



冷泉碳酸盐工厂的提出及古气候意义

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冷泉碳酸盐工厂的提出及古气候意义

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摘要 【意义】碳酸盐工厂的提出及其分类研究对于推动碳酸盐岩沉积学发展具有重要意义, 但现行分类方案不足以囊括所有碳酸盐沉积类型, 因此亟须从机理和过程层面对碳酸盐工厂类型予以梳理、扩充。【进展】传统碳酸盐工厂的碳源主要为大气—海洋中的无机碳库, 而一些特殊海相和陆相碳酸盐工厂的碳则主要源于外源碳库, 因而两者具有本质上的区别。后者往往对于追溯深时水体环境和气候事件具有重大意义。【结论与展望】以冷泉碳酸盐岩为例, 正式提出“冷泉碳酸盐工厂”概念, 综述了其沉积特征、生物组成及生物地球化学过程, 并举例阐述其古气候意义。基于外源碳库的碳酸盐工厂类型理应得到重视。

关键词 碳酸盐工厂; 冷泉; 外源碳库; 生物地球化学过程; 气候事件

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0 引言

碳酸盐岩主要是生物成因, 生物与环境相互作用决定了不同沉积环境中产生的碳酸盐沉积物也不相同^[1]。碳酸盐工厂即是指碳酸盐的形成过程及其产出位置^[2]。20世纪70年代以来, 沉积学家主要关注现代海洋碳酸盐沉积物中骨屑颗粒组合分布与海水温度和纬度的关系。Lees *et al.*^[3-4]评估了温度和盐度对温水和暖水陆架上底栖生物颗粒类型的影响, 将沿着温度梯度和盐度变化的独特生物组合归类为绿藻—珊瑚组合(chlorozoan)、仅发育绿藻的Chloragal组合和有孔虫—软体动物组合(foramol)。Nelson^[5]引入“非热带碳酸盐”一词, 论述了现代及深时位于北纬或南纬30°以上非热带大陆架碳酸盐的普遍存在, 并从中识别出苔藓虫—软体动物组合(bryomol)。Carannante *et al.*^[6]补充提出红藻石组合(rhodalgial)和软体动物—海胆—有孔虫组合(molechfor)。这些生物组合的分布主要与控制海水温度的纬度和水深有关, 同时也受海水盐度、营养物质浓度和光照强度等因素的影响。James *et al.*^[7]提出适用于整个显生宙的异养和光养碳酸盐工厂概念, 强调碳酸盐沉淀所需要的能量来自光合作用。Pomar^[8]在碳酸盐岩台地成因分类研究中, 区分出三

类主要与水深/光照强度有关的生物组合类型(真光带生物组合、弱光带生物组合和无光带生物组合), 并认为碳酸盐岩台地的沉积形态受三类生物组合分布的影响。

21世纪以来, 沉积学家为突出碳酸盐的形成机理及其生物学和海洋环境意义, 碳酸盐工厂类型被不断细化。Schlager^[2,9]根据显生宙海洋底栖碳酸盐沉淀路径, 提出可随时间和空间转变的热带浅水工厂、冷水工厂及灰泥丘/微生物工厂。随后, Reijmer^[10]将这三类工厂简化为T-工厂、C-工厂和M-工厂, 但又从冷水工厂中抽离出冷水珊瑚礁工厂(CWC-工厂)。Li *et al.*^[11]、李飞^[12]在研究二叠纪—三叠纪之交大规模海相碳酸盐鲕粒建造时, 提出了“鲕粒碳酸盐工厂”的概念。Pomar *et al.*^[13]进一步强调生产碳酸盐的“主角”, 将碳酸盐工厂划分为更多类型, 如底栖有孔虫—藻类骨屑工厂、底栖自生泥晶工厂、底栖—浮游共生骨屑工厂、骨骼工厂、珊瑚工厂、有孔虫工厂和海草工厂等。在最近的碳酸盐工厂分类研究中, Michel *et al.*^[14]和Laugié *et al.*^[15]将全球浅水碳酸盐产量与海洋学参数(温度、盐度、初级生产力)联系起来, 确定并分析了四类浅海碳酸盐工厂: 生物化学工厂、光养T型工厂、光养C型工厂、异养C型工厂。

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“冷泉工厂(cold seep factory)”一词于2013年由Taviani *et al.*^[16]研究地中海格拉盆地麻坑沉积时引入,用以描述与冷泉相关的化能共生生物群落和自生碳酸盐岩沉积。但自此之后,该术语却未被其他学者提及或使用,亦未引起同行的足够重视,其可能与Schlager^[2]和Reijmer^[17]将冷泉沉积物简单地归类为灰泥丘/微生物工厂或M-工厂有关。考虑到冷泉流体渗漏与现代及深时海洋物理化学环境和气候演变关系密切,本文正式提出“冷泉碳酸盐工厂”(cold seep carbonate factory)的概念,在系统综述冷泉碳酸盐岩岩石学、矿物学特征、生物组成及生物地球化学过程的同时,探讨其与前述“传统碳酸盐工厂”的本质区别。

1 冷泉及冷泉沉积

冷泉是一种天然流体渗漏现象,主要由水、烃类化合物(主要为甲烷)、硫化氢和细粒沉积物等组成的流体向上(海底方向)运移形成^[18]。冷泉与热泉相区别,其温度接近底层海水温度,通常与天然气水合物的失稳裂解有关^[19-20],并在渗漏区域发育以化学能

为能量来源的生物群落。自科学家首次在墨西哥湾水深3 200 m海底发现烃类流体并命名为冷泉(cold seep)以来^[21],大量活动的海底冷泉在世界范围内被相继发现和报道^[22-24]。

冷泉主要分布于大陆边缘斜坡沉积物—海水界面附近^[25](图1),常沿构造带和高渗透率地层带呈线状产出,有的冷泉集中分布于泥火山、俯冲带附近的挤压构造处或沿底辟顶部呈圆形冷泉群出现^[27]。全球气候变暖、海平面下降、地震、火山喷发、地温梯度上升等都可能引发冷泉。根据流体溢出速度不同,冷泉可分为产自泥火山、富甲烷且携带大量泥质沉积物的快速冷泉和富油或气的慢速冷泉,两者在空间上常过渡伴生。

在冷泉系统中,硫酸盐还原与甲烷厌氧氧化耦合作用是甲烷的主要消耗方式,也是地球碳循环的重要一环^[28-29]。冷泉流体向上运移至近海底的硫酸盐—甲烷过渡带时(接近沉积物—海水界面),与向下扩散的硫酸盐相遇,在甲烷氧化古菌和硫酸盐还原菌联合介导下发生甲烷厌氧氧化作用(图2)(公式1)^[30-31]:

