白垩纪大洋缺氧事件OAE2期间碳循环扰动的过程与机制

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2021-08-09 收稿, 2021-10-18 修回, 2021-10-19 接受, 2021-10-19 网络版发表

国家自然科学基金(42072118, 42050102)和中国地质调查局地质调查项目(DD20190057)资助

摘要 白垩纪大洋缺氧事件OAE2是一次全球性古环境突变事件,也是迄今研究程度最高的中生代古海洋事件之一。同时,由于它形成于全球极热气候时期,分析OAE2期间环境演化与形成机制对于研究极端温室气候条件下地球系统的演化过程具有重要意义。近年来,古气候和古海洋领域学者应用全球性古环境指标,对OAE2开展了精细研究,在其触发机制和地球系统反馈过程方面取得了诸多新认识。本文综述了这些方面的研究成果,从海水碳同位素($\delta^{13}\text{C}$)演化的角度分析了OAE2期间全球碳循环扰动过程及其控制因素。我们认为,大火成岩省岩浆作用是OAE2碳循环扰动的触发因素,海洋生产力提升和缺氧条件导致大规模有机质埋藏是OAE2期间海水 $\delta^{13}\text{C}$ 总体呈正偏的直接原因。古环境参数,如大陆风化强度、古温度、 CO_2 浓度、海洋生产力和海水氧化还原条件之间的相互影响,对OAE2期间次级 $\delta^{13}\text{C}$ 波动具有重要控制作用。本文分析了OAE2期间 $\delta^{13}\text{C}$ 演化在不同阶段主控因素的显著差异,并建立了全球环境演化及其对碳循环影响的模型。

关键词 白垩纪, 大洋缺氧, 大火成岩省, 有机质埋藏, 硅酸盐风化

20世纪70年代提出的大洋缺氧事件(oceanic anoxic event, OAE)^[1],用短时间大范围海洋缺氧来解释白垩纪某些特定时期全球广泛发育黑色页岩沉积。此后,OAE一直是地球科学中的热点领域之一,引领着白垩纪古海洋研究。经过40余年持续研究,已报道的全球性或区域性大洋缺氧事件包括Weissert事件(Valanginian期,~132 Ma)、OAE1a-1d(Aptian-Albian期)和OAE2(Cenomanian-Turonian之交,~94 Ma)等^[2,3]。研究表明,OAE期间地球气候为极端高温的状态,低纬地区海洋表层温度可高达45°C^[4],大气中 CO_2 分压($p\text{CO}_2$)相对背景值可成倍增加,最高达2000 ppmv(1 ppmv= 10^{-6} L/L)以上^[5],称为温室气候(hothouse)^[6]或极热事件(hyperthermal

events)^[7]。因此,它对于理解“深时”极端温室气候条件下古海洋的演化具有重要意义,也是预测未来全球变化的重要参照^[8,9]。

目前,OAE的触发因素主要被归因于大火成岩省(large igneous province, LIP)岩浆作用^[10,11]。岩浆作用释放大量温室气体和营养元素至海洋-大气系统,导致全球升温、生产力提升,并进而引发海洋中氧的溶解度降低、海水分层和溶解氧消耗增加。由于OAE期间地球深部释放大量的C,同时表层系统大规模有机质埋藏,引起全球碳循环发生重大扰动,表现为海水溶解无机碳库碳同位素值($\delta^{13}\text{C}_{\text{DIC}}$)在此过程中发生剧烈波动,导致沉积物中碳酸盐和有机质 $\delta^{13}\text{C}$ 值偏移^[12]。进一步

引用格式: 陈曦, 郭会芳, 姚翰威, 等. 白垩纪大洋缺氧事件OAE2期间碳循环扰动的过程与机制. 科学通报, 2022, 67: 1677–1688

Chen X, Guo H F, Yao H W, et al. Processes and forcing mechanisms of the carbon cycle perturbation during Cretaceous Oceanic Anoxic Event 2 (in Chinese). Chin Sci Bull, 2022, 67: 1677–1688, doi: [10.1360/TB-2021-0806](https://doi.org/10.1360/TB-2021-0806)

研究发现,虽然单个OAE期间沉积物 $\delta^{13}\text{C}$ 总体呈正偏或负偏,但也叠加万年至千年短尺度演化过程^[13-15].大洋缺氧事件期间的碳循环扰动与全球环境演化之间有何关联?这一问题的解答,将有助于对温室条件下地球系统演化机制的深入解析,也是大洋缺氧事件研究中的焦点.

