微生物成因白云石研究进展

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摘 要:"白云岩问题"一直是沉积地质学研究的热点和难点之一,白云岩在我国和世界范围内都是重要的油气储层。因此,深入认识白云岩成因对于碳酸岩油气勘探具有重要参考意义。白云岩成因有多种解释模式,如萨布哈蒸发模式、渗透回流模式、埋藏调节模式、混合水模式、潮汐泵模式等。近几十年来,随着低温白云石研究的不断深入,微生物白云石模式作为一种新的成因模式被提出并不断被完善。本文回顾了微生物成因白云石的研究进展,总结了低温白云石形成的3个动力学障碍(镁离子的高水合能、硫酸根的存在、碳酸根离子的低浓度和低活度),简要介绍了微生物成因白云石模式的建立、微生物成因白云石的生长过程及发育特征,系统分析了微生物在白云石形成过程中的调节作用,指出微生物(如硫酸盐还原菌、古甲烷菌)的存在可以改变溶液中的离子平衡,进而有利地克服白云石形成过程中的动力学障碍,并列举了低温微生物成因白云石的氧同位素指标在古温度恢复和过去气候变化研究中的应用,最后对微生物成因白云石相关研究方向(如多学科交叉、新技术应用等)加以展望。对微生物成因白云石模式的深入认识,将为正确解释"白云岩问题"提供新的途径,也将为石油学家关心的白云岩储层问题提供新的理论基础和研究思路。

关键词:白云石;微生物;硫酸盐还原菌

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The advances in the study of microbial dolomite

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Abstract: "Dolomite problem" has long been one of the focuses and difficulties in the study of sedimentary geology. Dolomite serves as an important reservoir of oil and gas both in China and abroad. Therefore, the understanding of the formation process of dolomite is significant for the exploration of oil and gas in carbonate rocks. There are many models to explain the origin of dolomite, such as the Sabhka evaporation model, the seepage-reflux model, the burial adjustment model, the mixing zone model, and the tidal pumping model. During the past decades, with the further research on the dolomite formation at low temperature, the microbial dolomite model, as a new dolomite origin model, was proposed and well developed. This paper reviews the progress of research on microbial dolomite. Three kinetic barriers of dolomite precipitation under earth surface conditions were listed, which are strong hydration energy of magnesium ion, the existence of sulfate ion and the low concentration and low activity of carbonate ion. The background for putting forward the microbial dolomite model and the growth process and morphological characteristics of microbial dolomite were briefly described. The mediation of microbe

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during the formation process of dolomite was explained in detail. It is pointed out that the existence of microbes (e.g., sulfate-reducing bacteria and ancient methane bacteria) could change the ion balance of solution and help dolomite to overcome the kinetic barriers during the precipitation process. The application of oxygen isotope of microbial dolomite to the reconstruction of palaeo-temperature and ancient climate change was discussed. The future orientations for research on microbial dolomite (e.g., multidisciplinary analysis, application of high technology etc.) were predicated. The further investigation into the microbial dolomite model will provide researchers with a new approach to understanding the "dolomite problem" and is also helpful to the study of dolomite reservoir in petroleum geology.

Key words: dolomite; microbial; sulfate-reducing bacterial

白云岩是碳酸盐岩油气勘探的一个重要目的层,从世界范围来看,目前50%的碳酸盐岩储层是白云岩(Zinger *et al*., 1980)。近年来,我国在海相碳酸盐岩油气勘探中不断取得突破,特别是在白云岩储层中发现了若干大型油气田,如塔里木盆地和田河气田、鄂尔多斯盆地苏里格气田、四川盆地普光超大型气田等,另外,塔里木盆地轮南-塔河大油田中也有部分储层为白云岩。因此,对白云岩储层成因及发育规律的研究是今后碳酸盐岩油气勘探能否取得更大突破的关键。白云岩的起源即"白云岩问题"早在200多年前就有人对其进行研究,并一直延续至今(Von Morlot, 1847; Skeats, 1905; Van Tuyl, 1918; Steidtmann, 1926; Hewett, 1928; Young, 1933; Riviere, 1939; Landes, 1946; Behre, 1947; Chave, 1952; Graf and Goldsmith, 1956; Fairbridge, 1957; Strakhov, 1958; Medlin, 1959; Baron, 1960; Wells, 1962; Alderman and Von der Borch, 1963; Friedman and Sanders, 1967)。白云岩成因有多种解释模式,如萨布哈蒸发模式、渗透回流模式、埋藏调节模式、混合水模式、潮汐泵模式等(Sherman *et al*., 1947; Adams and Rhodes, 1960; Goodell and Garman, 1969; Hanshow *et al*., 1971; Badiozamani, 1973; Fanning *et al*., 1981; Patterson and Kinsman, 1982; Saller, 1984; Carballo *et al*., 1987; Humphrey and Quinn, 1989; Daniel *et al*., 1990; Gill *et al*., 1995)。但目前白云岩的形成条件和机理仍然没有查清楚,对相关的地质模式也存在争议。近年来,白云石微生物成因假说的提出为解决"白云岩问题"提供新的途径。