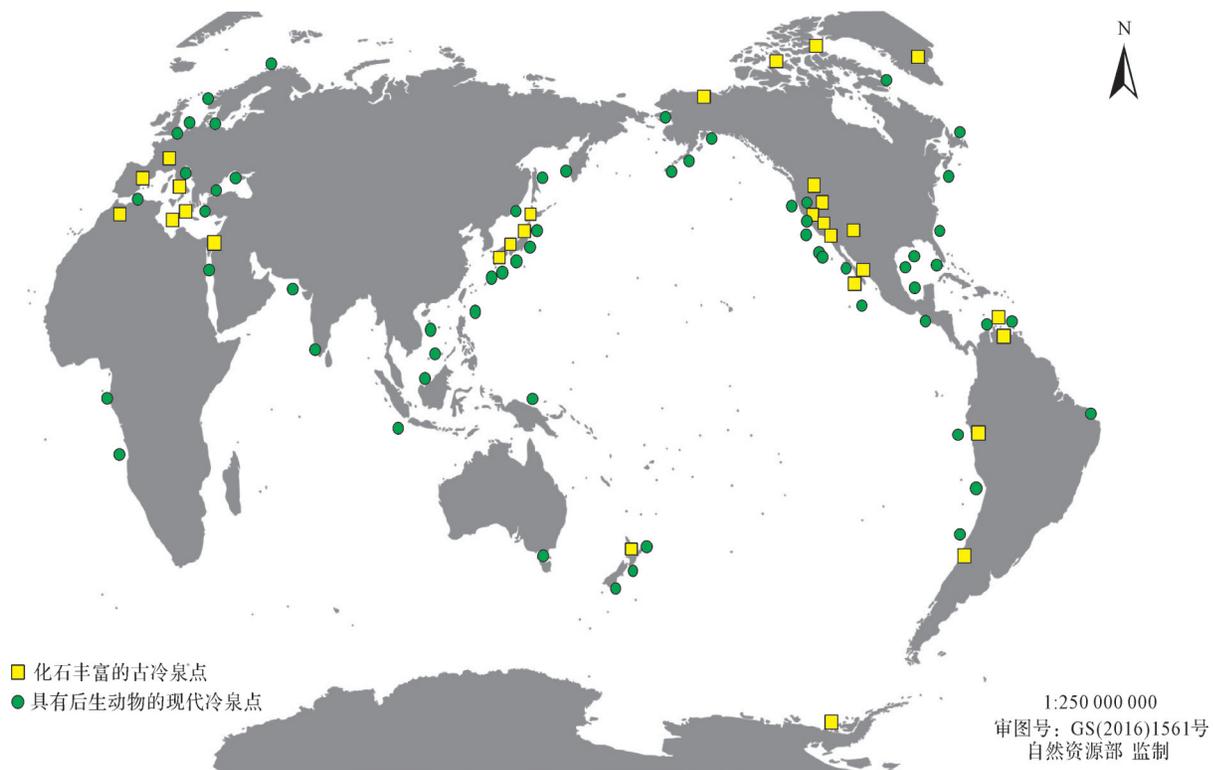
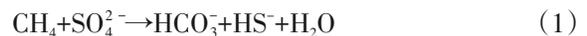


图1 显生宙全球海底冷泉分布(据文献[26]修改)

Fig.1 Global cold seep occurrences during the Phanerozoic (modified from reference [26])

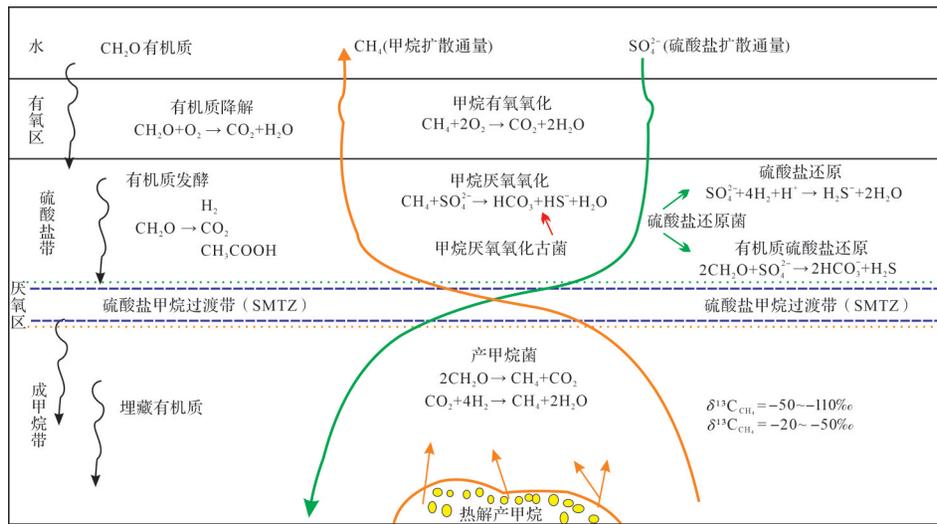


图2 海洋沉积物中微生物介导的有机物转化过程(据文献[30]修改)

Fig.2 Schematic diagram showing microbially mediated processes of organic matter transformation in marine sediments (modified from reference [30])

当冷泉附近的底层海水中缺乏硫酸盐时,微生物会利用其他电子受体(硝酸盐、 MnO_2 、 $FeOOH$ 等)进行甲烷厌氧氧化作用^[32]。这些过程会不断增加沉积物中孔隙水的碱度,碳酸氢根与孔隙水中的钙、镁等阳离子结合,当其过饱和时便在硫酸盐—甲烷过渡带形成自生碳酸盐矿物沉淀(公式2)^[28-33]:



碳酸盐岩是海底冷泉的主要沉积物。除此之外,冷泉碳酸盐岩中也常包含少量的硫化物、硫酸盐和磷酸盐矿物。硫化物常以草莓状黄铁矿形式出现^[34],硫酸盐则以重晶石和石膏为主。甲烷等烃类化合物和硫化物不断氧化产生化学能,供一些自养细菌繁殖和与这些细菌化学共生的宏体生物的生长,为冷泉生态系统提供了最基础的能量来源。

2 冷泉碳酸盐工厂

在温度、压力条件不足以形成一定规模天然气水合物的近海底位置,冷泉流体中的烃类化合物(主要为甲烷)在一系列微生物作用下与孔隙水或沉积物中的氧化剂(如硫酸盐、硝酸盐、铁锰氧化物等)发生生物化学反应,形成自生碳酸盐沉淀(生物诱导);相关反应形成的化学能常会原地供许多微生物群落和不同体型的钙质生物进行生命代谢活动(生物控制碳酸盐沉淀)。两者构成冷泉碳酸盐工厂沉积系统。与传统碳酸盐工厂相比^[2-17],冷泉碳酸盐工厂具有独特的岩石学、矿物学、生物组成和生物地球化学特征。

2.1 冷泉碳酸盐岩岩石学、矿物学特征

绝大多数冷泉碳酸盐岩都产自深海细碎屑岩中,规模从几厘米到上百米不等。其形态主要有层状^[35](图3a)、管状^[36](图3b)、结核状^[37](图3c)、烟卤状^[36](图3d)、圆柱状^[38](图3e)、和结壳状^[39](图3f),但少数也会在海底形成类似“生物礁”或“灰泥丘”的建隆。冷泉碳酸盐岩中常见丰富的孔洞、碎屑角砾、纹层状或凝块状结构及冷泉系统特有的生物化石等^[40-41]。冷泉流体的运移、自生碳酸盐矿物的溶蚀及天然气水合物的裂解释放易造成孔洞的形成。角砾的出现一般与冷泉流体的喷溢冲击或天然气水合物的结晶膨胀有关^[42]。与微生物岩相类似,冷泉附近微生物繁盛,微生物席的捕获、黏结与钙化作用趋向于形成纹层状或凝块状结构^[42-44]。

由于冷泉附近化学条件的时空差异,冷泉碳酸盐岩常包含不同比重的自生矿物,如文石、镁方解石、白云石、黄铁矿、菱铁矿、重晶石和磷灰石等^[45-46]。微观尺度下,冷泉碳酸盐岩的典型矿物相包括:微晶碳酸盐、带状/葡萄状文石胶结物、黄色方解石^[47](图4a)、边界模糊的微生物似球粒^[48](图4b)和草莓状黄铁矿^[49](图4c)等。微晶碳酸盐可由文石、镁方解石或白云石组成,常呈条带状^[35](图4d)、结节状^[35](图4e)或以胶结物形式存在。其矿物组成受甲烷通量、孔隙水中硫酸盐浓度和结晶基底等因素的影响。例如,当强烈的微生物活动去除孔隙水中的硫酸盐且Mg/Ca比值升高时,会形成具有不规则空心核、呈球

