. *Science*, 350: 434–438
- Fariás L, Sanzana K, Sanhueza-Guevara S, Yevenes M A. 2017. Dissolved methane distribution in the Reloncavi Fjord and adjacent marine system during austral winter (41°–43°S). *Estuar Coast*, 40: 1592–1606
- Fernández-Carrera A, Rogers K L, Weber S C, Chanton J P, Montoya J P. 2016. Deep Water Horizon oil and methane carbon entered the food web in the Gulf of Mexico. *Limnol Oceanogr*, 61: S387–S400
- Ferry J G, Lessner D J. 2008. Methanogenesis in marine sediments. *Ann New York Acad Sci*, 1125: 147–157
- Finster K, Tanimoto Y, Bak F. 1992. Fermentation of methanethiol and dimethylsulfide by a newly isolated methanogenic bacterium. *Arch Microbiol*, 157: 425–430
- Fischer D, Mogollón J M, Strasser M, Pape T, Bohrmann G, Fekete N, Spiess V, Kasten S. 2013. Subduction zone earthquake as potential trigger of submarine hydrocarbon seepage. *Nat Geosci*, 6: 647–651
- Florez-Leiva L, Damm E, Fariás L. 2013. Methane production induced by dimethylsulfide in surface water of an upwelling ecosystem. *Prog Oceanogr*, 112–113: 38–48
- Forster P, Ramaswamy V, Artaxo P, Bernsten T, Betts R, Fahey D W, Haywood J, Lean J, Lowe D C, Myhre G, Nganga J, Prinn R, Raga G, Schulz M, Dorland R V. 2007. Changes in atmospheric constituents and in radiative forcing. Chapter 2. In: Solomon S, Qin D, Manning M, Marquis M, Averyt K, Tignor M M, Miller H L, eds. *Climate Change 2007—The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. New York: Cambridge

- University Press
- Friedrich M W. 2005. Methyl-coenzyme M reductase genes: Unique functional markers for methanogenic and anaerobic methane-oxidizing Archaea. *Methods Enzymol*, 397: 428–442
- Frondel M, Oertel K, Rubbelke D. 2002. The domino effect in climate change. *Int J Environ Poll*, 17: 201–210
- Fu H, Metcalf W W. 2015. Genetic basis for metabolism of methylated sulfur compounds in *Methanosarcina* species. *J Bacteriol*, 197: 1515–1524
- Garcia J L, Patel B K C, Ollivier B. 2000. Taxonomic, phylogenetic, and ecological diversity of methanogenic Archaea. *Anaerobe*, 6: 205–226
- Geersen J, Scholz F, Linke P, Schmidt M, Lange D, Behrmann J H, Völker D, Hensen C. 2016. Fault zone controlled seafloor methane seepage in the rupture area of the 2010 Maule earthquake, Central Chile. *Geochem Geophys Geosyst*, 17: 4802–4813
- Geissler W H, Gebhardt A C, Gross F, Wollenburg J, Jensen L, Schmidt-Aursch M C, Krastel S, Elger J, Osti G. 2016. Arctic megaslide at presumed rest. *Sci Rep*, 6: 38529
- Gilly W F, Beman J M, Litvin S Y, Robison B H. 2013. Oceanographic and biological effects of shoaling of the oxygen minimum zone. *Annu Rev Mar Sci*, 5: 393–420
- Glasby G P. 2003. Potential impact on climate of the exploitation of methane hydrate deposits offshore. *Mar Pet Geol*, 20: 163–175
- Ghosh A, Patra P K, Ishijima K, Umezawa T, Ito A, Etheridge D M, Sugawara S, Kawamura K, Miller J B, Dlugokencky E J, Krummel P B, Fraser P J, Steele L P, Langenfelds R L, Trudinger C M, White J W C, Vaughn B, Saeki T, Aoki S, Nakazawa T. 2015. Variations in global methane sources and sinks during 1910–2010. *Atmos Chem Phys*, 15: 2595–2612
- Glass J B, Orphan V J. 2012. Trace metal requirements for microbial enzymes involved in the production and consumption of methane and nitrous oxide. *Front Microbio*, 3: 61
- Greening C, Ahmed F H, Mohamed A E, Lee B M, Pandey G, Warden A C, Scott C, Oakeshott J G, Taylor M C, Jackson C J. 2016. Physiology, Biochemistry, and Applications of F_{420} - and F_o -Dependent Redox Reactions. *Microbiol Mol Biol Rev*, 80: 451–493
- Gruber N. 2011. Warming up, turning sour, losing breath: Ocean biogeochemistry under global change. *Philos Trans R Soc A-Math Phys Eng Sci*, 369: 1980–1996
- Gutjahr M, Ridgwell A, Sexton P F, Anagnostou E, Pearson P N, Pälike H, Norris R D, Thomas E, Foster G L. 2017. Very large release of mostly volcanic carbon during the Palaeocene-Eocene Thermal Maximum. *Nature*, 548: 573–577
- Hamdan L J, Wickland K P. 2016. Methane emissions from oceans, coasts, and freshwater habitats: New perspectives and feedbacks on climate. *Limnol Oceanogr*, 61: S3–S12