本文综述了地球表生白云石形成的动力学障碍及微生物在白云石形成过程中的作用,并初步提出今后白云石相关研究的发展趋势。

1 地球表生条件下白云石形成的3个动力学障碍

白云石广泛存在于古老的碳酸盐中(Zinger *et al*., 1980; Warren, 1999),在全新世沉积物中却相对罕见。早期研究认为地球表生的低温低压条件不利于白云石的形成(Garrels and Thompson, 1962)。Land(1998)曾试图在25℃条件下沉淀出白云石,但经过32年的试验都未能成功,最终得出"白云石问题是一个动力学问题"的结论。

归纳当时室内模拟地球表生条件沉淀白云石试验失败的原因,可能是白云石形成过程中存在着动力学能量障碍,抑制了它的形成(Krauskopf and Bird, 1995)。这种抑制作用主要来自3方面:① 镁离子的高水合能(Lippmann, 1973)。低温条件下镁离子与水结合紧密,不易进入白云石晶格,只有当温度升高时,镁离子与水结合的紧密程度才会降低(Gains, 1980);② 硫酸根的存在。硫酸根可以和镁离子形成中性粒子对,进而显著增加硫酸根的溶解度,而溶液中的硫酸根可以抑制白云石的均匀成核作用(Baker and Kastner, 1981)。升温后的实验结果显示出,即便溶液中存在少量硫酸根离子,甚至只有300~400 mg/L,也会阻止白云石的形成(Baker and Kastner, 1981; Kastner, 1986; Morrow and Ricketts, 1988);③ 碳酸根离子浓度和活度过低(Garrels and Thompson, 1962),且碳酸根离子不能克服镁离子外面的水合层而和镁结合(Lippmann, 1973)。

要克服上述动力学障碍,溶液(海水)需要被浓缩、加热、冷却、稀释、降低硫酸根离子水平或升高碳酸根离子活度。因此,室内模拟的地球表生低温低压条件,不能克服白云石形成的这些动力学障碍。

2　微生物成因白云石

2.1　微生物在白云石问题中的引入

澳大利亚南部的 Coorong 地区出现的大量现代白云石已被证实为原生沉淀(Von der Borch and Lock, 1979;Rosen *et al.*, 1988;Wright, 1999), Lagoa Vermelha 地区也发现了原生白云石的沉淀(Vasconcelos, 1994)。自然界现代白云石是如何克服动力学障碍而形成的呢?Nadson(1928)曾在厌氧微生物实验中发现了与镁相关的碳酸盐矿物的沉淀,并认为可能是白云石。Neher(1959)也曾报道在厌氧微生物实验中有白云石晶体沉淀出来。众多研究者发现,在现代盐湖或泻湖等自然条件下,微生物对于诱导白云石的形成可能起到重要作用(Skinner, 1963;Von der Borch, 1976;Von der Borch and Jones, 1976;Kelts and McKenzie, 1982;Lock, 1982;Baker and Burns, 1985;Ahmad and Hostetler, 1988, 1994;Compton, 1988;Rosen *et al.*, 1988, 1989;Warren, 1988, 1990;Slaughter and Hill, 1991;Botz and Von der Borch 1984;Mazzullo *et al.*, 1995;Vasconcelos *et al.*, 1995;Vasconcelos and McKenzie, 1997;Wright, 1997, 1999, 2000;Gournay *et al.*, 1999;Burns *et al.*, 2000;Teal *et al.*, 2000;Warthmann *et al.*, 2000;Wacey, 2002;Van Lith *et al.*, 2003;Wright and Wacey, 2004, 2005;Wright and Oren, 2005)。Folk(1992, 1993a, 1993b)通过对晶面内部或表层毫微米大小的球粒体的观察,认为这反映了早期细菌体的形态,并进一步强调了微生物对矿物形成的影响。Vasconcelos 等(1995)通过 Lagoa Vermelha 微生物培养成功沉淀出低温条件下的白云石,进一步证实了微生物因素在白云石形成过程中的重要作用。据此,Vasconcelos 和 McKenzie(1997)提出了一种新的白云石成因模式,即微生物白云石模式(图 1),图中盐湖湖底形成黑色富有机质软泥,呈缺氧状态,高盐度使硫酸盐含量变高,为嗜硫细菌作用提供了物质来源,同时 Mg 含量也增高,并以镁方解石或钙白云石沉淀下来,软泥中微生物活动的调整使得这些原始碳酸盐岩沉积并埋藏变老。随后 Warthmann 等(2000)对这一模型作了进一步验证,实验证实硫酸盐还原菌的参与可以诱导白云石的形成,而没有细菌参与的低温条件下根本无法形成白云石。