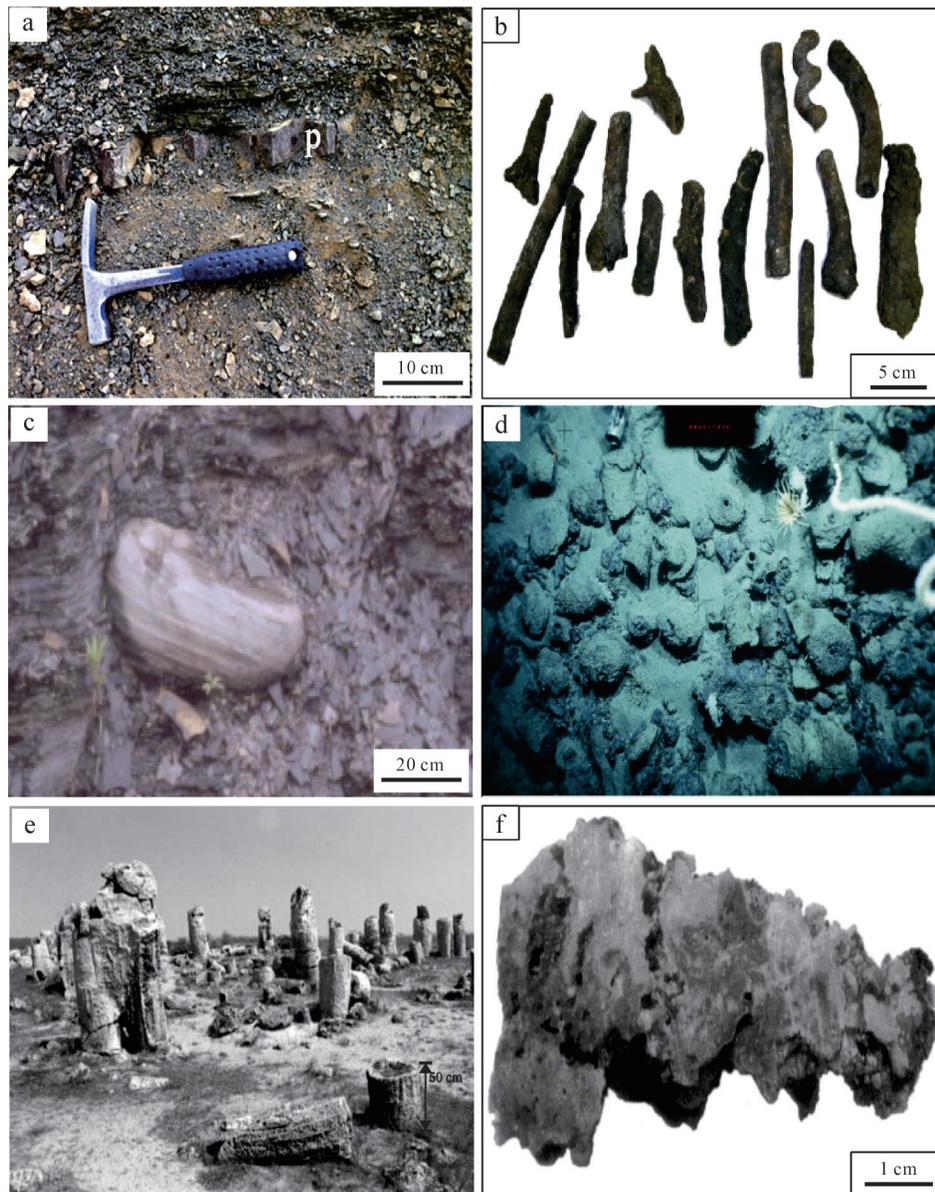


图3 不同形态的冷泉碳酸盐岩

(a)拉萨地块申扎地区早二叠世冷泉沉积物中发育的碳酸盐岩层(p)^[35]; (b)现代南海海底冷泉口处发育的呈实心管状、螺旋状碳酸盐岩^[36]; (c)纽约西部上泥盆统黑色页岩中发育的钙质结核^[37]; (d)现代南海海底冷泉口处发育的烟筒状冷泉碳酸盐岩^[36]; (e)保加利亚东北部始新世古冷泉口处垂直的圆柱状冷泉碳酸盐岩^[38]; (f)现代黑海结壳状冷泉碳酸盐岩, 深色部分为泥晶碳酸盐岩, 浅色部分为亮晶胶结物^[39]

Fig.3 Different morphological forms of cold seep carbonates

状或哑铃状的白云石矿物^[42]。带状/葡萄状文石胶结物由大量放射状文石扇构成,显示多期次生长特征,一般形成于高甲烷厌氧氧化速率环境,常与黄色方解石伴生,形成“千层糕”式结构^[50]。草莓状黄铁矿多分布于孔隙或自生碳酸盐基质,有时也围绕溶蚀碳酸盐边界生长(“黄铁矿套”)^[43]。除此之外,在冷泉碳酸盐岩中还可观察到网状有机脉^[39](图4f)、微裂隙和定向排列的碎屑角砾等特殊微观沉积组构,它们均与冷泉流体/气体的喷溢或运移有关。

2.2 冷泉碳酸盐岩生物地球化学特征

2.2.1 碳、氧同位素地球化学

冷泉碳酸盐岩通常具有低 $\delta^{13}\text{C}$ 值(一般低于 -25‰ ^[44,51-52]),表明其继承了冷泉流体中主要烃类化合物(甲烷)的碳同位素组成特征。海洋沉积物中的甲烷主要通过二氧化碳还原或发酵产生,即生物成因甲烷($\delta^{13}\text{C}=-110\text{‰}\sim-50\text{‰}$)^[53];二是在深埋藏环境下,由有机质和/或长链烃类化合物受热裂解形成,即热成因甲烷($\delta^{13}\text{C}=-50\text{‰}\sim-30\text{‰}$)^[54]。除甲烷外,冷泉

