海洋惰性溶解有机碳库与海侵黑色页岩

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海洋是地球上重要的碳储库, 是大气碳储库的50多倍, 包括颗粒无机碳(particulate inorganic carbon, PIC)、溶解无机碳(dissolved inorganic carbon, DIC)、颗粒有机碳(particulate organic carbon, POC)和溶解有机碳(dissolved organic carbon, DOC)四大类^[1]. 现代海洋的DOC库约为 $(662 \pm 32) \times 10^{15}$ g碳^[2], 远大于POC库, 占海洋总有机碳库的90%以上^[3]. 根据生物可利用性, 又可将DOC分为很容易被降解的活性溶解有机碳(labile dissolved organic carbon, LDOC)、可被缓慢降解的半活性溶解有机碳(semi-labile dissolved organic carbon, SLDOC)和难以被降解的惰性溶解有机碳(refractory/recalcitrant organic carbon, RDOC)三类^[3]. LDOC与SLDOC活性较高, 在水中仅可存在几天到几十天就被降解或被生物利用, 而且只占很少一部分, 约为 $(20 \pm 3) \times 10^{15}$ g碳^[2]. RDOC是DOC的主体, 占比超过95%, 约为 $(642 \pm 32) \times 10^{15}$ g碳^[2], 总量与大气碳库相当, 可以在海洋中保存数千年^[4-7]. 根据碳同位素地质记录推测, RDOC也可能存在于地质历史时期的海洋中, 尤其是在新元古代晚期, 海洋中可能存在超大型的RDOC库, 是目前海洋RDOC库的百倍甚至千倍^[4]. 如果这一推测是正确的, 那么如此巨大的RDOC库是如何消减或者消失的? 有没有可能进入地质储库? 如何进入地质储库? 自生碳酸盐矿物在海洋中沉淀时是否可以部分RDOC转移到地质储库还有待进一步研究证实^[1,8,9]. 本文依据黏土矿物对有机物的吸附作用和黑色页岩富含有机质的特性提出大胆猜测, 认为海平面快速上升的海侵超覆过程以及远洋深层水上涌, 可将深水的RDOC运输到浅水区域或者风化剥蚀面之上, 与黏土沉积物混合并被吸附后沉积形成黑色页岩. 因此, RDOC可能对海侵黑色页岩中的有机质有重要贡献.

1 RDOC库的形成与演化

学术界对RDOC组成的认识还有待不断地提高和完善. RDOC主要以固相可萃取的溶解有机物(SPE-DOM)为代表, 是数千种组分的混合物, H/C和O/C元素比超出常规蛋白质、脂类和碳水化合物范围, 富含羧酸盐和稠脂环碳, 与多环脂具有相似的结构特征^[10]. RDOC主要在远洋水体, 浓度约为 $34\sim 45 \mu\text{mol/kg}$ ^[11]. RDOC的来源曾困惑学术界近半个世纪^[12]. 目前学术界普遍认为微型生物碳泵(microbial carbon

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pump, MCP)是RDOC产生的主要机制^[3,4,12-14]. 细菌和古菌的胞外分泌作用、病毒的裂解作用以及浮游动物的撒漏摄食、分泌和排泄等作用都可以产生RDOC^[4], 可以概括为3种来源: (1) 直接来源于细胞物质; (2) 来源于颗粒有机碳降解的产物; (3) 微生物利用LDOC和SLDOC后的剩余产物^[12]. 微生物培养实验研究表明, 细菌可以将LDOC(例如葡萄糖和谷氨酸)高效地转化为RDOC^[15].