- Handwerker A L, Rempel A W, Skarbek R M. 2017. Submarine landslides triggered by destabilization of high-saturation hydrate anomalies. *Geochem Geophys Geosyst*, 18: 2429–2445
- Hansen J, Kharecha P, Sato M, Masson-Delmotte V, Ackerman F, Beerling D J, Hearty P J, Hoegh-Guldberg O, Hsu S L, Parmesan C, Rockstrom J, Rohling E J, Sachs J, Smith P, Steffen K, Van Susteren L, von Schuckmann K, Zachos J C. 2013. Assessing “dangerous climate change”: Required reduction of carbon emissions to protect young people, future generations and nature. *Plos One*, 8: e81648
- Hansen J, Sato M, Kharecha P, Russell G, Lea D W, Siddall M. 2007. Climate change and trace gases. *Philos Trans R Soc A-Math Phys Eng Sci*, 365: 1925–1954
- Hesselbo S P, Gröcke D R, Jenkyns H C, Bjerrum C J, Farrimond P, Morgans Bell H S, Green O R. 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature*, 406: 392–395
- Hester K C, Brewer P G. 2009. Clathrate hydrates in nature. *Annu Rev Mar Sci*, 1: 303–327
- Higgins J A, Schrag D P. 2006. Beyond methane: Towards a theory for the Paleocene-Eocene Thermal Maximum. *Earth Planet Sci Lett*, 245: 523–537
- Holmes M E, Sansone F J, Rust T M, Popp B N. 2000. Methane production, consumption, and air-sea exchange in the open ocean: An evaluation based on carbon isotopic ratios. *Glob Biogeochem Cycle*, 14: 1–10
- Horsman G P, Zechel D L. 2017. Phosphonate biochemistry. *Chem Rev*, 117: 5704–5783
- Hove-Jensen B, Zechel D L, Jochimsen B. 2014. Utilization of glyphosate as phosphate source: Biochemistry and genetics of bacterial carbon-phosphorus lyase. *Microbiol Mol Biol Rev*, 78: 176–197
- Hunter S J, Goldobin D S, Haywood A M, Ridgwell A, Rees J G. 2013. Sensitivity of the global submarine hydrate inventory to scenarios of future climate change. *Earth Planet Sci Lett*, 367: 105–115
- Iino T, Tamaki H, Tamazawa S, Ueno Y, Ohkuma M, Suzuki K, Igarashi Y, Haruta S. 2013. *Candidatus Methanogranum caenicola*: A novel methanogen from the anaerobic digested sludge, and proposal of *Methanomassiliicoccaceae* fam. nov. and *Methanomassiliicoccales* ord. nov., for a methanogenic lineage of the class *Thermoplasmata*. *Microb Environ*, 28: 244–250
- Isaksen I S A, Gauss M, Myhre G, Walter Anthony K M, Ruppel C. 2011. Strong atmospheric chemistry feedback to climate warming from Arctic methane emissions. *Glob Biogeochem Cycle*, 25: GB2002
- Jabłoński S, Rodowicz P, Łukaszewicz M. 2015. Methanogenic archaea

- database containing physiological and biochemical characteristics. *Int J Systatic Evolary Microbiol*, 65: 1360–1368
- James R H, Bousquet P, Bussmann I, Haeckel M, Kipfer R, Leifer I, Niemann H, Ostrovsky I, Piskozub J, Rehder G, Treude T, Vielstädte L, Greinert J. 2016. Effects of climate change on methane emissions from seafloor sediments in the Arctic Ocean: A review. *Limnol Oceanogr*, 61: S283–S299
- Jarrell K F. 1985. Extreme oxygen sensitivity in methanogenic archaeobacteria. *BioScience*, 35: 298–302
- Jiao N, Robinson C, Azam F, Thomas H, Baltar F, Dang H, Hardman-Mountford N J, Johnson M, Kirchman D L, Koch B P, Legendre L, Li C, Liu J, Luo T, Luo Y W, Mitra A, Romanou A, Tang K, Wang X, Zhang C, Zhang R. 2014. Mechanisms of microbial carbon sequestration in the ocean-future research directions. *Biogeosciences*, 11: 5285–5306
- Kallistova A Y, Merkel A Y, Tarnovetskii I Y, Pimenov N V. 2017. Methane formation and oxidation by prokaryotes. *Microbiology*, 86: 671–691
- Karl D M, Beversdorf L, Björkman K M, Church M J, Martinez A, Delong E F. 2008. Aerobic production of methane in the sea. *Nat Geosci*, 1: 473–478
- Karl D M, Tilbrook B D. 1994. Production and transport of methane in oceanic particulate organic matter. *Nature*, 368: 732–734
- Karol I L, Kiselev A A, Genikhovich E L, Chicherin S S. 2013. Reduction of short-lived atmospheric pollutant emissions as an alternative strategy for climate-change moderation. *Izv Atmos Ocean Phys*, 49: 461–478
- Karthikeyan O P, Chidambarampadmavathy K, Cirés S, Heimann K. 2015. Review of sustainable methane mitigation and biopolymer production. *Critical Rev Environ Sci Tech*, 45: 1579–1610