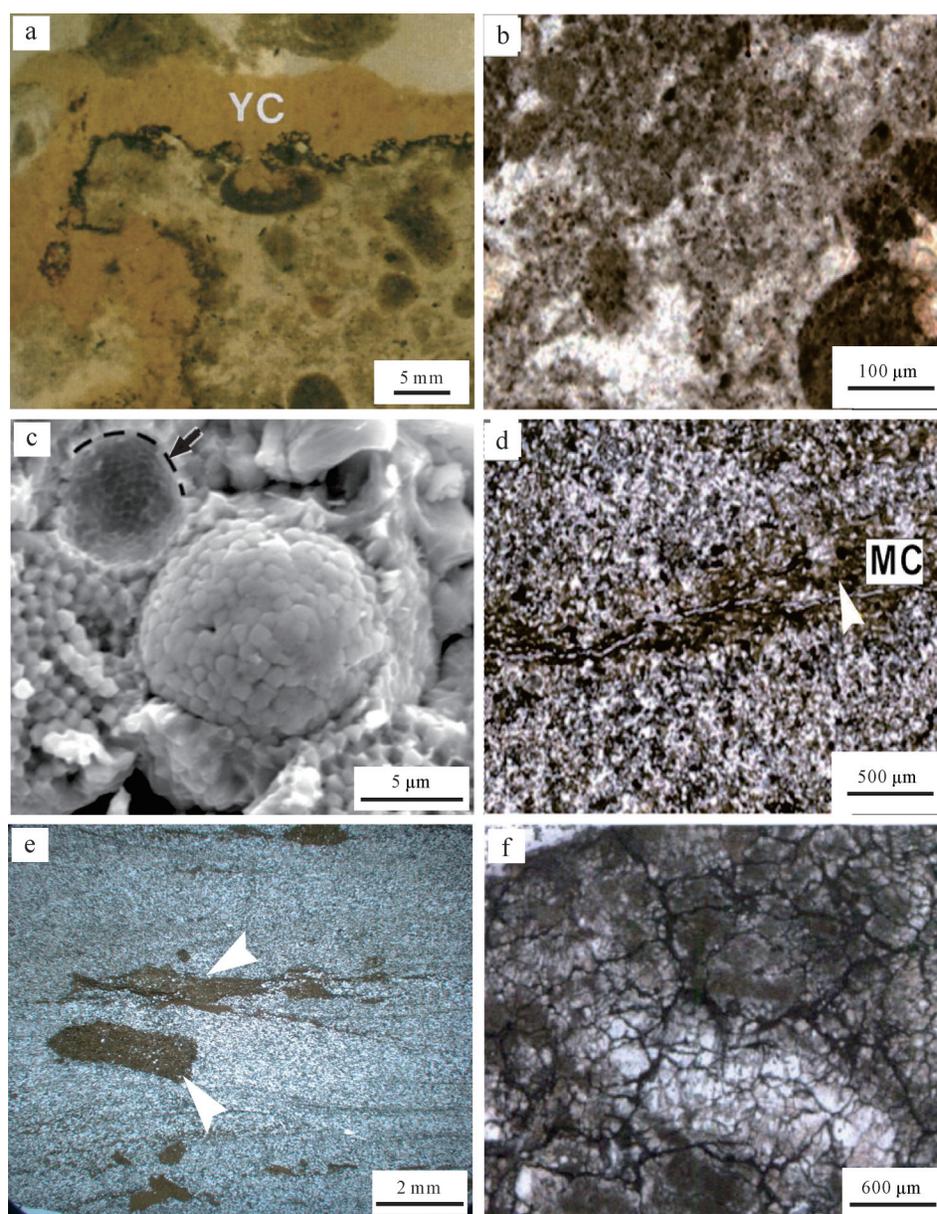


图4 冷泉碳酸盐岩中典型的微观矿物相和构造

(a)黄色方解石(YC)^[47]; (b)边界模糊的微生物似球粒^[48]; (c)草莓状黄铁矿^[49]; (d)条带状泥晶方解石(MC)^[35]; (e)深棕色泥晶方解石结节^[55]; (f)网状有机脉, 在单偏光显微镜下为黑色^[39]

Fig.4 Typical microscopic mineral phases and structures in cold seep carbonates

流体中还可能包含石油重烃,其 $\delta^{13}\text{C}$ 值通常介于 -30‰ ~ -25‰ ^[55]。由于自生碳酸盐在其形成过程中,冷泉流体与周围海水/孔隙水存在不同程度的混合,或在埋藏成岩过程中受产甲烷作用的影响^[56],冷泉碳酸盐岩一般具有混合的碳同位素信号。这些混合信号主要源于海水溶解无机碳库($\delta^{13}\text{C}=-2\text{‰}$ ~ 2‰)、有机质早期成岩降解产生的碳($\delta^{13}\text{C}=-15\text{‰}$ ~ -35‰)和产甲烷作用残留的 CO_2 ($\delta^{13}\text{C}=5\text{‰}$ ~ 24‰)^[44,51,57-59]。Campbell *et al.*^[60]汇编了14个现代冷泉附近自生碳酸盐岩的碳同位素组成(范围为 -61‰ 至 9‰), $\delta^{13}\text{C}$ 值

明显大于溶解无机碳库的点位,表明其受到产甲烷作用剩余二氧化碳的影响^[61-62]。

冷泉碳酸盐岩氧同位素值一般介于 -14‰ ~ 8‰ (VPDB)^[63-64]。天然气水合物结晶时会发生氧同位素分馏,与初始孔隙水相比,水合物晶格中的水相对富集 ^{18}O ($\delta^{18}\text{O}$ 值偏正 2‰ ~ 3‰),因此,水合物分解后形成的冷泉碳酸盐岩氧同位素通常具有更重的 $\delta^{18}\text{O}$ 值^[65]。此外,黏土矿物(蒙脱石、伊利石)的脱水作用也能导致孔隙水中富集 ^{18}O ,这种孔隙水沿通道到达冷泉系统,也可产生富 ^{18}O 的自生碳酸盐岩^[66]。由于

大气降水明显亏损 ^{18}O , 深时冷泉碳酸盐岩极易与其发生氧同位素交换, 导致冷泉碳酸盐岩的 $\delta^{18}\text{O}$ 值逐渐偏负^[39,43], 而 $\delta^{13}\text{C}$ 值逐渐偏正, 因此, 冷泉碳酸盐岩的 $\delta^{13}\text{C}$ 与 $\delta^{18}\text{O}$ 值通常具有显著的负相关关系^[27,67]。

2.2.2 硫同位素地球化学

冷泉碳酸盐工厂沉积系统中含硫的自生矿物主要为黄铁矿^[68-69]和重晶石^[70-71], 它们的硫同位素组成与硫酸盐还原过程密切相关^[72]。硫酸盐还原作用涉及的硫同位素分馏主要受有机质基底类型、数量和硫酸盐浓度控制^[32]。有机质硫酸盐还原作用(图2)产生的黄铁矿和硫酸盐库之间的最大分馏为 $\sim 45\text{‰}$, 更大的分馏可能与黄铁矿氧化和微生物介导的还原硫中间体歧化反应有关^[73-76]。因此, 当黄铁矿 $\delta^{34}\text{S}$ 值低于 -45‰ (CDT)时, 表明其源于有机质硫酸盐还原作用。而冷泉碳酸盐岩中的黄铁矿 $\delta^{34}\text{S}$ 值通常较高, 反映其形成于硫酸盐浓度较低的沉积环境^[35]。不过, 这类黄铁矿并不是冷泉所特有, 亦见于富有机质海洋环境^[77-78]。多硫同位素遵循质量分馏原理, 可利用硫的三个稳定同位素(^{32}S 、 ^{33}S 、 ^{34}S)探索冷泉生物地球化学过程中多硫同位素分馏机制^[33]。Masterson *et al.*^[79]和 Pellerin *et al.*^[80]通过对加利福尼亚—墨西哥边缘(Alfonso盆地)沉积体系孔隙水硫酸盐多硫同位素分析表明, 由有机质硫酸盐还原作用形成的沉积物表层黄铁矿会呈现 $\delta^{34}\text{S}$ - $\delta^{33}\text{S}$ 正相关性, 但随着埋藏深度的增加, 硫酸盐驱动的甲烷厌氧氧化作用形成黄铁矿机制将占主导, 其 $\delta^{34}\text{S}$ - $\delta^{33}\text{S}$ 将逐渐转变为负相关关系^[81]。Gong *et al.*^[82]对墨西哥湾五个冷泉点收集的重晶石样品进行多硫同位素研究, 发现与甲烷厌氧氧化耦合的硫酸盐还原作用形成的重晶石, 其 $\delta^{34}\text{S}$ - $\delta^{33}\text{S}$ 也呈明显的负相关性。

2.2.3 稀土元素地球化学

冷泉碳酸盐岩的稀土元素(REE)总量和页岩标准化配分模式具有一定规律^[20,83]。通常情况下, 早期成岩比晚期成岩形成的碳酸盐矿物REE总量高(如微晶碳酸盐>块状亮晶胶结物); 准同期形成的碳酸盐矿物, 受有机矿化影响的或结晶速度较慢的矿物REE总量高(如微晶碳酸盐>葡萄状文石胶结物)^[84-85]。对于稀土元素配分模式而言, 正常开阔氧化海水中形成的碳酸盐岩往往表现为重稀土富集^[86], 而冷泉碳酸盐矿物形成时, 铁、锰氧化物还原作用会释放大量中稀土元素至孔隙水中, 导致冷泉碳酸盐岩常表现为中稀土富集特点^[83,87]。