OAE2发生于Cenomanian-Turonian期之交,是白垩纪两次全球性大洋缺氧事件之一^[3].其沉积记录在全球范围内广泛分布(图1)^[16],是现今研究程度最高的一期大洋缺氧事件.根据不同的估算结果,该事件持续时间在400~870 ka之间^[15,18,19].近年来,国际上对于OAE2期间碳循环扰动的过程分析愈加详细,对事件期间古环境演化的过程刻画得越来越精细,为探讨全球环境与碳循环扰动的关系提供了重要基础.本文在近年来国际研究动态的基础上,系统讨论关于OAE2期间碳循环扰动过程与机制的研究进展.

1 OAE2碳循环特征

1.1 $\delta^{13}\text{C}$ 演化过程

在全球不同地区,OAE2期间海洋沉积物的碳同位素值正偏幅度平均约为3‰,其中碳酸盐碳同位素($\delta^{13}\text{C}_{\text{carb}}$)的正偏幅度主要为2‰~4‰,而有机质碳同位素($\delta^{13}\text{C}_{\text{org}}$)正偏幅度在2‰~7‰之间^[20].OAE2的沉积记录主要为黑色页岩,沉积速率较低,难以获得高分辨率

图1 白垩纪大洋缺氧事件OAE2研究剖面或钻孔位置(橙色圆点)^[16].~100 Ma古地理底图来自Hay^[17],红色圆点为西藏贡扎剖面和英国Eastbourne剖面位置.红色虚线区域为大火成岩省位置^[10].1,北极大火成岩省;2,加勒比大火成岩省;3,马达加斯加大火成岩省;4,翁通爪哇大火成岩省

Figure 1 Locations of OAE2 sections in the continents and drilling sites in the oceans (orange dots)^[16]. The paleogeographic map of ~100 Ma is sourced from Hay^[17]. Red dots show the localities of Gongzha section of Tibet and Eastbourne section of England. The enclosed areas marked by red dashed lines indicate coeval large igneous provinces (LIP)^[10]. 1, High Arctic LIP; 2, Caribbean LIP; 3, Madagascar LIP; 4, Ontong Java LIP

$\delta^{13}\text{C}$ 演化曲线.我国西藏特提斯喜马拉雅带贡扎剖面OAE2沉积物主要为灰岩,沉积速率高,厚度可达30 m^[21],为揭示OAE2期间的 $\delta^{13}\text{C}$ 提供了良好的材料. Li等人^[15]基于西藏贡扎剖面 $\delta^{13}\text{C}_{\text{carb}}$ 的研究,结合全球碳同位素地层对比,将OAE2及其上下层位的 $\delta^{13}\text{C}$ 曲线划分为6个主要阶段,分别命名为C1~C6,主要特征如下(图2).

(1) C1阶段为OAE之前, $\delta^{13}\text{C}$ 值相对稳定,在全球不同地区的 $\delta^{13}\text{C}_{\text{carb}}$ 值一般在1‰~3‰之间.

(2) C2阶段紧邻于OAE之下,持续时间约为50 ka. $\delta^{13}\text{C}$ 值出现较小幅度的高频波动, $\delta^{13}\text{C}_{\text{carb}}$ 和 $\delta^{13}\text{C}_{\text{org}}$ 值的波动幅度在1‰左右^[15,23,24].需要指出的是,有些地区该阶段特征表现不明显^[19,25,26].

(3) C3阶段为 $\delta^{13}\text{C}$ 快速上升阶段,持续时间约为280 ka^[15]. $\delta^{13}\text{C}$ 值在C3顶部达到整个OAE2期间的最高值.高分辨率分析结果显示,该阶段 $\delta^{13}\text{C}$ 演化可进一步划分为3个次级阶段,自下而上分别命名为C3a、C3b和C3c,持续时间分别为110、80和90 ka.其中,C3a和C3c为 $\delta^{13}\text{C}$ 正偏,C3b的 $\delta^{13}\text{C}$ 为短期小幅度负偏.

(4) C4阶段 $\delta^{13}\text{C}$ 值略低于C3顶部,但仍处于高值,整体变化较小,持续时间约为370 ka^[15].

(5) C5阶段 $\delta^{13}\text{C}$ 快速下降,最终恢复到与C1相近的 $\delta^{13}\text{C}$ 值,该阶段持续时间约为170 ka.此后 $\delta^{13}\text{C}$ 值保持相对稳定,即为C6阶段^[15]. Li等人^[15]未明确标示C6阶段的终止层位,根据前人研究,该阶段可持续至Turonian早期 $\delta^{13}\text{C}$ 正偏事件,即Holywell事件.

上述 $\delta^{13}\text{C}$ 演化特征是OAE2进行全球对比的重要工具. OAE2的起始标志为C3阶段底部,但国际上对其终止层位有两种主要观点.一是认为OAE2结束于C4顶部^[25],二是认为OAE2结束于C5顶部^[12].