- Katz M E, Pak D K, Dickens G R, Miller K G. 1999. The source and fate of massive carbon input during the latest Paleocene Thermal Maximum. *Science*, 286: 1531–1533
- Kennedy M, Mrofka D, von der Borch C. 2008. Snowball Earth termination by destabilization of equatorial permafrost methane clathrate. *Nature*, 453: 642–645
- Kennett J P, Cannariato K G, Hendy I L, Behl R J. 2003. Methane hydrates in Quaternary climate change: The clathrate gun hypothesis. AGU, Washington D C. 217
- Khadem A F, Pol A, Jetten M S M, Op den Camp H J M. 2010. Nitrogen fixation by the verrucomicrobial methanotroph ‘*Methylocidiphilum fumariolicum*’ SolV. *Microbiology*, 156: 1052–1059
- Kiene R P, Oremland R S, Catena A, Miller L G, Capone D G. 1986. Metabolism of reduced methylated sulfur compounds in anaerobic sediments and by a pure culture of an estuarine methanogen. *Appl Environ Microbiol*, 52: 1037–1045
- Kirschke S, Bousquet P, Ciais P, Saunois M, Canadell J G, Dlugokencky E J, Bergamaschi P, Bergmann D, Blake D R, Bruhwiler L, Cameron-Smith P, Castaldi S, Chevallier F, Feng L, Fraser A, Heimann M, Hodson E L, Houweling S, Josse B, Fraser P J, Krummel P B, Lamarque J F, Langenfelds R L, Le Quéré C, Naik V, O’Doherty S, Palmer P I, Pison I, Plummer D, Poulter B, Prinn R G, Rigby M, Ringeval B, Santini M, Schmidt M, Shindell D T, Simpson I J, Spahn R, Steele L P, Strode S A, Sudo K, Szopa S, van der Werf G R, Voulgarakis A, van Weele M, Weiss R F, Williams J E, Zeng G. 2013. Three decades of global methane sources and sinks. *Nat Geosci*, 6: 813–823
- Knittel K, Boetius A. 2009. Anaerobic oxidation of methane: Progress with an unknown process. *Annu Rev Microbiol*, 63: 311–334
- Kretschmer K, Biastoch A, Rüpke L, Burwicz E. 2015. Modeling the fate of methane hydrates under global warming. *Glob Biogeochem Cycle*, 29: 610–625
- Krishnakumar A M, Sliwa D, Endrizzi J A, Boyd E S, Ensign S A, Peters J W. 2008. Getting a handle on the role of coenzyme M in alkene metabolism. *Microbiol Mol Biol Rev*, 72: 445–456
- Krüger M, Treude T, Wolters H, Nauhaus K, Boetius A. 2005. Microbial methane turnover in different marine habitats. *Palaeogeogr Palaeoclimatol Palaeoecol*, 227: 6–17
- Krumhardt K M, Lovenduski N S, Iglesias-Rodriguez M D, Kleypas J A. 2017. Coccolithophore growth and calcification in a changing ocean. *Prog Oceanogr*, 159: 276–295
- Kudela R M, Seeyave S, Cochlan W P. 2010. The role of nutrients in regulation and promotion of harmful algal blooms in upwelling systems. *Prog Oceanogr*, 85: 122–135
- Kvenvolden K A. 1988. Methane hydrates and global climate. *Glob Biogeochem Cycle*, 2: 221–229
- Lambert G, Schmidt S. 1993. Reevaluation of the oceanic flux of methane: Uncertainties and long term variations. *Chemosphere*, 26: 579–589
- Lamontagne R A, Swinnerton J W, Linnenbom V J. 1971. Nonequilibrium of carbon monoxide and methane at the air-sea interface. *J Geophys Res*, 76: 5117–5121
- Leifer I, Luyendyk B P, Boles J, Clark J F. 2006. Natural marine seepage blowout: Contribution to atmospheric methane. *Glob Biogeochem Cycle*, 20: GB3008
- Lenhart K, Klitzsch T, Langer G, Nehrke G, Bunge M, Schnell S, Keppler F. 2016. Evidence for methane production by the marine algae *Emiliania huxleyi*. *Biogeosciences*, 13: 3163–3174
- Levin L A, Le Bris N. 2015. The deep ocean under climate change. *Science*, 350: 766–768
- Liu Y, Whitman W B. 2008. Metabolic, phylogenetic, and ecological diversity of the methanogenic archaea. *Ann New York Acad Sci*,

- 1125: 171–189
- Lloyd K. 2015. Beyond known methanogens. *Science*, 350: 384
- Lomans B P, Maas R, Luderer R, Op den Camp H J, Pol A, van der Drift C, Vogels G D. 1999. Isolation and characterization of *Methanomethylovorans hollandica* gen. nov., sp. nov., isolated from freshwater sediment, a methylotrophic methanogen able to grow on dimethyl sulfide and methanethiol. *Appl Environ Microbiol*, 65: 3641–3650
- Loulergue L, Schilt A, Spahni R, Masson-Delmotte V, Blunier T, Lemieux B, Barnola J M, Raynaud D, Stocker T F, Chappellaz J. 2008. Orbital and millennial-scale features of atmospheric CH₄ over the past 800000 years. *Nature*, 453: 383–386