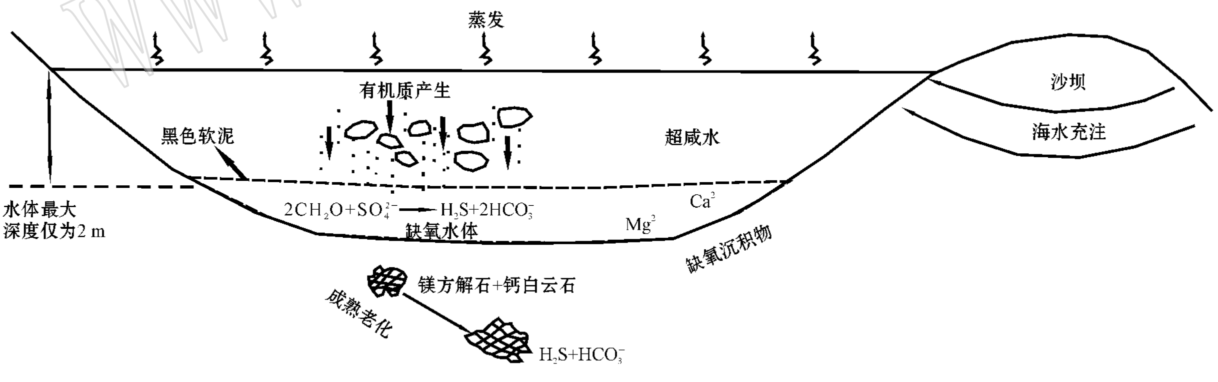

图 1　巴西 Lagoa Vermelha 微生物白云石形成示意图(据 Vasconcelos 和 Mckenzie,1997)

Fig. 1　Sketch of microbial dolomite formation in Lagoa Vermelha, Brazil (after Vasconcelos and McKenzie,1997)

2.2　微生物成因白云石的形态特征

微生物成因白云石的形态完全不同于高温条件下化学沉淀的白云石,其颗粒的形态和大小与细菌体相似,多为亚微米级大小,最小的颗粒的形态表现为次球状和椭球状细菌形态的核,周围被白云石所包裹,而较大的颗粒是由众多小颗粒聚集而成(Wright,1999)。Warthmann 等(2000)在实验室内详细观察了白云石晶体生长过程,发现随着白云石的生长,其晶形不断变化(图 2)。最初的生长开始于细菌细胞末端不连续的微晶,1~2 周后发育成卵形(图 2a) 持续生长 4~6 周后从一个卵的中心分裂成两个卵,外形上酷似哑铃(图 2b) 随着细菌在“哑铃”上的不断附着,白云石的生长也在继续(图 2c) ;一直生长到多个“哑铃”末端相互接触并结合,最终形成

半球状或花椰菜状(图2d)。Van Lith 等(2003)的实验也观察到哑铃形的白云石集合体的形成。在我国青海湖沉积物中发现的现代微生物成因的白云石为粒度约3微米的次球-球状白云石集合体,这些集合体多呈球状和椭球状,内部具有特定的、规则的显微结构形态,且广泛发育有亚微米级的孔隙(图3)(于炳松等,2007;Deng *et al*.,2010)。