稀土元素中的铈(Ce)、铕(Eu)异常, 可反映冷泉碳酸盐岩形成的环境条件及流体性质^[45,83,88-90]。在富氧海水中, Ce^{3+} 被迅速氧化为 Ce^{4+} , Ce^{4+} 水解形成高度不溶的 $\text{Ce}(\text{OH})_4$, 从而产生Ce负异常。 $\text{Ce}(\text{OH})_4$ 在进入缺氧环境后, 又被还原成可溶的 Ce^{3+} 重新进入水体, 形成Ce正异常。显著的Ce正异常见于南海北部、刚果扇和加迪斯湾等地区的冷泉碳酸盐岩中, 指示其形成于缺氧环境^[20]。但是, 由于冷泉附近生物地球化学条件复杂多变, 一些冷泉碳酸盐岩也常表现为Ce负异常特点, 暗示其也可以形成于短暂的氧化环境^[88]。

在水岩交换过程中, Eu^{3+} 被还原为更可溶的 Eu^{2+} , 形成Eu正异常, 但此还原反应需要高温的热液环境支持($>200\text{ }^\circ\text{C}$)^[91]。冷泉碳酸盐岩中出现Eu正异常可能存在两种解释: 其一是铁镁质火山岩中富Eu矿物(如斜长石)发生溶解, 释放大量的 Eu^{2+} 至冷泉流体运移系统; 其二是在硫酸盐还原带较浅的状态下, 含有大量还原性化合物的高通量冷泉流体涌向海底, 导致孔隙水中形成极端还原的环境^[92]。

2.3 冷泉碳酸盐岩的生物组成特征

甲烷等烃类化合物源源不断地涌向海底, 导致冷泉口及附近发育大量的微生物菌群和微生物席, 其生产、代谢速率高。甲烷厌氧氧化和硫酸盐还原耦合作用常形成自生碳酸盐岩建造出露于海底。孔隙水中高浓度的硫化物和甲烷为自由生活和共生的细菌提供了生物化学反应基质, 其与丰富的食物来源(有机质)和坚硬的栖息基底(自生碳酸盐岩), 共同促进了冷泉生态系统的形成^[22]。因此, 冷泉生态系统, 特别是其中的微生物席和钙质生物体, 也属于冷泉碳酸盐工厂的重要组成部分。

化能自养生物是海底冷泉生态系统的工程师^[93], 其具有丰度高、分异度低和垂直—水平分带等特点^[94], 以管状蠕虫、贻贝和蛤最为常见, 有时也包含其他双壳类、须腕蠕虫、枝状海绵、腹足类和海虾等^[95]。这些生物与甲烷氧化菌和/或硫化物氧化菌共生, 通过甲烷和/或硫化物氧化反应为其提供生命代谢活动所需之能量^[94]。除此之外, 冷泉系统还滋养了一批单纯以微生物或其他化能自养生物为食的后生动物, 如龙介虫、介形虫、藤壶、有孔虫、螃蟹、扁形虫、海葵和多毛动物等^[22]。

现代海底冷泉环境中尚未发现腕足动物, 但其广泛存在于许多古生代和中生代冷泉碳酸盐岩

中^[96-97]。传统观点认为,白垩纪中期之后,双壳类已替代腕足成为冷泉生态系统中最主要的生物^[98]。但随着摩洛哥上志留统和中泥盆统^[99-100]以及土耳其上三叠统^[101-102]中含腕足动物却以双壳类为主的冷泉动物群的发现,人们对两种生物竞争关系的认识得以发生改变。研究表明,冷泉腕足动物极有可能是异养生物,主要以冷泉附近的有机质(如浮游细菌)为食,而冷泉生态系统中的双壳类则是典型的化能自养生物,与硫化物氧化细菌密切共生^[103]。

2.4 与传统碳酸盐工厂的本质区别

大气通过与海洋进行物质交换使CO₂进入海水,形成溶解无机碳库。海洋中的溶解无机碳主要包括水合二氧化碳分子、碳酸氢根和碳酸。海水表层(10~100 m)溶解的二氧化碳是浮游植物的重要碳源,它们通过光合作用使海水中一定量的CO₂转变成有机碳,形成初级生产力,同时伴随碳酸盐沉淀和氧气的释放^[104]。初级生产力生成的颗粒有机碳除被浮游动物摄食外,大部分在海水中被微生物降解,转化成CO₂和惰性溶解有机碳,仅有20%的颗粒有机碳沉降到海底^[105]。沉降的颗粒有机碳会进一步被底栖微生物利用或被海洋生物所摄食。可以说,传统的碳酸盐工厂(包括浮游碳酸盐工厂和底栖碳酸盐工厂)所利用的碳主要源于大气—海洋系统中的溶解无机碳。相比之下,冷泉碳酸盐工厂的碳源则主要为海洋沉积物中的甲烷等烃类化合物,本质上属于对外

源碳的固定(图5)。碳源的差异决定了两类工厂在沉积特征、生物组成和生物地球化学特征等方面也存在不同。因此,从碳源角度出发,冷泉碳酸盐工厂与传统碳酸盐工厂存在本质上的区别,可视为一个独立的工厂(图6)。

3 冷泉碳酸盐工厂的古气候意义

海洋沉积物中的天然气水合物是目前地球上已知的最大的甲烷储库,其推测的碳储量介于5 000~10 000 Gt(1 Gt = 10¹⁵ g),构成近地表最大的可交换碳库^[106]。当温度和压力变化达到天然气水合物失稳的临界条件时,大量甲烷气体将释放到海洋和大气系统中,造成全球重大碳循环波动和气候变化^[107]。例如,Dickens *et al.*^[108]认为,古新世与始新世之交的极热事件(PETM)与海洋沉积物中天然气水合物的快速裂解及释放巨量(>2 000 Gt)的甲烷气体有关。晚第四纪冰芯记录显示大气中甲烷气体浓度与温度变化高度吻合,Kennett *et al.*^[109]提出“甲烷水合物枪假说”予以解释,认为海洋沉积物中甲烷水合物的周期性裂解在很大程度上导致了全球气候在米兰科维奇和千年尺度上的变化。除此之外,新元古代雪球地球的结束^[110]、二叠纪—三叠纪之交的超级温室气候^[111]及中新世初期的冰消事件^[112]等也被认为与海洋沉积物中天然气水合物的裂解存在因果关系。