- Lyimo T J, Pol A, Op den Camp H J, Harhangi H R, Vogels G D. 2000. *Methanosarcina semesiae* sp. nov., a dimethylsulfide-utilizing methanogen from mangrove sediment. *Int J Systematic Evolary Microbiol*, 50: 171–178
- Lyu Z, Lu Y. 2018. Metabolic shift at the class level sheds light on adaptation of methanogens to oxidative environments. *ISME J*, 12: 411–423
- MacCracken M C. 2008. Prospects for future climate change and the reasons for early action. *J Air Waste Manage*, 58: 735–786
- MacDougall A H, Knutti R. 2016. Enhancement of non-CO₂ radiative forcing via intensified carbon cycle feedbacks. *Geophys Res Lett*, 43: 5833–5840
- McKinley G A, Pilcher D J, Fay A R, Lindsay K, Long M C, Lovenduski N S. 2016. Timescales for detection of trends in the ocean carbon sink. *Nature*, 530: 469–472
- Marín-Moreno H, Giustiniani M, Tinivella U, Piñero E. 2016. The challenges of quantifying the carbon stored in Arctic marine gas hydrate. *Mar Pet Geol*, 71: 76–82
- Marín-Moreno H, Minshull T A, Westbrook G K, Sinha B, Sarkar S. 2013. The response of methane hydrate beneath the seabed offshore Svalbard to ocean warming during the next three centuries. *Geophys Res Lett*, 40: 5159–5163
- Martínez A, Ventouras L A, Wilson S T, Karl D M, DeLong E F. 2013. Metatranscriptomic and functional metagenomic analysis of methylphosphonate utilization by marine bacteria. *Front Microbiol*, 4: 340
- Marty D G, Nival P, Yoon W D. 1997. Methanoarchaea associated with sinking particles and zooplankton collected in the Northeastern tropical Atlantic. *Oceanol Acta*, 20: 863–869
- Maslin M, Owen M, Betts R, Day S, Dunkley Jones T, Ridgwell A. 2010. Gas hydrates: Past and future geohazard? *Philos Trans R Soc A-Math Phys Eng Sci*, 368: 2369–2393
- Maslin M, Owen M, Day S, Long D. 2004. Linking continental-slope failures and climate change: Testing the clathrate gun hypothesis. *Geology*, 32: 53–56
- Masson D G, Harbitz C B, Wynn R B, Pedersen G, Løvholt F. 2006. Submarine landslides: Processes, triggers and hazard prediction. *Philos Trans R Soc A-Math Phys Eng Sci*, 364: 2009–2039
- Masuda S, Awaji T, Sugiura N, Matthews J P, Toyoda T, Kawai Y, Doi T, Kouketsu S, Igarashi H, Katsumata K, Uchida H, Kawano T, Fukasawa M. 2010. Simulated rapid warming of abyssal North Pacific waters. *Science*, 329: 319–322
- Matthews E. 1994. Assessment of methane sources and their uncertainties. *Pure Appl Chem*, 66: 154–162
- McNeill D, Halloran P R, Good P, Betts R A. 2011. Analyzing abrupt and nonlinear climate changes and their impacts. *WIREs Clim Change*, 2: 663–686
- Mestdagh T, Poort J, De Batist M. 2017. The sensitivity of gas hydrate reservoirs to climate change: Perspectives from a new combined model for permafrost-related and marine settings. *Earth-Sci Rev*, 169: 104–131
- Metcalf W W, Griffin B M, Cicchillo R M, Gao J, Janga S C, Cooke H A, Circello B T, Evans B S, Martens-Habbena W, Stahl D A, van der Donk W A. 2012. Synthesis of methylphosphonic acid by marine microbes: A source for methane in the aerobic ocean. *Science*, 337: 1104–1107
- Mondav R, Woodcroft B J, Kim E H, McCalley C K, Hodgkins S B, Crill P M, Chanton J, Hurst G B, VerBerkmoes N C, Saleska S R, Hugenholtz P, Rich V I, Tyson G W. 2014. Discovery of a novel methanogen prevalent in thawing permafrost. *Nat Commun*, 5: 3212
- Montzka S A, Dlugokencky E J, Butler J H. 2011. Non-CO₂ greenhouse gases and climate change. *Nature*, 476: 43–50
- Mora C, Wei C L, Rollo A, Amaro T, Baco A R, Billett D, Bopp L, Chen Q, Collier M, Danovaro R, Gooday A J, Grupe B M, Halloran P R, Ingels J, Jones D O B, Levin L A, Nakano H, Norling K, Ramirez-Llodra E, Rex M, Ruhl H A, Smith C R, Sweetman A K, Thurber A R, Tjiputra J F, Usseglio P, Watling L, Wu T, Yasuhara M. 2013. Biotic and human vulnerability to projected changes in ocean biogeochemistry over the 21st century. *Plos Biol*, 11: e1001682
- Naqvi S W A, Bange H W, Farias L, Monteiro P M S, Scranton M I, Zhang J. 2010. Marine hypoxia/anoxia as a source of CH₄ and N₂O. *Biogeosciences*, 7: 2159–2190
- Navid D. 1989. The international law of migratory species: The Ramsar convention. *Nat Res J*, 29: 1001–1016