RDOC不易降解, 不易沉降, 可长时间保存在海洋水体中. 现代海洋的RDOC库是动态变化的体系, 据有关研究估计, 完全更新需要16000~30000年时间^[10,16]. 一方面微生物碳泵向水体供给RDOC, 另一方面随着水体的循环与老龄化, RDOC会有所损耗或流失. 例如, 有研究显示太平洋深部海水中的RDOC库正以 $\sim 0.003 \mu\text{mol}/(\text{kg a})$ 的速率缩减^[17]. 目前对RDOC库消减机制的研究还不是十分全面系统^[18], 虽然已有一些有价值的观点, 例如: 紫外线辐射可能导致表层水体中的RDOC氧化^[19,20], 海平面上产生的气溶胶可以带走一部分RDOC^[21], 水体循环的稀释与扩散、颗粒吸附RDOC后沉降、海底热液的改造、RDOC自我凝聚成凝胶沉降等作用可能会导致深水区的RDOC库缓慢地消减, 但是还需要进一步的深入研究^[2,22].

根据RDOC的形成机制推断, 动态变化的RDOC库也会存在于地质历史时期的海洋中. 有研究认为, 古新世到始新世转变时期的全球变暖事件就是由海洋RDOC库向大气排放

碳所致^[23]。古海洋学家通过对地质历史时期的有机碳和无机碳的稳定同位素记录的分析研究推测, RDOC可能在古海洋中普遍存在, 新元古代晚期巨大的RDOC库可能是现代海洋的数百倍甚至上千倍^[4,24-26]。古海洋中的RDOC是否与现代海洋中的RDOC相似, 由哪些分子组成, 碳库有多大, 在地质历史时期是如何发生动态变化的? 要回答这一系列问题, 首先需要深入研究RDOC是否可以沉积并保存在地质记录中, 其次是如何从地质记录中识别出古代的RDOC。

2 黏土矿物对RDOC的吸附作用

黏土矿物是指具有层状结构的含水铝硅酸盐矿物, 主要包括高岭石族、蒙脱石族、伊利石族、绿泥石族等矿物。黏土矿物通常是岩石风化的终端产物, 因此是构成土壤的重要组成部分。黏土沉积物颗粒细小, 直径一般为几微米到几十微米, 可以较长时间悬浮在水体中, 经长距离搬运后沉积在离物源较远的区域, 因而是构成泥岩和页岩的主要矿物成分^[27,28]。

黏土矿物颗粒细小, 比表面积大(蒙脱石: $800\text{ m}^2/\text{g}$; 伊利石: $30\text{ m}^2/\text{g}$; 高岭石和绿泥石: $< 20\text{ m}^2/\text{g}$)^[29], 层间域有较大的胀缩性, 八面体结构中富含金属元素, 表面具有裸露的羟基官能团。因此, 它们不仅具有很强的亲水性, 而且还具有吸附土壤、沉积物和水体中溶解有机碳的特性^[30]。尤其是蒙脱石黏土和伊利石-蒙脱石混合黏土, 因为巨大的活性表面可以大量吸附水体和空隙溶液中的DOC^[29]。实验研究表明, 每克伊利石-高岭石黏土可吸附 29.2 mg DOC , 每克蒙脱石黏土可吸附 77.5 mg DOC , 每克水铝英石黏土可吸附 123.5 mg DOC ^[30]。DOC可以被吸附在矿物外表面, 绝大部分被吸附在黏土矿物的层间域^[26]。而且, DOC被黏土矿物蒙脱石、伊利石等吸附后很不容易降解^[31], 尤其是被束缚在黏土矿物层间域的有机物, 很难再被微生物利用^[29]。在沉积物或土壤中, 有机物可以与铁的氧化物或者氢氧化物(例如水铁矿)结合, 形成矿物与有机物的复合体, 对有机质的降解也有很强的抑制作用^[32]。因此, 黏土矿物对有机质在黏土沉积物中的富集和长期保存起重要作用。研究发现, 黑色页岩总有机碳(total organic carbon, TOC)的含量与黏土矿物活性表面的大小呈正相关关系, 并因此提出黏土矿物的活性表面大小是黑色页岩有机质埋藏和保存的一级控制因素^[29]。地层中富有机质的黑色页岩与贫有机质的岩层截然交替出现的现象很可能与水体或空隙溶液中DOC浓度的周期性变化有关^[29]。