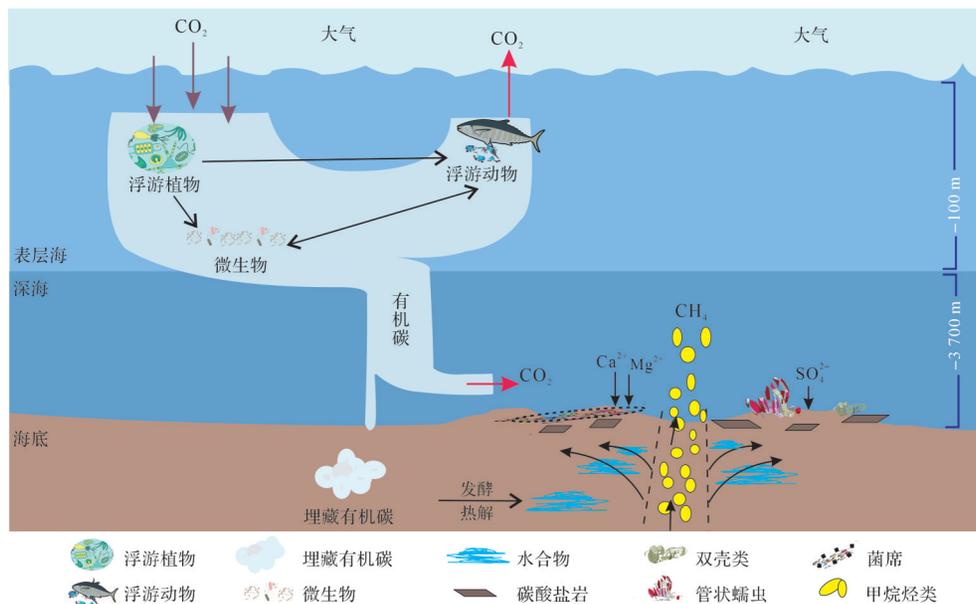


图5 海洋碳循环过程

Fig.5 Oceanic carbon cycle

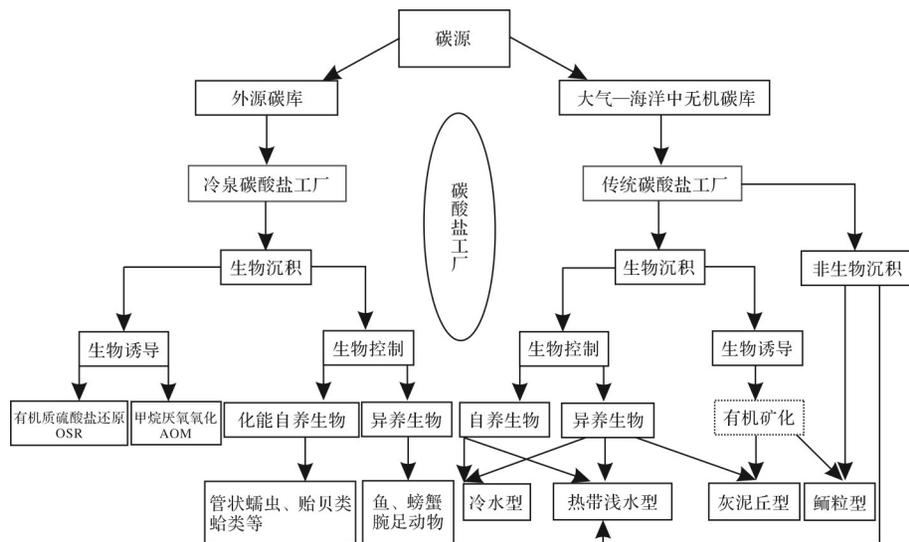


图6 基于碳源的碳酸盐工厂划分方案(据文献[11]修改)

AOM. 甲烷厌氧氧化作用; OSR. 有机质硫酸盐还原

Fig.6 Classification of carbonate factories by carbon source (modified from reference [11])

冷泉碳酸盐工厂的工作机理即是在沉积物—海水界面附近对上涌的冷泉流体中的外源碳(甲烷等烃类化合物)进行固定。研究表明,在现代海洋中,超过90%的冷泉甲烷在溢出海底前就被甲烷厌氧氧化作用所消耗^[113]。但当冷泉碳酸盐工厂生产效率不高时,大量的甲烷气体势必会进入到海洋和大气系统中,造成海洋大面积缺氧和全球气候变暖。这种情形通常与冷泉甲烷的快速释放和/或底层海水中缺乏硫酸盐等电子受体有关^[114-115]。下面以西藏申扎地区早二叠世空谷期昂杰组中的冷泉碳酸盐工厂为例^[35],依据其岩石学、矿物学和生物地球化学特征,阐述冷泉碳酸盐工厂的古气候意义。

申扎地区的冷泉碳酸盐岩发育于昂杰组泥页岩中,主要呈层状和结核状(图7),其内部典型的微观矿物相包括微晶方解石条带(图7b)、结节(图7c)、草莓状黄铁矿(图7d)或黄铁矿假晶(图7g)、葡萄状文石扇(图7f、图8a)和早期沥青(图7b)等。碳酸盐层和钙质结核的稳定碳、氧同位素组成呈显著和谐的负相关关系(图8b),通过上延法获得冷泉流体中烃类化合物的碳同位素值为 $-38‰$,表明热成甲烷和石油重烃是其主要碳源。虽碳源一致,两者形成的环境条件却有很大差异(图9)。钙质结核的自生碳酸盐矿物含量(6%~14%)远低于碳酸盐层(53%~89%),暗示前者的形成位置相对更深(数米)。特别是水平黑色页岩直接覆盖在含“帐篷”构造的碳酸盐层上(图7e),证明碳酸盐层形成于冷泉流体上涌刷

烈的近海底位置。而钙质结核中保存了原始的水平或“前积”纹层,且其碳同位素组成相对更重(图8b; $-19.1‰\sim-11.5‰$ vs. $-34.7‰\sim-16.7‰$),表明其形成于弥漫性冷泉流体渗漏环境。

除形成环境迥异外,碳酸盐层还经历了不同的生物地球化学过程(图9)。在硫酸盐—甲烷过渡带,甲烷厌氧氧化和硫酸盐还原耦合作用会优先利用含 ^{32}S 的硫酸盐,导致溶解 H_2S 库的 $\delta^{34}\text{S}$ 值随硫酸盐的消耗逐渐变重。这种变重的信号会直接传递到黄铁矿中。碳酸盐层中的黄铁矿 $\delta^{34}\text{S}$ 与碳酸盐晶格硫 $\delta^{34}\text{S}$ 值接近(图8c),暗示碳酸盐层生长于高甲烷通量、高甲烷厌氧氧化速率和硫酸盐极度匮乏($\text{TS}<0.008 \text{ wt.}\%$; 图8a)的海底环境。硫酸盐不足会引起先前形成的重晶石发生部分溶解,表现为在葡萄状和泥晶胶结物中发育较多具港湾状构造、多孔的重晶石集合体(图7g)。硫酸盐不足还会触发甲烷厌氧氧化与铁氧化物还原耦合作用^[32],证据包括:(1)在碳酸盐层上部文石扇中,自生碳酸盐矿物含量与铁含量呈显著的正相关关系(图8a);(2)铁氧化物驱动的甲烷厌氧氧化速率较低,文石扇晶体自下而上生长速率变缓(对应晶体由小变大),更多海水无机碳混入上部晶体,导致碳酸盐层自下而上 $\delta^{13}\text{C}$ 值逐渐变重(图8a);(3)铁氧化物驱动的甲烷厌氧氧化作用增加了孔隙水中 Fe^{2+} 和 HCO_3^- 的浓度,在缺乏硫化物的情况下,促进了菱铁矿(图7h)和铁方解石的形成。