- Nobu M K, Narihiro T, Kuroda K, Mei R, Liu W T. 2016. Chasing the elusive Euryarchaeota class WSA2: Genomes reveal a uniquely fastidious methyl-reducing methanogen. *ISME J*, 10: 2478–2487
- Norris R D, Röhl U. 1999. Carbon cycling and chronology of climate warming during the Palaeocene/Eocene transition. *Nature*, 401:

- 775–778
- Obzhairov A I. 2013. Gas component increase during seismo-tectonics and the role of gas in earthquake origination (Okhotsk Sea). *Russ J Pac Geol*, 32: 86–89
- Offre P, Spang A, Schleper C. 2013. Archaea in biogeochemical cycles. *Annu Rev Microbiol*, 67: 437–457
- Orcutt B N, LaRowe D E, Biddle J F, Colwell F S, Glazer B T, Reese B K, Kirkpatrick J B, Lapham L L, Mills H J, Sylvan J B, Wankel S D, Wheat C G. 2013. Microbial activity in the marine deep biosphere: Progress and prospects. *Front Microbiol*, 4: 189
- Oremland R S. 1979. Methanogenic activity in plankton samples and fish intestines A mechanism for in situ methanogenesis in oceanic surface waters. *Limnol Oceanogr*, 24: 1136–1141
- Oremland R S, Kiene R P, Mathrani I, Whiticar M J, Boone D R. 1989. Description of an estuarine methylotrophic methanogen which grows on dimethyl sulfide. *Appl Environ Microbiol*, 55: 994–1002
- Ortiz-Llorente M J, Alvarez-Cobelas M. 2012. Comparison of biogenic methane emissions from unmanaged estuaries, lakes, oceans, rivers and wetlands. *Atmos Environ*, 59: 328–337
- Paulo L M, Ramiro-Garcia J, van Mourik S, Stams A J M, Sousa D Z. 2017. Effect of nickel and cobalt on methanogenic enrichment cultures and role of biogenic sulfide in metal toxicity attenuation. *Front Microbiol*, 8: 1341
- Pernthaler A, Dekas A E, Titus Brown C, Goffredi S K, Embaye T, Orphan V J. 2008. Diverse syntrophic partnerships from deep-sea methane vents revealed by direct cell capture and metagenomics. *Proc Natl Acad Sci USA*, 105: 7052–7057
- Phrampus B J, Hornbach M J. 2012. Recent changes to the Gulf Stream causing widespread gas hydrate destabilization. *Nature*, 490: 527–530
- Poehlein A, Daniel R, Seedorf H. 2017. The draft genome of the non-host-associated *Methanobrevibacter arboriphilus* strain DH1 encodes a large repertoire of adhesin-like proteins. *Archaea*, 2017: 1–9
- Pohlman J W, Greinert J, Ruppel C, Silyakova A, Vielstädte L, Casso M, Mienert J, Bünz S. 2017. Enhanced CO₂ uptake at a shallow Arctic Ocean seep field overwhelms the positive warming potential of emitted methane. *Proc Natl Acad Sci USA*, 114: 5355–5360
- Prather M J, Holmes C D. 2017. Overexplaining or underexplaining methane's role in climate change. *Proc Natl Acad Sci USA*, 114: 5324–5326
- Purwantini E, Torto-Alalibo T, Lomax J, Setubal J A C, Tyler B M, Mukhopadhyay B. 2014. Genetic resources for methane production from biomass described with the Gene Ontology. *Front Microbiol*, 5: 634
- Rakowski C V, Magen C, Bosman S, Rogers K L, Gillies L E, Chanton J P, Mason O U. 2015. Methane and microbial dynamics in the Gulf of Mexico water column. *Front Mar Sci*, 2: 69
- Rasmussen R A, Khalil M A K. 1981. Atmospheric methane (CH₄): Trends and seasonal cycles. *J Geophys Res*, 86: 9826–9832
- Ravishankara A R, Daniel J S, Portmann R W. 2009. Nitrous oxide (N₂O): The dominant ozone-depleting substance emitted in the 21st century. *Science*, 326: 123–125
- Reagan M T, Moridis G J. 2007. Oceanic gas hydrate instability and dissociation under climate change scenarios. *Geophys Res Lett*, 34: L22709
- Reagan M T, Moridis G J. 2008. Dynamic response of oceanic hydrate deposits to ocean temperature change. *J Geophys Res*, 113: C12023
- Reeburgh W S. 2007. Oceanic methane biogeochemistry. *Chem Rev*, 107: 486–513
- Repeta D J, Ferrón S, Sosa O A, Johnson C G, Repeta L D, Acker M, DeLong E F, Karl D M. 2016. Marine methane paradox explained by bacterial degradation of dissolved organic matter. *Nat Geosci*, 9: 884–887
- Rhee T S, Kettle A J, Andreae M O. 2009. Methane and nitrous oxide emissions from the ocean: A reassessment using basin-wide observations in the Atlantic. *J Geophys Res*, 114: D12304