1.2 $\delta^{13}\text{C}_{\text{carb}}$ 与 $\delta^{13}\text{C}_{\text{org}}$ 差值及 $p\text{CO}_2$

OAE2期间 $\delta^{13}\text{C}_{\text{carb}}$ 与 $\delta^{13}\text{C}_{\text{org}}$ 的演化趋势是相似的,这是因为两者均反映海水 $\delta^{13}\text{C}_{\text{DIC}}$ 演化.通常 $\delta^{13}\text{C}_{\text{carb}}$ 与 $\delta^{13}\text{C}_{\text{org}}$ 呈显著正相关,表明二者均未受到成岩作用的影响^[27].但在不同时期二者变化幅度有所差异,前人研究认为,这是由于生物在光合作用过程中碳同位素分馏系数(ϵ_p)随时间变化所致^[28,29].而 ϵ_p 与海水中的 CO_2 浓度呈线性关系^[30],后者与大气 CO_2 分压($p\text{CO}_2$)是动态平衡的.换言之,沉积物 $\delta^{13}\text{C}_{\text{carb}}$ 与 $\delta^{13}\text{C}_{\text{org}}$ 的差值(用 $\Delta^{13}\text{C}$ 表示)可定性地表征 $p\text{CO}_2$. $\Delta^{13}\text{C}$ 指标的使用前提是地层中的岩性和有机质来源没有明显变化,因此不太适用于长周期 CO_2 浓度的重建,而在持续时间<1 Ma的大洋缺氧

图2 OAE2期间碳循环与全球古环境演化过程。图中显示了PCE事件层位(蓝色区域)^[22], $\delta^{13}\text{C}$ 演化阶段划分方案及持续时间^[15], $\delta^{13}\text{C}$ ^[12]和 $p\text{CO}_2$ 演化过程^[12,22], 大火成岩省岩浆作用强度、有机碳埋藏通量和大陆风化强度^[33]

Figure 2 Evolution of the carbon cycle and major environmental changes during OAE2. The interval of Plenus Cold Event (PCE, blue shaded area)^[22], the segments and their durations of the $\delta^{13}\text{C}$ curve^[15], $\delta^{13}\text{C}$ ^[12], idealized CO_2 fluctuations^[12,22] and the trends in rate of LIP magmatic activity, organic matter burial and silicate weathering intensity are shown^[33]

事件研究中获得应用, 且与植物气孔指数定量重建的 $p\text{CO}_2$ 结果具有相同的演化趋势^[5,12]。

前人在原北大西洋邻近区域和西特提斯通过 $\Delta^{13}\text{C}$ 重建了OAE2期间 $p\text{CO}_2$ 的演化历史(图2), 结果显示在不同区域 $\Delta^{13}\text{C}$ 具有相似的趋势。 $\Delta^{13}\text{C}$ 突出特点是在C3阶段降低并达到OAE2期间的极低值, 而在C4阶段初期恢复。这种演化过程与海洋表层温度及古生物记录吻合。Gale和Christensen^[31]指出在C3阶段北方域箭石出现在特提斯域, 表明了全球降温。有机质古温度计 TEX_{86} 重建的海洋表层温度也表明在该阶段出现约 3°C 的降温^[32]。OAE2期间这一显著降温事件被称为Plenus冷事件(Plenus Cold Event, PCE)^[22,31]。但在不同地区 $\Delta^{13}\text{C}$ 和古气候演化过程有如下细微差异: (1) $\Delta^{13}\text{C}$ 极低值多数出现于C3a顶部, 但也有些地区出现在C3b或C3c中, 即 $\Delta^{13}\text{C}$ 记录的古气候演化在空间上具有穿时性^[22,33]。(2) 古生物记录和古温度指标显示PCE可进一步细分为两次降温事件^[31,34], 但 $\Delta^{13}\text{C}$ 演化中并不易分

辨两次变冷事件。目前, OAE2期间 $\Delta^{13}\text{C}$ 的研究还较少, 进一步在全球范围内开展高分辨率研究, 有望为解释上述差异提供依据。

2 OAE2碳循环扰动的控制因素

2.1 碳循环与生物泵

海洋表层植物通过光合作用吸收 CO_2 , 部分以颗粒有机碳形式保存下来, 这一过程称为生物碳泵作用。生物光合作用优先利用轻碳, 是导致海水 $\delta^{13}\text{C}_{\text{DIC}}$ 变化的重要机制。在正常海洋条件下, 生物富集轻碳, 但在有机质沉降过程中或沉降之后, 有机质的分解会使大部分轻碳重返海洋-大气系统中。在这种动态平衡下, 海洋沉积物的 $\delta^{13}\text{C}$ 值不会发生显著改变。而当海洋初级生产力快速提升或者海洋缺氧时, 会导致大量有机质埋藏, 使海水 $\delta^{13}\text{C}_{\text{DIC}}$ 正偏。