黏土矿物与有机化合物的相互作用是很复杂的过程, 与两者自身的物理化学性质息息相关, 主要有以下几种吸附机制: 配位键交换作用、离子交换作用、阳离子桥作用、范德华力作用和氢键作用等。不同类型黏土矿物的吸附机制不尽相同, 不同机制的吸附能力差别很大, 对不同类型的有机物也有一定的选择性。具体关系十分复杂, 请参阅文献^[33,34], 这里暂不赘述。

3 黑色页岩与海侵黑色页岩

黑色页岩是富含黏土矿物和有机质的细碎屑岩(泥页岩), 黏土沉积物含量一般大于50%, TOC含量大于1%, 通常为2%~10%^[35-37], 造成“黑色”的主要原因是较高的有机质和黄铁矿含量^[37]。黑色页岩不仅是石油和天然气生成和储藏的重要地质体, 而且富含Ni、Mo、Cu、Zn、Ag、Cr、V、U等10多种金属元素, 具有很高的经济价值^[35], 因此在地球科学领域很受关注。黑色页岩在时间和空间上分布广泛, 在各主要大陆元古宙以来的海相或陆相沉积地层中广泛发育, 沉积环境变化多样, 可以形成于深海、浅海陆棚、泻湖、陆相湖泊等沉积环境^[35,36]。

过去很长一段时间, 地质学研究通常认为黑色页岩与滞流、缺氧和深水条件有关, 沉积环境类似于现代的黑海, 底层海水盐度高、缺氧, 海底主要是富含有机质的黑色淤泥, 因此提出“黑海淤泥”沉积模型^[35,37]。但是, 通过对地质历史时期的黑色页岩的沉积环境研究发现, 黑色页岩可以形成于开阔的陆表海环境, “黑海淤泥”模型不能够解释所有的黑色页岩的成因^[35,37], 于是又提出了多达10余种黑色页岩沉积模型^[35,38]。这些沉积模型主要考虑三大因素: (1) 有机质的生产与供给; (2) 有机质的降解或者氧气的消耗速率; (3) 陆源黏土沉积物的沉积速率^[36,39,40]。可见, 黑色页岩的形成首先是有有机质的供给要相对充足, 可以是原地生产并沉积的有机质, 也可以从异地输入。其次, 有机质的降解不能太快, 或者说氧气的需求要大于供给, 否则有机质无法积累。再次, 沉积速率也不能太快, 如果陆源黏土物质输入过快, 有机质会被稀释, TOC的含量达不到1%, 即便是有机质的生产和供给相对充足也无法形成黑色页岩。如果只考虑这3种因素, 在有机质供给相对过剩、沉积速率相对较慢、底层水氧化的条件下也可以形成富含有机质的泥质沉积物。但是保存在沉积物中的有机质还可以被继续氧化分解, 或者通过发酵作用、厌氧呼吸作用、产烷作用等被微生物进一步分解。因此, 还应考虑黏土矿物对黑色页岩中有机质长期保存的特殊贡献。

黑色页岩可以形成于开阔的深水陆棚环境, 也可以在海平面快速升高, 海侵超覆过程中形成于近岸浅水环境, 即海侵黑色页岩(transgressive black shale)^[37,38,40]。海侵黑色页岩的沉积开始于盆地内部, 逐渐向盆地边缘扩张^[36,37]。与最大洪泛相关的黑色页岩可形成于高水位体系域^[36,37]。海侵黑色页岩发育在海侵沉积序列的下部, 与下伏浅水台地相地层截然不同, 通常位于海侵序列底部滞留凝缩段或者不整合面之上^[36,40], 可以包含直径为10~100 cm的大型碳酸盐岩结核^[41]。我国华南广泛发育有新元古代至寒武纪的海侵黑色页岩, 例如埃迪卡拉统陡山沱组^[42], 及寒武系下部的牛蹄塘组、石岩头组等^[43]。尤其是, 寒武系下部的牛蹄塘组(局部地区称水井沱组、郭家坝组等)与下伏地层呈突变(图1(a))或不整合接触关系(图1(c), (d)), 含有直径可达1 m的灰岩结核(图1(b)), 是很