- Ruppel C D, Kessler J D. 2017. The interaction of climate change and methane hydrates. *Rev Geophys*, 55: 126–168
- Sabine C L, Feely R A, Gruber N, Key R M, Lee K, Bullister J L, Wanninkhof R, Wong C S, Wallace D W R, Tilbrook B, Millero F J, Peng T H, Kozyr A, Ono T, Rios A F. 2004. The oceanic sink for anthropogenic CO₂. *Science*, 305: 367–371
- Sakai S, Imachi H, Hanada S, Ohashi A, Harada H, Kamagata Y. 2008. *Methanocella paludicola* gen. nov., sp. nov., a methane-producing archaeon, the first isolate of the lineage 'Rice Cluster I', and proposal of the new archaeal order *Methanocellales* ord. nov.. *Int J Systematic Evolary Microbiol*, 58: 929–936
- Sansone F J, Popp B N, Gasc A, Graham A W, Rust T M. 2001. Highly elevated methane in the eastern tropical North Pacific and associated isotopically enriched fluxes to the atmosphere. *Geophys Res Lett*, 28: 4567–4570
- Sasakawa M, Tsunogai U, Kameyama S, Nakagawa F, Nojiri Y, Tsuda A. 2008. Carbon isotopic characterization for the origin of excess methane in subsurface seawater. *J Geophys Res*, 113: C03012
- Schäfer G, Engelhard M, Müller V. 1999. Bioenergetics of the Archaea. *Microbiol Mol Biol Rev*, 63: 570–620
- Schink B. 1997. Energetics of syntrophic cooperation in methanogenic degradation. *Microbiol Mol Biol Rev*, 61: 262–280
- Schleuning M, Fründ J, Schweiger O, Welk E, Albrecht J, Albrecht M, Beil M, Benadi G, Blüthgen N, Bruehlheide H, Böhning-Gaese K, Dehling D M, Dormann C F, Exeler N, Farwig N, Harpke A, Hickler T, Kratochwil A, Kuhlmann M, Kühn I, Michez D, Mudri

- Stojnić S, Plein M, Rasmont P, Schwabe A, Settele J, Vujić A, Weiner C N, Wiemers M, Hof C. 2016. Ecological networks are more sensitive to plant than to animal extinction under climate change. *Nat Commun*, 7: 13965
- Schmale O, Wäge J, Mohrholz V, Wasmund N, Gräwe U, Rehder G, Labrenz M, Loick-Wilde N. 2018. The contribution of zooplankton to methane supersaturation in the oxygenated upper waters of the central Baltic Sea. *Limnol Oceanogr*, 63: 412–430
- Scranton M I, Brewer P G. 1977. Occurrence of methane in the near-surface waters of the western subtropical North-Atlantic. *Deep Sea Res*, 24: 127–138
- Sela-Adler M, Ronen Z, Herut B, Antler G, Vigderovich H, Eckert W, Sivan O. 2017. Co-existence of methanogenesis and sulfate reduction with common substrates in sulfate-rich estuarine sediments. *Front Microbiol*, 8: 766
- Semrau J D, DiSpirito A A, Gu W, Yoon S. 2018. Metals and methanotrophy. *Appl Environ Microbiol*, 84: e02289–17
- Shakhova N, Semiletov I, Salyuk A, Yusupov V, Kosmach D, Gustafsson O. 2010. Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf. *Science*, 327: 1246–1250
- Shepherd J G, Brewer P G, Oschlies A, Watson A J. 2017. Ocean ventilation and deoxygenation in a warming world: Introduction and overview. *Philos Trans R Soc A-Math Phys Eng Sci*, 375: 20170240
- Showstack R. 2013. Carbon Dioxide Tops 400 ppm at Mauna Loa. Hawaii: Eos Trans AGU, 94: 192
- Sieburth J N, Johnson P, Macario A, Conway de Macario E. 1993. C1 bacteria in the water column of Chesapeake Bay USA. II. The dominant O₂- and H₂S-tolerant methylotrophic methanogens, coenriched with their oxidative and sulphate reducing bacterial consort, are all new immunotypes and probably include new taxa. *Mar Ecol Prog Ser*, 95: 81–89
- Solomon S, Daniel J S, Sanford T J, Murphy D M, Plattner G K, Knutti R, Friedlingstein P. 2010. Persistence of climate changes due to a range of greenhouse gases. *Proc Natl Acad Sci USA*, 107: 18354–18359
- Solomon S, Plattner G K, Knutti R, Friedlingstein P. 2009. Irreversible climate change due to carbon dioxide emissions. *Proc Natl Acad Sci USA*, 106: 1704–1709
- Sonnemann G R, Grygalashvily M. 2014. Global annual methane emission rate derived from its current atmospheric mixing ratio and estimated lifetime. *Ann Geophys*, 32: 277–283
- Sorokin D Y, Makarova K S, Abbas B, Ferrer M, Golyshin P N, Galinski E A, Ciordia S, Mena M C, Merkel A Y, Wolf Y I, van Loosdrecht M C M, Koonin E V. 2017. Discovery of extremely halophilic, methyl-reducing euryarchaea provides insights into the evolutionary origin of methanogenesis. *Nat Microbiol*, 2: 17081