OAE2期间, 黑色页岩在全球范围内广泛分布, 尤

其是在西特提斯域、原北大西洋和南大西洋浅海区域^[20]。在边缘海远滨环境, 沉积物总有机碳(total organic carbon, TOC)含量较高, 特别是有上升洋流区域, 如北非摩洛哥地区。OAE2黑色页岩的TOC含量主体在2%~15%之间^[20], 最高可达45%以上(DSDP367站位)^[35]。根据全球不同地区沉积物中的总有机碳含量估算, Owens等人^[20]发现OAE2期间全球埋藏大约70 Eg(1 Eg=10¹⁸ g)碳, 通量是现今海洋碳埋藏通量的2倍多。通过碳同位素质量平衡模型计算, OAE2期间海水 $\delta^{13}\text{C}_{\text{DIC}}$ 值发生3‰正偏, 需要全球有机碳埋藏量约为90 Eg^[20]。因此, 大规模有机质埋藏是OAE2期间海洋 $\delta^{13}\text{C}$ 整体正偏的主要原因。

已有研究指出, 海洋表层生产力提升和海洋缺氧状态导致了OAE2期间沉积物中有机质含量增加^[23,36,37]。一方面, 大火成岩省的强烈岩浆作用向海洋输入大量生物营养元素, 而高温、高CO₂条件促使全球水文循环加强和大陆风化增强, 进一步提升海洋中生物营养元素的含量^[3,36]。上述过程刺激海洋表层生产力, 可能是OAE2期间大规模有机质埋藏的一个原因。另一方面, 有机质降解消耗海水溶解氧, 高温条件下氧气溶解度下降等, 引起OAE2期间海洋缺氧。而在缺氧条件下, 营养元素P从沉积物中释放, 进一步促进生产力提升^[37]。因此, 生产力增强和缺氧条件形成正反馈, 增加了沉积物中有机质输入通量, 也改善了有机质保存条件, 共同促使有机质埋藏量增加。

近年来的研究表明, 大陆风化带来的黏土矿物输入增加、缺氧条件下形成有机硫化物对有机质保存具有促进作用^[38-41], 有助于提升生物泵效率。

2.2 碳循环与LIP

前人通过非传统金属同位素研究提出, 白垩纪大洋缺氧事件主要由大火成岩省岩浆作用触发导致^[10,42-44]。OAE2之前20~50 ka海水Os和Ca等同位素剧烈漂移表明了OAE2与大火成岩省之间具有直接成因联系^[45-47]。在此期间活跃的大火成岩省包括加勒比、马达加斯加、翁通爪哇和北极大火成岩省(High Arctic LIP)等^[11]。大火岩省岩浆作用会将深部大量的CO₂释放到地球表层。研究表明, 深部释放CO₂的 $\delta^{13}\text{C}$ 值相对于地球表层碳库是一个显著的轻碳源^[48]。理论上, 大洋缺氧事件之前的大火成岩省岩浆作用将会降低海水的 $\delta^{13}\text{C}_{\text{DIC}}$ 值, 导致C2阶段沉积物 $\delta^{13}\text{C}$ 值负偏^[49]。然而, 全球OAE2沉积记录在C2阶段具有显著差异。有些地区在

C2阶段 $\delta^{13}\text{C}$ 值负偏, 幅度可达1‰~2‰, 如我国西藏特提斯喜马拉雅带、太平洋西部的日本地区和南大洋Kerguelen高原等^[15]。在西特提斯、欧洲北方域、原北大西洋等地区, 多数剖面C2阶段 $\delta^{13}\text{C}$ 值相对稳定^[15,25,32]。早期成岩作用导致的沉积物 $\delta^{13}\text{C}$ 负偏, 不在本文讨论范畴。如摩洛哥地区C2阶段碳酸盐 $\delta^{13}\text{C}$ 负偏幅度可达4‰, 可能是早期成岩阶段有机质降解的轻碳形成了自生碳酸盐胶结物^[50]。

OAE2期间的大规模岩浆活动主要发生于海底^[7,10]。海底岩浆喷发引起海水升温、氧气的溶解度下降和海洋缺氧以及区域有机质埋藏增加等过程, 可能是导致不同区域碳同位素响应有所差异的主要原因。C2阶段 $\delta^{13}\text{C}$ 值负偏在开阔大洋地区表现更为明显, 而在相对局限的海域, 其趋势差异显著。这一结果进一步表明, 区域因素可能是影响C2阶段 $\delta^{13}\text{C}$ 值演化的重要控制条件。