图 1 华南寒武纪早期海侵黑色页岩与下伏地层的接触关系。(a) 湖南张家界三岔剖面, 寒武纪牛蹄塘组斜坡相黑色页岩覆盖在埃迪卡拉纪灯影组台地相碳酸盐岩之上(界线在地质锤位置); (b) 湖北长阳地区寒武纪水井沱组黑色页岩中的大型灰岩结核; (c) 湖北长阳地区岩芯样品, 展示寒武纪水井沱组黑色页岩平行不整合覆盖在埃迪卡拉纪灯影组之上; (d) 陕西汉中地区岩芯样品, 展示寒武纪郭家坝组黑色页岩平行不整合覆盖在埃迪卡拉纪灯影组之上

Figure 1 Transgressive black shales from the lower Cambrian of South China abruptly overlying the late Ediacaran Dengying Formation of carbonate platform facies. (a) Outcrop in Sancha, Zhangjiajie, Hunan, showing the sharp contact between the early Cambrian slope black shales and the underlying platform carbonates of the late Ediacaran Dengying Formation (pointed by a geological hammer); (b) a huge limestone nodule in the Shuijingtuo black shales, Changyang, Hubei; (c) drill core sample from Changyang, Hubei, showing the black shale of the Shuijingtuo Formation unconformably resting on the Dengying Formation; (d) drill core sample from Hanzhong, Shaanxi, showing the black shale of the Guojiaba Formation unconformably resting on the Dengying Formation

典型的海侵黑色页岩^[43]。

4 RDOC的沉积和地质封存

针对海侵黑色页岩的成因, 前人已经提出一些沉积模型, 例如深海淤泥扩张模型和底层海水上涌模型^[38,40]。事实上, 这些模型在本质上有雷同之处, 主要沉积机制为: 地壳下沉或气候变化等地球动力作用引起的海平面快速上升, 驱动较深部缺氧、富营养(磷和氮等)的水体上涌至浅水陆棚环境, 或者驱动最低含氧带(oxygen minimum zone, OMZ)向浅水区域移动, 导致表层水体生产力加强, 有机质供给过剩, 氧消耗过

多, 从而会进一步导致表层水间歇性缺氧, 有机质沉降加速, 形成黑色页岩^[38]。沉积过程与现代纳米比亚和秘鲁外海上升流发育区域类似^[38,40]。这一沉积机制认为表层水体富营养造成的生产力过剩是有机质的主要来源, 没有提到有机质沉积后的保存问题, 没有考虑巨大的RDOC库的贡献, 也没有考虑黏土矿物在有机质富集和保存方面的特殊作用。

本文依据RDOC在现代和古海洋中的普遍性和巨大的储库, 结合黏土矿物可吸附溶解有机碳的特点, 提出另外一种海侵黑色页岩的沉积模型, 即RDOC的沉积与保存模型(图2)。深层海水上涌(图2(b)), 或者在全球尺度的大海侵时期(例如

图2 海洋惰性溶解有机碳的沉积与地质封存机制。(a) 海侵前；(b) 深部海水上涌将RDOC运输到较浅水区，与黏土沉积物混合沉积形成黑色页岩；(c) 海侵时RDOC与黏土沉积物混合并被吸附后沉积形成黑色页岩

Figure 2 Mechanism of RDOC deposition and preservation as an alternative model for the origin of transgressive black shales. (a) Before transgression; (b) sedimentation of black shales driven by upwelling of RDOC-rich water bodies; (c) sedimentation of RDOC-rich clay sediments following mixture and adsorption between clays and RDOC during the transgression