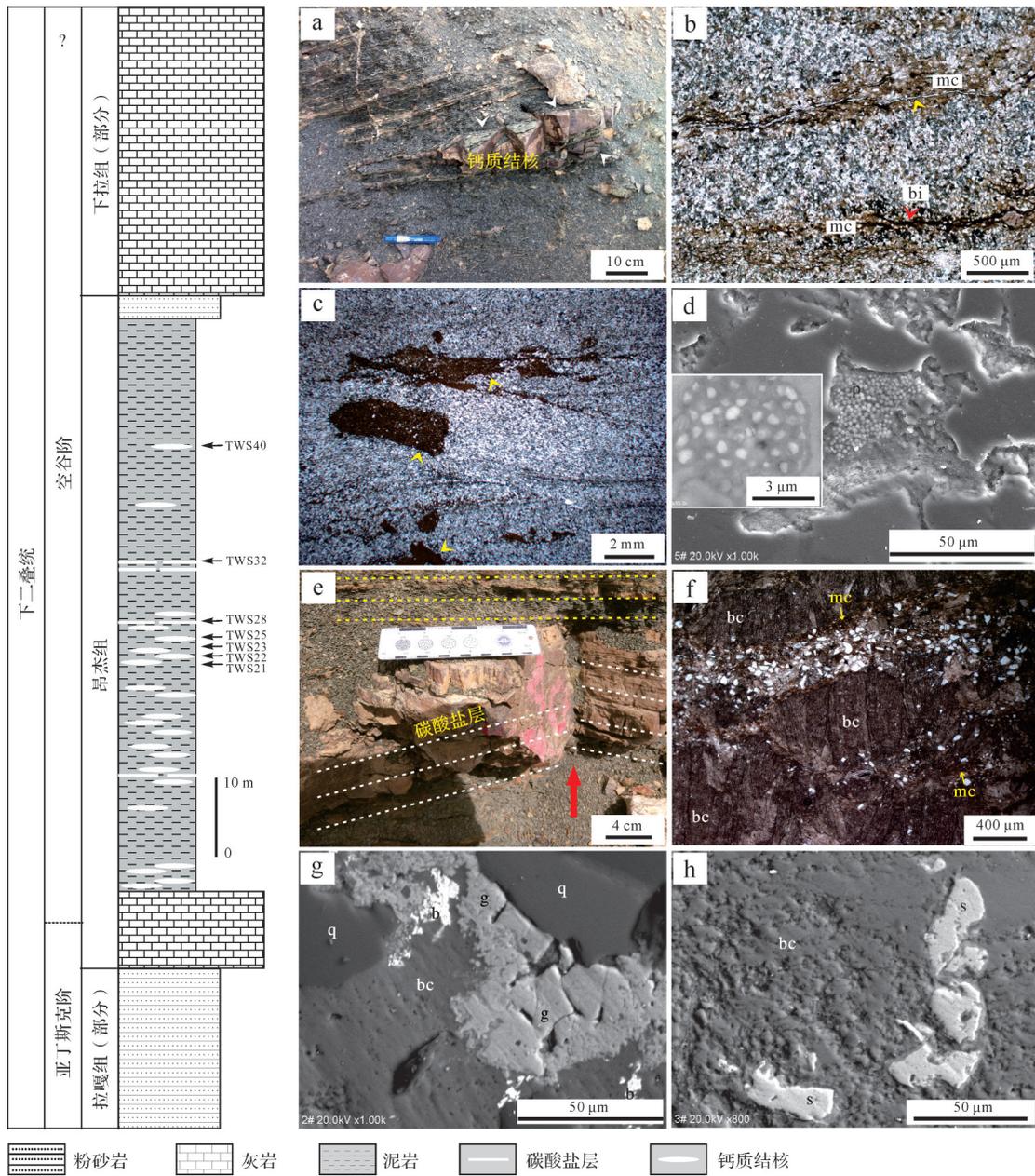


图7 申扎地区早二叠世冷泉碳酸盐岩的地层、岩相学、矿物相特征(据文献[35])

(a) 昂杰组泥页岩中的钙质结核(箭头所示);(b) 钙质结核中的淡黄色泥晶胶结物(mc)和充填冷泉流体微运移管道的沥青(bi);(c) 钙质结核中的泥晶结节(箭头所示);(d) 钙质结核中的草莓状黄铁矿(p);(e) 昂杰组泥页岩中的碳酸盐层,注意被水平黑色页岩覆盖的“帐篷”构造;(f) 碳酸盐岩层中的葡萄状方解石(bc)和褐色泥晶胶结物(mc);(g) 葡萄状方解石和泥晶胶结物中发育较多具港湾状构造、多孔重晶石(b)集合体,q,石英,g,针铁矿;(h) 碳酸盐层上部的葡萄状方解石中发育较多的菱铁矿(s)

Fig.7 Stratigraphical, lithological and mineral features of the Early Permian cold seep carbonates from the Xainza area (after reference [35])

考虑到碳酸盐层中发育的“帐篷”构造指示剧烈上涌的冷泉流体周期性地喷出海底,同时考虑到铁氧化物驱动的甲烷厌氧氧化比硫酸盐驱动的甲烷厌氧氧化速率慢8.7倍^[32],申扎地区早二叠世空谷期的冷泉碳酸盐工厂对外源碳的固定效率并不高,这将导致大量的甲烷气体进入海洋—大气系统。前人研究表明,亚

丁斯克晚期在澳大利亚和拉萨地块均发育明显的大陆冰川活动^[117-118],而在空谷早期,冈瓦纳北缘开始出现大范围海侵^[119-120]。这一气候转暖事件与申扎地区冷泉活动的发生时限相当。Liu *et al.*^[121]通过碳平衡定量计算,认为甲烷释放在很大程度上导致了同期的全球碳循环异常,并推动地球气候从冰室到温室转换。