尽管越来越多的证据表明LIP岩浆活动是导致OAE2的直接原因^[10], 但OAE2启动时C同位素在全球有所差异。这与白垩纪另一次全球性大洋缺氧事件OAE1a形成明显差别, 后者在事件启动层位出现一次全球性 $\delta^{13}\text{C}$ 负偏, 其负偏幅度在3‰以上^[51,52]。在整个OAE2期间, $\delta^{13}\text{C}$ 突出特征是正偏, 但在C3阶段中部(C3b)呈全球同步的小幅度负漂。没有证据表明在C3b阶段LIP活动更强, 反而有其他证据指示这次负漂事件与气候变冷^[22]、陆源输入^[36]和底层水氧化还原条件改变^[53,54]有关。综上所述, LIP岩浆活动导致了地球系统碳循环扰动, 但海水 $\delta^{13}\text{C}$ 演化是多种因素共同作用的综合结果。

2.3 碳循环与海水氧化还原条件

海洋氧化还原条件是大洋缺氧事件研究中的一个热点, 用于OAE研究中的指标包括Mn、V、Cr、Mo、U等氧化还原敏感元素^[55-57], 黄铁矿化指数^[24], 生物标志化合物^[58], 铁组分^[59], I/Ca比值^[60], Ce异常^[61], N同位素^[62], Mo同位素^[63], U同位素^[64], Tl同位素^[65]等。其中, 碳酸盐相U同位素和Tl同位素能够反映全球性海水的氧化还原状态, 而其他指标往往指示区域水体信息。

研究表明, OAE2期间, 在原北大西洋和西特提斯等相对局限的区域, 海洋底层水主要呈缺氧状态, 而在太平洋和东特提斯等开阔大洋主要为氧化状态^[24]。OAE2时期, 水体氧化还原条件在时间和空间上均有动态演化的特征。PCE期间在北大西洋及周边地区显示水

体氧化^[36,66], 被称为OAE2期间的海洋再氧化^[22], 或底层水氧化事件(Benthic Oxidic Event)^[66]. 但在东特提斯地区西藏贡扎剖面V/Cr比值略有增加^[67], 指示向还原条件转变. 通过铁组分和等温剩磁分析, Li等人^[68]研究了贡扎剖面OAE2层C3阶段氧化还原状态演化的过程, 与北大西洋域摩洛哥Tarfaya剖面对比, 发现二者呈现同步、氧化还原状态相反的变化^[68,69]. 有学者提出, 白垩纪中期局限和开阔大洋水体的氧化还原状态呈“跷跷板”式动态变化^[70], 即当原北大西洋水体为铁化条件时, 铁向太平洋输入, 导致太平洋生产力提升, 有机降解过程中消耗溶解氧, 导致太平洋地区水体向还原状态转变. 而当原北大西洋为更加缺氧的硫化状态时, 向太平洋输入铁的通量降低, 使太平洋可维持在较为氧化状态^[70]. 这可能是OAE2期间全球不同区域海洋氧化还原状态有明显差异的机制. 因此, OAE2期间海洋氧化还原状态在时间和空间上具有复杂性, 要分析其与全球碳循环扰动的关系, 需要对全球海水的氧化还原状态进行更为精确的评估.

碳酸盐相U同位素结合地球化学模拟研究, 揭示了在OAE2期间全球大洋缺氧的程度及其演化规律, 发现在此期间海底缺氧面积可达8%~15%^[64]. 海底大面积缺氧, 导致有机质保存条件好, 同时在还原条件下生物营养元素P难以形成磷酸盐沉淀在孔隙水中, 而游离到上层水体, 进一步刺激生产力, 形成“缺氧-生产力提升-进一步缺氧”的正反馈过程, 提升了生物泵效率, 最终导致海水 $\delta^{13}\text{C}$ 能够长时间维持在高值^[37]. 另一方面, 在硫化水体中可形成有机硫化物, 亦可改善有机质保存条件^[39]. 前人研究发现, 虽然OAE2期间海洋缺氧面积扩张, 但PCE期间 $\delta^{238}\text{U}$ 值正偏约0.2‰(图3), 估算海底缺氧面积减少至约5%^[64]. 在原北大西洋周边地区开展的OAE2期间海水Zn同位素演化研究, 也表明PCE期间原北大西洋及邻近地区海水经历了再氧化过程^[53,54]. 因此, OAE2期间海水氧化还原状态具有早期缺氧、PCE期再氧化和后期缺氧的三阶段演化特征. 综合以上分析, 本文认为OAE2早期大规模沉积的有机质在PCE期间被氧化, 可将大量轻碳输入海水储库. 这一过程可能是导致C3b阶段碳同位素负漂的重要原因.