- Sosa O A, Repeta D J, Ferrón S, Bryant J A, Mende D R, Karl D M, DeLong E F. 2017. Isolation and characterization of bacteria that degrade phosphonates in marine dissolved organic matter. *Front Microbiol*, 8: 1786
- Sowers T. 2006. Late Quaternary atmospheric CH₄ isotope record suggests marine clathrates are stable. *Science*, 311: 838–840
- Stranne C, O'Regan M, Jakobsson M. 2017. Modeling fracture propagation and seafloor gas release during seafloor warming-induced hydrate dissociation. *Geophys Res Lett*, 44: 8510–8519
- Svensen H, Planke S, Malthes-Sørensen A, Jamtveit B, Myklebust R, Rasmussen Eidem T, Rey S S. 2004. Release of methane from a volcanic basin as a mechanism for initial Eocene global warming. *Nature*, 429: 542–545
- Sydeman W J, García-Reyes M, Schoeman D S, Rykaczewski R R, Thompson S A, Black B A, Bograd S J. 2014. Climate change and wind intensification in coastal upwelling ecosystems. *Science*, 345: 77–80
- Tallant T C, Krzycki J A. 1997. Methylthiol:coenzyme M methyltransferase from *Methanosarcina barkeri*, an enzyme of methanogenesis from dimethylsulfide and methylmercaptopropionate. *J Bacteriol*, 179: 6902–6911
- Tallant T C, Paul L, Krzycki J A. 2001. The MtsA subunit of the methylthiol:coenzyme M methyltransferase of *Methanosarcina barkeri* catalyses both half-reactions of corrinoid-dependent dimethylsulfide: Coenzyme M methyl transfer. *J Biol Chem*, 276: 4485–4493
- Teikari J E, Fewer D P, Shrestha R, Hou S, Leikoski N, Mäkelä M, Simojoki A, Hess W R, Sivonen K. 2018. Strains of the toxic and bloom-forming *Nodularia spumigena* (cyanobacteria) can degrade methylphosphonate and release methane. *ISME J*, 12: 1619–1630
- Thatcher K E, Westbrook G K, Sarkar S, Minshull T A. 2013. Methane release from warming-induced hydrate dissociation in the West Svalbard continental margin: Timing, rates, and geological controls. *J Geophys Res-Solid Earth*, 118: 22–38
- Tholen A, Pester M, Brune A. 2007. Simultaneous methanogenesis and oxygen reduction by *Methanobrevibacter cuticularis* at low oxygen fluxes. *Fems Microbiol Ecol*, 62: 303–312
- Tilbrook B D, Karl D M. 1995. Methane sources, distributions and sinks from California coastal waters to the oligotrophic North Pacific gyre. *Mar Chem*, 49: 51–64
- Tseng H C, Chen C T A, Borges A V, DelValls T A, Chang Y C. 2017. Methane in the South China Sea and the Western Philippine Sea. *Cont Shelf Res*, 135: 23–34
- Tsunogai U, Maegawa K, Sato S, Komatsu D D, Nakagawa F, Toki T, Ashi J. 2012. Coseismic massive methane release from a submarine

- mud volcano. *Earth Planet Sci Lett*, 341-344: 79–85
- Tsuruta A, Aalto T, Backman L, Hakkarainen J, van der Laan-Luijckx I T, Krol M C, Spahn R, Houweling S, Laine M, Dlugokencky E, Gomez-Pelaez A J, van der Schoot M, Langenfelds R, Ellul R, Arduini J, Apadula F, Gerbig C, Feist D G, Kivi R, Yoshida Y, Peters W. 2017. Global methane emission estimates for 2000–2012 from CarbonTracker Europe-CH₄ v1.0. *Geosci Model Dev*, 10: 1261–1289
- Upstill-Goddard R C, Barnes J. 2016. Methane emissions from UK estuaries: Re-evaluating the estuarine source of tropospheric methane from Europe. *Mar Chem*, 180: 14–23
- Valentine D L. 2011. Emerging topics in marine methane biogeochemistry. *Annu Rev Mar Sci*, 3: 147–171
- van der Maarel M J E C, Hansen T A. 1997. Dimethylsulfoniopropionate in anoxic intertidal sediments: A precursor of methanogenesis via dimethyl sulfide, methanethiol, and methiolpropionate. *Mar Geol*, 137: 5–12
- Van Mooy B A S, Krupke A, Dyhrman S T, Fredricks H F, Frischkorn K R, Ossolinski J E, Repeta D J, Rouco M, Seewald J D, Sylva S P. 2015. Major role of planktonic phosphate reduction in the marine phosphorus redox cycle. *Science*, 348: 783–785
- Vanwonterghem I, Evans P N, Parks D H, Jensen P D, Woodcroft B J, Hugenholtz P, Tyson G W. 2016. Methylophilic methanogenesis discovered in the archaeal phylum Verstraetearchaeota. *Nat Microbiol*, 1: 16170
- Vizza C, West W E, Jones S E, Hart J A, Lamberti G A. 2017. Regulators of coastal wetland methane production and responses to simulated global change. *Biogeosciences*, 14: 431–446