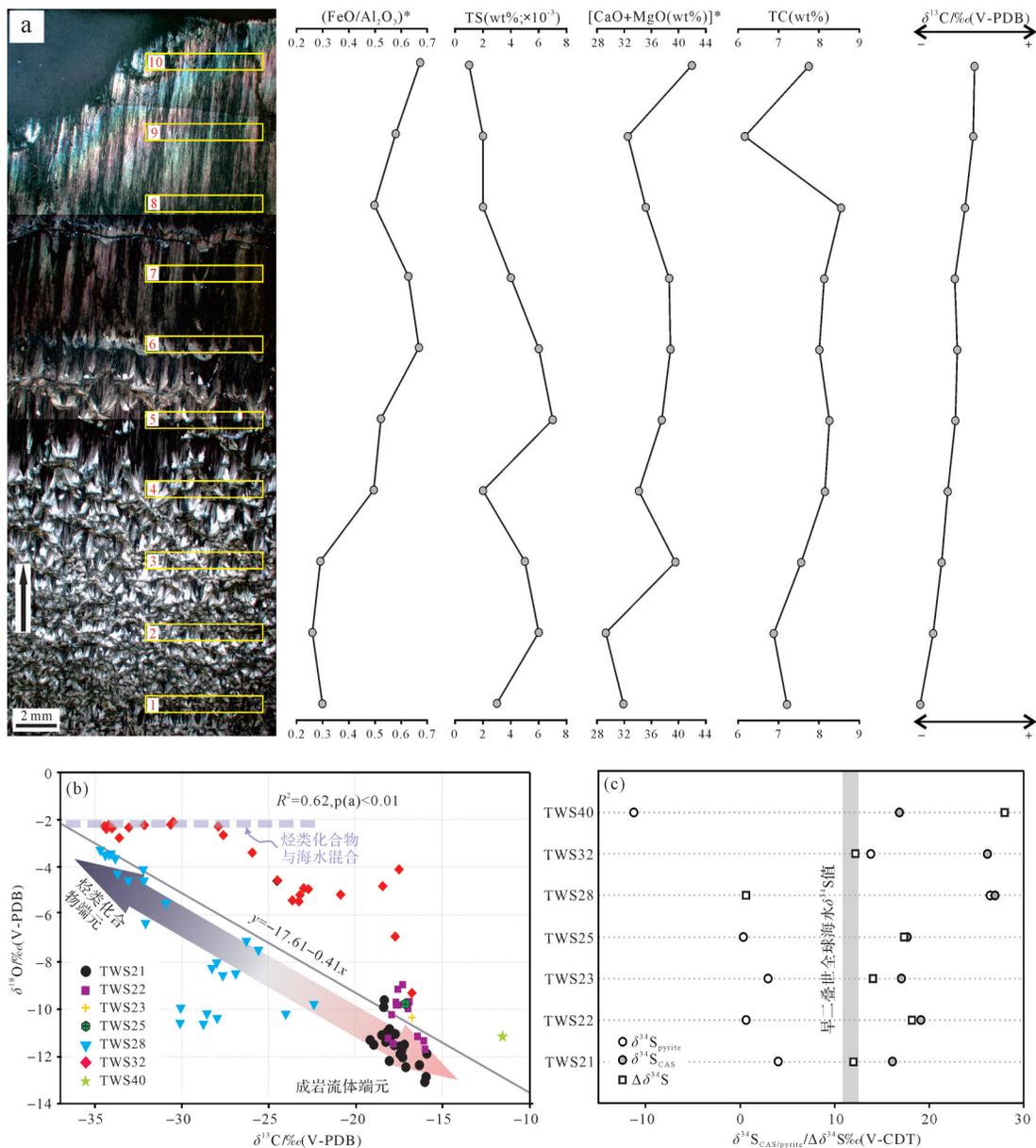


图8 申扎地区早二叠世冷泉碳酸盐岩的典型地球化学特征(据文献[35])

(a)通过电子探针和碳硫仪分析碳酸盐层中葡萄状文石扇微区的元素含量;(b)碳酸盐层和钙质结核微区的 $\delta^{13}\text{C}$ 和 $\delta^{18}\text{O}$ 值的交会图,显示两者具有显著的负相关关系($r=-0.79, p(a)<0.01, n=88$);(c)昂杰组上段钙质结核和碳酸盐层的 $\delta^{34}\text{S}_{\text{CAS}}, \delta^{34}\text{S}_{\text{Sprite}}$ 和 $\delta^{34}\text{S}$ 值,早二叠世全球海水 $\delta^{34}\text{S}$ 值范围引自文献[116]

Fig.8 Typical geochemical characteristics of Early Permian cold seep carbonates from the Xainza area (after reference [35])

4 结语

在显生宙,不同类型的碳酸盐工厂皆是地球重要的碳汇。在温度、压力条件不足以形成一定规模天然气水合物的近海底位置,冷泉流体中的烃类化合物在一系列微生物作用下与孔隙水或沉积物中的氧化剂发生生物化学反应,形成自生碳酸盐沉淀;相关反应形成的化学能常会原地供许多微生物群落和不同体型的钙质生物进行生命代谢活动。两者构成

冷泉碳酸盐工厂沉积系统,其具有独特的岩石学、矿物学、生物组成和生物地球化学特征。从碳源角度出发,冷泉碳酸盐工厂与传统碳酸盐工厂存在本质上的区别:传统碳酸盐工厂所利用的碳主要源于大气—海洋系统中的溶解无机碳,而冷泉碳酸盐工厂的碳源则主要为海洋沉积物中的甲烷等烃类化合物(属外源碳库)。考虑到冷泉碳酸盐工厂对于追溯深时水体环境和气候事件具有重大意义,基于外源碳库的碳酸盐工厂类型理应得到重视。

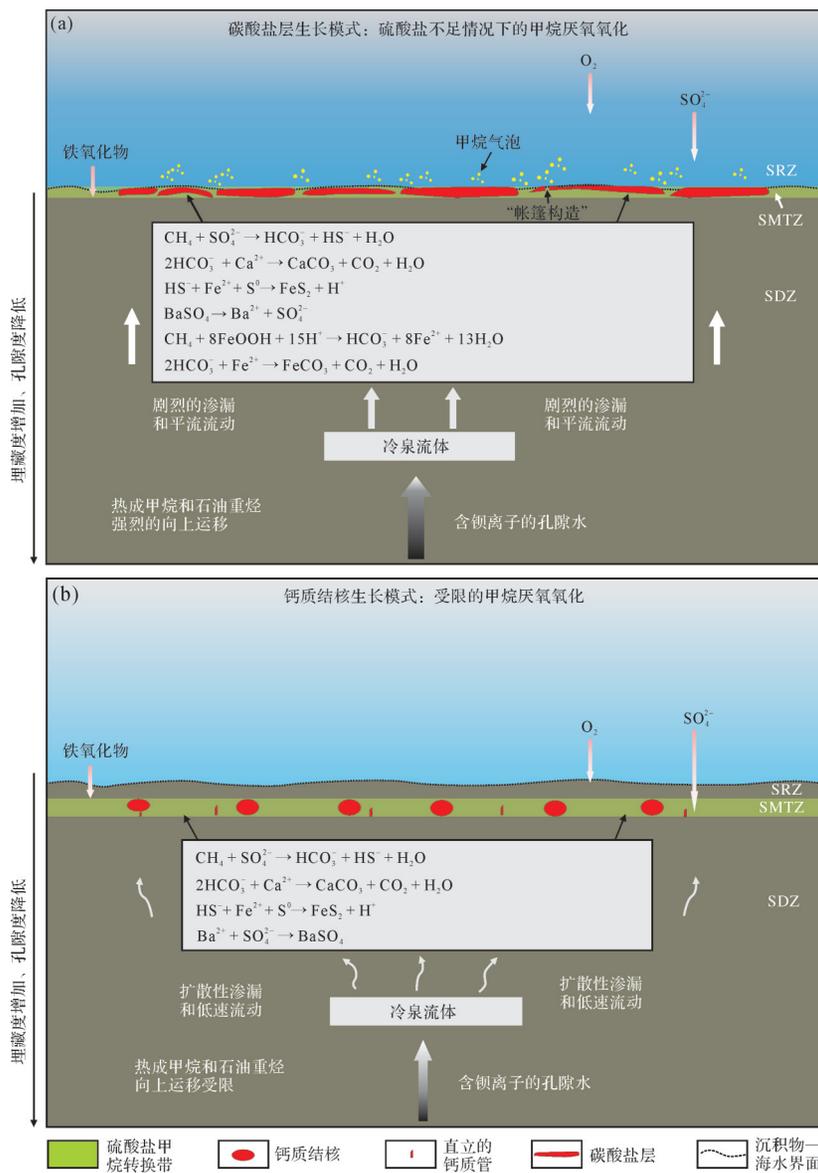


图9 申扎地区早二叠世冷泉碳酸盐岩层和钙质结核生长模式图(据文献[35])

SRZ.硫酸盐还原带;SMTZ.硫酸盐甲烷转换带;SDZ.贫硫酸盐带

Fig.9 Growth patterns of Early Permian cold seep carbonate concretions and layers from the Xainza area (after reference [35])

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Proposal of Cold Seep Carbonate Factory and Its Paleoclimatic Significance

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Abstract: [Significance] The proposal of a carbonate factory and its classification study are of great significance for promoting the development of carbonate sedimentology. However, the current classification scheme is not sufficient to cover all carbonate sediments, so it is urgent to clarify different carbonate factories at the level of mechanism and process. [Progress] The carbon used by traditional carbonate factories mainly comes from atmospheric and oceanic inorganic carbon pools, whereas certain marine and continental carbonate factories mainly fix carbon from exogenous carbon pools, so the two are fundamentally different. The latter is often highly significant for tracing deep water environments and climate events. [Conclusions and prospects] As an example, this study takes hydrocarbon seep carbonate, and formally puts forward the concept of a “cold seep carbonate factory”. In addition, its sedimentary characteristics, biological composition and biogeochemical processes are summarized, and an example is discussed to address its geological significance. The type of carbonate factory based on an exogenous carbon pool deserves much attention.

Key words: carbonate factory; cold seep; exogenous carbon pools; biogeochemical processes; climate events