同时, U同位素演化指示海洋脱氧过程的启动时间在碳同位素演化的C2阶段, 略早于OAE2, 与前人通过Os同位素^[45]揭示的岩浆作用增强的层位相当, 也与Li同位素揭示的洋底新鲜玄武岩风化增强^[71]处于同一层位. Ostrander等人^[65]通过Ti同位素研究也提出海洋开

始脱氧早于OAE2启动约43 ka. 海洋缺氧导致的有机质保存削弱了大火成岩省岩浆作用输入轻碳对海水 $\delta^{13}\text{C}_{\text{DIC}}$ 的影响. 海洋开始脱氧时, 优先影响的区域是相对局限的海洋, 而开阔大洋的氧化还原状态可能变化相对较小. 因此, 本文认为, 这种C2阶段海洋脱氧是导致在局限海洋中 $\delta^{13}\text{C}$ 值无明显负偏的一个重要原因. 在此过程中, LIP带来的营养物质刺激表层生产力可能是另一个原因.

2.4 碳循环与硅酸盐风化作用

缺氧事件期间水文循环增强, 陆地向海洋输入通量增加^[36,73]. 硅酸盐风化通过3个过程可对地球表层激增的 CO_2 起到负反馈作用: 一是风化带来的黏土矿物对于有机质的保存具有重要作用^[74]. 二是风化输入大量营养物质, 可提升海洋表层生产力; 三是硅酸盐风化消耗 CO_2 . 前两者可导致海水 $\delta^{13}\text{C}$ 上升, 后者带来陆地有机质的大量输入, 有机质降解会导致海水 $\delta^{13}\text{C}$ 值降低.

近年来, Li、Ca、Zn等同位素研究^[67,71,72]揭示了在OAE2期间硅酸盐风化强度具有两个差异明显的阶段(图3): OAE2初期~200 ka内(C3阶段)风化持续增强; OAE2后期风化逐渐减弱. 风化增强阶段与 $\delta^{13}\text{C}$ 持续正偏几乎同步, 指示风化输入的黏土矿物和营养物质对于生产力提升和有机质保存条件改善的促进作用. 风化强度在C3阶段上部达到峰值, 与OAE2期间 CO_2 含量最低值及PCE对应(图3). 上述结果表明, 在OAE2初期, 风化强度提升和生物泵作用增强共同促进了大气-海洋系统中过量的 CO_2 消耗, 这种负反馈机制调节了地球气候.

在此之后, 海洋再一次进入缺氧状态, 并持续了300 ka^[19]甚至600 ka^[15], 即C4和C5阶段. 风化强度减弱而岩浆作用仍然活跃导致 CO_2 含量上升和全球升温可能是其主要原因. 在此阶段, 海洋生产力提升和缺氧条件是生物泵固碳及海水 $\delta^{13}\text{C}_{\text{DIC}}$ 增加的主要因素.

3 OAE2碳循环扰动期间全球环境演化过程

综合上述可知, 在OAE2期间全球碳循环受到LIP岩浆作用、海水氧化还原条件、海洋表层生产力和有机质保存条件、大陆风化等因素共同影响. 海水碳同位素演化直接反映了上述因素对全球碳循环影响的结果(图4). OAE2期间碳同位素演化分为6个阶段, 其中C1与C6为背景状态, C2~C5阶段为碳循环扰动期. 本

图3 西藏贡扎剖面Zn同位素^[67]和英国Eastbourne剖面Li^[71]、Ca同位素^[72]记录,反映了硅酸盐风化强度在OAE2初期加剧、后期减弱的演化过程. Eastbourne剖面U同位素^[64]记录显示在PCE期间海洋经历了再氧化的演化阶段. 灰色箭头表示在OAE2初期200 ka硅酸盐风化强度快速提升. **Figure 3** Zn isotope plot from Gongzha section of Tibet^[67] and Li^[71] and Ca^[72] isotope plots from Eastbourne section of England. These curves indicate that the silicate weathering intensity enhanced in the early stage of OAE2 and decreased in the later stage of this event. The U isotope curve from Eastbourne section^[64] indicates a re-oxygenation during the PCE interval. The gray arrows show the rapid increase of silicate weathering intensity in the initial ~200 ka of OAE2

文通过上述分析将OAE2期间碳同位素及其控制因素的演化过程总结如下.