- Vojvoda J, Lamy D, Sintès E, Garcia J, Turk V, Herndl G. 2014. Seasonal variation in marine-snow-associated and ambient-water prokaryotic communities in the northern Adriatic Sea. *Aquat Microb Ecol*, 73: 211–224
- Wang D, Gouhier T C, Menge B A, Ganguly A R. 2015. Intensification and spatial homogenization of coastal upwelling under climate change. *Nature*, 518: 390–394
- Wang J, Yuan J, Liu D, Xiang J, Ding W, Jiang X. 2016. Research progresses on methanogenesis pathway and methanogens in coastal wetlands. *Chin J Appl Ecol*, 27: 993–1001
- Weller D I, Law C S, Marriner A, Nodder S D, Chang F H, Stephens J A, Wilhelm S W, Boyd P W, Sutton P J H. 2013. Temporal variation of dissolved methane in a subtropical mesoscale eddy during a phytoplankton bloom in the southwest Pacific Ocean. *Prog Oceanogr*, 116: 193–206
- Welsh D T. 2000. Ecological significance of compatible solute accumulation by micro-organisms: From single cells to global climate. *Fems Microbiol Rev*, 24: 263–290
- Welte C, Deppenmeier U. 2014. Bioenergetics and anaerobic respiratory chains of acetoclastic methanogens. *Biochim Biophys Acta*, 1837: 1130–1147
- Wen X, Yang S, Horn F, Winkel M, Wagner D, Liebner S. 2017. Global biogeographic analysis of methanogenic archaea identifies community-shaping environmental factors of natural environments. *Front Microbiol*, 8: 1339
- Wilson S T, Ferrón S, Karl D M. 2017. Interannual variability of methane and nitrous oxide in the North Pacific Subtropical Gyre. *Geophys Res Lett*, 44: 9885–9892
- Wright J J, Konwar K M, Hallam S J. 2012. Microbial ecology of expanding oxygen minimum zones. *Nat Rev Micro*, 10: 381–394
- Wuebbles D J, Hayhoe K. 2002. Atmospheric methane and global change. *Earth-Sci Rev*, 57: 177–210
- Xiao K Q, Beulig F, Kjeldsen K U, Jørgensen B B, Risgaard-Petersen N. 2017. Concurrent methane production and oxidation in surface sediment from Aarhus Bay, Denmark. *Front Microbiol*, 8: 1198
- Xiao L, Xie B, Liu J, Zhang H, Han G, Wang O, Liu F. 2017. Stimulation of long-term ammonium nitrogen deposition on methanogenesis by Methanocellaceae in a coastal wetland. *Sci Total Environ*, 595: 337–343
- Yvon-Durocher G, Allen A P, Bastviken D, Conrad R, Gudas C, St-Pierre A, Thanh-Duc N, del Giorgio P A. 2014. Methane fluxes show consistent temperature dependence across microbial to ecosystem scales. *Nature*, 507: 488–491
- Zeebe R E, Ridgwell A, Zachos J C. 2016. Anthropogenic carbon release rate unprecedented during the past 66 million years. *Nat Geosci*, 9: 325–329
- Zehnder A J B, Wuhrmann K. 1977. Physiology of a *Methanobacterium* strain AZ. *Arch Microbiol*, 111: 199–205
- Zhang B, Tian H, Lu C, Chen G, Pan S, Anderson C, Poulter B. 2017. Methane emissions from global wetlands: An assessment of the uncertainty associated with various wetland extent data sets. *Atmos Environ*, 165: 310–321
- Zhang G L, Zhang J, Kang Y B, Liu S M. 2004. Distributions and fluxes of methane in the East China Sea and the Yellow Sea in spring. *J Geophys Res*, 109: C07011
- Zhang G L, Zhang J, Liu S, Ren J, Xu J, Zhang F. 2008. Methane in the Changjiang (Yangtze River) Estuary and its adjacent marine area: Riverine input, sediment release and atmospheric fluxes. *Biogeochemistry*, 91: 71–84
- Zhang Y, Zhai W D. 2015. Shallow-ocean methane leakage and degassing to the atmosphere: Triggered by offshore oil-gas and methane hydrate explorations. *Front Mar Sci*, 2: 34
- Zhou H Y, Yin X J, Yang Q H, Wang H, Wu Z J, Bao S X. 2009. Distribution, source and flux of methane in the western Pearl River

Estuary and northern South China Sea. [Mar Chem](#), 117: 21–31

Zickfeld K, Solomon S, Gilford D M. 2017. Centuries of thermal sea-level rise due to anthropogenic emissions of short-lived greenhouse gases. [Proc Natl Acad Sci USA](#), 114: 657–662

Zindler C, Bracher A, Marandino C A, Taylor B, Torrecilla E, Kock A, Bange H W. 2013. Sulphur compounds, methane, and phytoplankton: Interactions along a north-south transit in the western Pacific Ocean. [Biogeosciences](#), 10: 3297–3311

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