寒武纪早期)的海平面快速上升(图2(c)), 将海洋深部的RDOC运输到泥页岩沉积环境, 甚至可达风化剥蚀面之上, 与那里的黏土沉积物充分混合, 形成富含RDOC与黏土沉积物的浑浊流体, 黏土矿物吸附RDOC后沉降, 并持续吸附孔隙溶液中的RDOC, 从而将RDOC长期保存在沉积物中, 经成岩作用后形成黑色页岩(图2(b), (c)). 黏土矿物不仅有巨大的活性表面, 可以吸附大量的RDOC, 不同类型的黏土矿物吸附能力差别较大, 每克可吸附30~120 mg的RDOC, 完全可以达到黑色页岩大于1%有机碳的含量. 此外, 黏土矿物有层状结构, 束缚在黏土矿物层间域的RDOC很难再被氧化分解或被微生物利用^[31], 因此可以长久地被封存在黑色页岩中. RDOC的沉积与保存模型不排斥已有的海侵黑色页岩沉积模型, 在沉积机制上有共同之处, 表现在所有模型都强调海平面上升驱动深层水上涌的上升流的作用. 不同之处在于有机质的来源, 以往的模型强调生产力增强导致大量的POC沉积; 新模型强调RDOC库的重要贡献, 但不排斥生产力过剩或POC输入对有机碳的贡献. 另外, 新模型突出黏土矿物的特殊作用, 不仅能

吸附而且还有助于RDOC的长期保存. 在埃迪卡拉纪晚期与寒武纪早期, 全球范围内分别发生过一次无机碳同位素的超大型负漂移和一次较大型负漂移事件, 与有机碳同位素记录呈非耦合关系(文献[4]的图7), 反映了在埃迪卡拉纪晚期海洋中存在超大型的RDOC库, 在寒武纪早期海洋中存在较大型的RDOC库^[4]. 这两个RDOC库的消失是否与黑色页岩沉积事件有关值得深入研究.

上文中提到, 华南广泛发育的牛蹄塘组是寒武纪早期海侵过程中形成的黑色页岩, TOC含量在空间上很不均匀. 上斜坡边缘的黑色页岩TOC高达25%, 富集C、P、Fe、Ba, 指示较高的生产力和较强的C、P、Fe循环. 在外陆棚形成的黑色页岩TOC含量普遍低于10%, 与P、Fe含量为对偶关系(antithetic relationship), Ba含量也相对较低, 显示较低的生产力以及C、P、Fe循环临时性解耦现象^[43]. Yeasmin等人^[43]依据牛蹄塘组黑色页岩在空间上的不均一性和多种反映氧化还原条件的地球化学指标推测, 在上斜坡边缘的较浅水区域存在生产力很旺盛的楔形水体, 局部生产力终止的区域可能存

在楔形硫化水体. 关于形成机制, Yeasmin等人^[43]强调上升流的重要作用, 认为信风驱动底层水上涌, 导致表层水体生产力过剩, 从而导致有机质富集. 如果考虑到RDOC库存在的普遍性和黏土矿物的特殊属性, 牛蹄塘组黑色页岩的形成机制也可以套用本文提出的RDOC沉积与保存模型. Yeasmin等人^[43]提出的高生产力楔形水体还有可能代表的是高浓度的楔形RDOC库, 与黏土沉积物在上斜坡浅水区域混合, 被吸附后沉积到海底并被束缚到黏土矿物层间域, 经成岩作用后形成牛蹄塘组黑色页岩.

5 问题与展望

RDOC库是由MCP产生的巨型海洋溶解有机碳库, 是海洋碳循环研究关注的重要对象^[12]. 黑色页岩是油气资源和多种稀有金属矿产的地质载体, 因而是油气资源勘查、找矿勘探、基础地质学等领域共同关注的研究对象. 本文提出的

RDOC沉积与保存模型架起了RDOC与黑色页岩之间的“桥梁”, 为RDOC找到了可能的“地质归宿”. 从RDOC到黑色页岩可能代表海洋碳循环的一种重要途径. 需要强调的是, RDOC的沉积与保存模型暂时还是一种猜测或者假说, 为RDOC从海洋储库到地质储库提供一种可能的途径, 目前还缺乏强有力的证据支撑, 需要开展广泛的研究去证实或证伪.