C2阶段(图4(a))LIP岩浆活动剧烈,释放大量轻碳至地球表层,理论上将导致海洋 $\delta^{13}\text{C}_{\text{DIC}}$ 负偏,开阔海域沉积物记录了C2阶段 $\delta^{13}\text{C}$ 的负偏特征.但在局限海域,由于热液和陆地风化带来营养物质,刺激海洋生产力快速提升,同时海底缺氧范围开始扩张,利于有机质保存. OAE2期间 $\delta^{13}\text{C}_{\text{org}}$ 值为 -25‰ 左右^[12,19],若要使C2阶段全球海水同位素不发生 1‰ 漂移,则该阶段碳埋藏较背景值增量约为 $1800 \times 10^{15} \text{ g}$ ^[48].该阶段持续时间约为50 ka,因此埋藏速率增量约为 $0.04 \times 10^{15} \text{ g/a}$.假设白垩纪中期碳埋藏通量背景值与现今相近为 $0.16 \times 10^{15} \text{ g/a}$ ^[74],C2阶段碳埋藏速率增加约25%,则可导致 $\delta^{13}\text{C}_{\text{DIC}}$ 值无明显变化.

C3a阶段(图4(b))大陆风化和海底火山岩风化作用显著增强,导致海洋化学条件急剧变化.在海洋营养物

质增加、海洋缺氧面积持续扩张的情况下,生物泵固碳作用不断增强,而导致海洋-大气系统中的 CO_2 消耗、有机质埋藏和海水 $\delta^{13}\text{C}_{\text{DIC}}$ 快速正偏. C3b-c阶段(图4(c))硅酸盐风化作用持续增强,导致了OAE2期间一段全球海洋再氧化和气候转凉时期.风化导致陆地输入的有机质增多,并且C3阶段在风化和生物光合作用下,导致大气氧含量上升,促使陆地野火事件增多^[75],可进一步增强陆地有机质输入通量增加.大量陆源有机质和海底前期沉积的富有机质页岩,在氧化作用下释放轻碳导致 $\delta^{13}\text{C}$ 负偏.

C4阶段(图4(d))硅酸盐风化强度减弱,并且该阶段初期LIP岩浆活动强,导致了全球海洋返回到缺氧、高生产力状态,二者通过营养元素循环和有机质降解耗氧,形成正反馈^[37].导致海水 $\delta^{13}\text{C}$ 升高到OAE2期间最高值,并持续 $\sim 370 \text{ ka}$ ^[15].此后,岩浆活动减弱,风化强度降低,海洋营养盐限制,生产力降低而打破上述正反

图 4 OAE2期间碳循环扰动与古环境演化相互作用模式图。(a) C2阶段; (b) C3a阶段; (c) C3b~C3c阶段; (d) C4阶段; (e) C5阶段

Figure 4 Cartoon showing the interactions between carbon cycle perturbation and the evolution of major environmental changes during OAE2. (a) Segment C2; (b) segment C3a; (c) segment C3b~C3c; (d) segment C4; (e) segment C5

馈循环,使得在C5阶段(图4(e))海洋生物固碳作用减弱, $\delta^{13}\text{C}$ 逐步降低到OAE2之前水平,海洋碳循环扰动事件得以终止。

4 总结

通过海水 $\delta^{13}\text{C}_{\text{DIC}}$ 演化及其控制因素分析,本文综述了OAE2期间全球环境演化过程及其对碳循环的影响:大火成岩省岩浆作用是OAE2碳循环扰动的触发因素,海洋生产力和缺氧条件是导致海水 $\delta^{13}\text{C}$ 演化的直接原因,大陆风化强度和海水氧化还原条件动态演化对OAE2期间 $\delta^{13}\text{C}$ 次级波动具有重要影响。如同地质历史中多次全球性重大事件一样,大规模火山作用所引起的全球剧烈环境变化^[76],是导致OAE2碳循环扰动的根本原因。

目前在OAE2期间碳循环扰动与控制因素方面仍存在一些问题有待解决。从长周期看,碳循环扰动在C5

阶段末期结束,但古温度记录显示此时仍为极端高温时期。即,高效率生物泵作用并未能导致全球气候转凉^[77]。从短周期看,在C3阶段大陆风化增强是持续的,但古温度记录往往显示气候变化具有突变的特点。这一方面反映了在极端温室条件下,全球气候演化的控制因素具有复杂性。另一方面,地球系统中其他重要因素,例如溶解有机碳库对全球碳循环和气候演化的影响,特别是微生物碳泵的作用^[78],还欠缺相关研究。此外,古温度和古生物记录表明C3c阶段为OAE2期间最冷时期,但多数地区的 $p\text{CO}_2$ 重建结果显示在C3a顶部达到最低值,二者在时间上不一致。是否预示着白垩纪极端温室条件下海水温度与大气 CO_2 浓度在一定程度上解耦^[79],目前还无法回答其形成机制。未来的工作,需要获得更高时、空分辨率古环境演化数据,对地球系统中的因素进行全面研究,才可能使得OAE2期间碳循环与古气候演化得到更好理解。

致谢 感谢中国地质大学(武汉)David Kemp教授对英文摘要的修改。

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Summary for “白垩纪大洋缺氧事件OAE2期间碳循环扰动的过程与机制”

Processes and forcing mechanisms of the carbon cycle perturbation during Cretaceous Oceanic Anoxic Event 2

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Oceanic Anoxic Event 2 (OAE2, ~94 Ma) was one of two global oceanic anoxic events in the Cretaceous and has been one of the most studied paleoceanographic events of the Mesozoic. Owing to the hyperthermal climate state during OAE2, it serves as a key event in the study of Earth system evolution during extreme greenhouse warmth. Recently, high temporal and spatial resolution studies and the application of globally representative paleoenvironmental proxies have permitted major advances in our understanding of the triggering mechanisms and feedbacks of the Earth system during OAE2. By reviewing these findings, this paper analyzes the detailed processes involved in the OAE2 carbon cycle perturbation and associated environmental changes to elucidate the mechanisms that forced the evolution of carbon isotopes ($\delta^{13}\text{C}$) in seawater through the event. The most remarkable feature of OAE2 is a sharp positive $\delta^{13}\text{C}$ excursion recorded globally, indicating a major perturbation of carbon cycle during the event. Outgassing from massive magmatism associated with large igneous province (LIP) emplacement was the major trigger of this carbon cycle perturbation. Increased primary productivity and extensive anoxia were responsible for the long-term positive $\delta^{13}\text{C}$ excursion during OAE2. Interactions between paleoenvironmental parameters, such as weathering intensity, paleotemperature, CO_2 concentration, primary productivity and seawater redox condition controlled the short-term $\delta^{13}\text{C}$ changes, which are superimposed on the long-term positive excursion of the entire OAE2 event.

In this paper, we present a comprehensive model for the interactions between paleoenvironment changes and $\delta^{13}\text{C}$ fluctuations through OAE2. The $\delta^{13}\text{C}$ curve across the OAE2 has been previously divided into six segments by Li et al. (2017), labeled as C1 to C6, among which the major carbon cycle perturbation interval spans segments C2 to C5. During segment C2, a minor negative excursion in $\delta^{13}\text{C}$ with a magnitude of ~1‰ is observed in open marine settings and relates to outgassing from LIP magmatic activity. However, enhanced productivity and deoxygenation of seawater during C2, especially in restricted marine settings, promoted the preservation of organic matter and this in turn led to an increase of $\delta^{13}\text{C}$. Based on simple mass balance calculation, we suggest that a 25% increase in the burial rate of organic carbon could diminish the effects of LIP outgassing on $\delta^{13}\text{C}$ values in seawater and lead to relatively stable $\delta^{13}\text{C}$ values during C2 in restricted seas.

Segment C3 is characterized by a rapid increase in $\delta^{13}\text{C}$ values that lasted for ~280 ka. Significantly enhanced biological fixation of carbon is suggested to be responsible for the positive excursion in $\delta^{13}\text{C}$. A globally recorded negative excursion in $\delta^{13}\text{C}$ has been found in the middle of this segment, which is consistent with an interval of maximum weathering intensity and global cooling. We suggest that reoxygenation of bottom water owing to cooling and consequent respiration of organic carbon from enhanced continental input and organic rich sediments could be the major cause of this decrease in $\delta^{13}\text{C}$ in the middle of segment C3.

Within the lower part of segment C4, LIP magmatism remained active and weathering intensity decreased, which led to a return to anoxic conditions and a highly fertilized state within the oceans. Consequent high burial rate of organic matter resulted in the positive trend in $\delta^{13}\text{C}$. Meanwhile, the sediment retention potential for nutrients (e.g., P) decreased under anoxic conditions, which led to sustained high primary productivity and high $\delta^{13}\text{C}$ ($\delta^{13}\text{C}$ plateau) that lasted for ~370 ka. After this peak in $\delta^{13}\text{C}$, nutrient supply from weathering and LIP magmatism reached a minimum threshold to maintain a productivity-anoxia feedback, which in turn led to the inevitable recovery of $\delta^{13}\text{C}$ (segment C5) to pre-OAE values and the termination of OAE2.

Cretaceous, oceanic anoxia, large igneous province, burial of organic matter, silicate weatheringdoi: [10.1360/TB-2021-0806](https://doi.org/10.1360/TB-2021-0806)