未来需要加强有机质与黏土矿物之间相互作用的实验研究, 查明不同种类的黏土矿物、在不同的温压和氧化还原条件下可以吸附哪些RDOC分子, 能吸附多少, 吸附在什么位置, 吸附的机制是什么, 吸附后能否长久保存等关键的科学问题. 如果RDOC在古海洋中也广泛存在, 从理论上讲, 必然会有一部分RDOC进入沉积物, 记录在黑色页岩等富含有机质的沉积岩中. 如何从岩石中有效地识别出RDOC的组分, 首先需要建立判别RDOC贡献的地质指标. 另外, 量化评估不同地质历史时期古海洋中RDOC库大小的变化也是非常重要的研究.

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Summary for “海洋惰性溶解有机碳库与海侵黑色页岩”

Marine refractory dissolved organic carbon and transgressive black shales

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The marine refractory dissolved organic carbon (RDOC) pool, derived from the microbial carbon pump (MCP), holds a tremendous amount of carbon, as much as that in today's atmosphere; hence, an understanding of this pool is crucial for investigating carbon cycling and climate change at the global scale. The size of the RDOC pool dynamically evolves over time. In the geological past, particularly during the Neoproterozoic to Cambrian transition, the marine RDOC pool might have reached a hundred to a thousand times its present size. However, the patterns of the reduction in the RDOC pool through time and the means by which RDOC was transferred into the geological reservoir have been poorly known to science.

Black shales, which are the source rocks of oil and gas reservoirs and are enriched in many rare metals, are economically important sedimentary rocks. Black shale is characterized by the enrichment of clay sediments and organic matter (total organic carbon (TOC) >1%). At least a dozen depositional models have been proposed to interpret various types of black shales based on the depositional environments and three major controls on organic content, i.e., the production and supply of organic matter, the demand and consumption of oxygen, and the rate of sedimentation. Organo-clay interactions and potential organic sources of the bulk RDOC in ancient oceans have not been fully considered. Clay minerals, e.g., smectite and illite, are well known for their capability of adsorption and preservation of dissolved organic matter in significant quantities. Organic compounds adsorbed by clays are present dominantly within interlayer sites and thus are difficult to be decomposed or used by microbes.

Accordingly, here, I propose a hypothetical mechanism of RDOC deposition and preservation, which also functions as an alternative model for the origin of transgressive black shales that always abruptly contact the underlying rock unit. The proposed mechanism is outlined as follows: During global-scale sea level rise driven by crustal subsidence or climate change, upwelling currents transport RDOC-rich water bodies from deep oceans to clay-rich shallow sea depositional environments, where clay sediments mix well with the RDOC; the mixture triggers the interplay between clay minerals and organic matter, and thus leads to large amounts of RDOC being absorbed by clay sediments; after deposition, the clay sediments are able to absorb organic matter from pore water; finally, the organic-rich transgressive clay sediments form black shales through diagenesis. Experiments indicate clays are capable of absorbing as much as 12% or more dissolved organic matter, far more than the minimal 1% TOC in black shales. Therefore, it is reasonable to assume that the RDOC is an important organic source in transgressive black shales.

The new model provides a potential link between ancient marine RDOC and black shales; hence, it might offer a mechanism for transferring marine RDOC into the geological carbon reservoir and thereby present an additional path of marine carbon cycling. Unlike the previous model that invoked primary production as the major organic source, the present model emphasizes the contribution of RDOC to the organic matter of black shales. However, it does not refute the contributions of any other organic source or any other model for transgressive black shales. To test this hypothesis, future work may include enhanced experimental studies of the interplay between clay minerals and organic compounds under different settings of temperature, pressure, and redox state, establish a set of geological criteria to recognize RDOC from organic-rich rocks, e.g., black shales; and quantitatively model the evolution of RDOC over geological time. Each of these tests would provide critical information for understanding the global carbon cycles of the past, present, and future.

refractory dissolved organic carbon (RDOC), deposition and preservation, black shale, transgression, unconformity, Cambrian

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