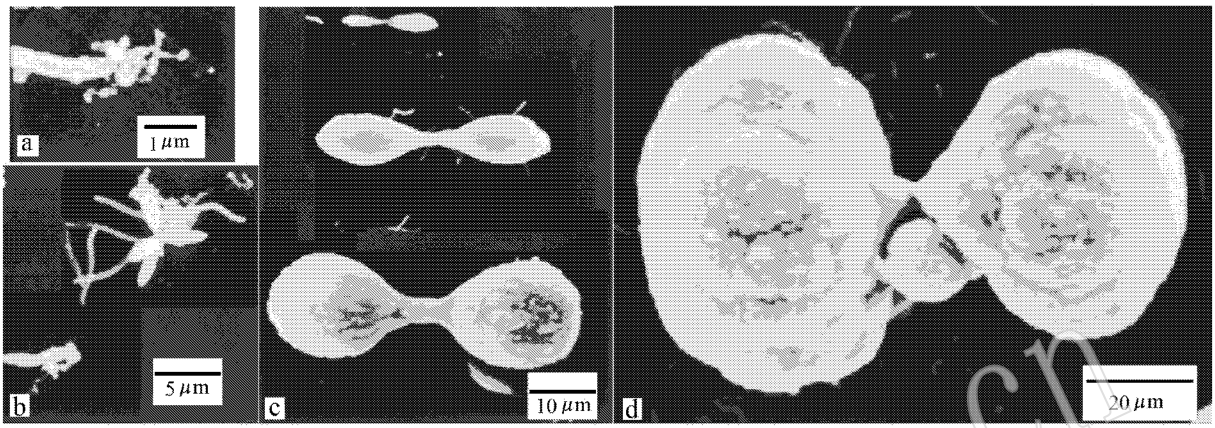

图2 微生物成因白云石生长过程(据 Warthmann 等,2000)

Fig. 2 The microbial dolomite formation process (after Warthmann *et al*.,2000)

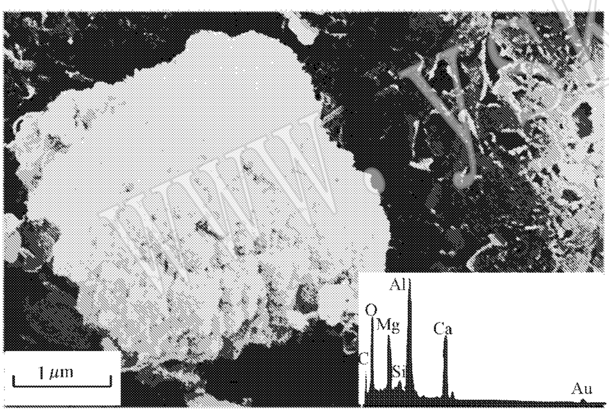

图3 青海湖底沉积物中白云石集合体扫描电镜照片及能谱分析结果(据 Deng 等,2010)

Fig. 3 SEM image and EDS analytical result of dolomite aggregates in Qinghai Lake sediments (after Deng *et al*.,2010)

2.3 微生物白云石形成机理

实验室观察发现碳酸盐的成核作用发生于细菌、微细菌或外表细胞聚合的物质上(Folk,1993a;1993b;Vasconcelos *et al*.,1995;Vasconcelos and McKenzie,1997;Warthmann *et al*.,2000),因此,微生物在白云石沉淀过程中起结晶核的作用(Wright and Wacey,2004)。硫酸盐还原菌或与甲烷古菌共同作用,将硫酸根离子还原,一方面解离了$(MgSO_4)^0$离子对,增加了镁离子活度,提高了细胞周围微环境的镁离子浓度(Van Lith *et al*.,2003);另一方面,由于细菌和微生物的细胞壁带负电,可以吸引阳离子,为矿物成核创造了有利的微环境(Beveridge,1989;Folk,1993a)。这两方面有利于克服前文提到的白云石形成的动力学障碍之一。同时,硫酸根由于被微生物还原而减少($SO_4^{2-}+2CH_2O+H_2O \rightarrow H_2S+2HCO_3^-$ 或 $CH_4+SO_4^{2-} \rightarrow HCO_3^-+HS^-+H_2O$)(Gunatilaka,1987;Peckmann and Thiel;2004),这克服了低温白云石沉淀动力学障碍之二。细菌活动还会控制溶液中CO_3^{2-}的可利用性(Wright,1999;Wright and Wacey,2004)。厌氧环境下,硫酸盐还原菌利用硫酸根作为末端电子接收者而消耗有机质。有机质中的氨基酸通过微生物降解释放出易溶的氨气,氨气溶解增加溶液的碱度,升高pH值,使碳酸盐平衡向CO_3^{2-}方向移动($NH_3+H_2O \rightarrow NH_4^++OH^-$,$OH^-+HCO_3^- \rightarrow H_2O+CO_3^{2-}$)(Berner,1980;Durand,1980;Slaughter and Hill,1991),进而提高了CO_3^{2-}的浓度,有利于克服白云石动力学障碍之三。

可见,微生物(硫酸盐还原菌及甲烷古菌)在白云石形成过程中起到催化剂的作用(Wacey *et al*.,2007)。微生物/细菌的代谢活动显著地影响了周围微环境的变化,通过提高pH值、CO_3^{2-}和Mg^{2+}浓

度，降低 SO_4^{2-} 浓度，进而克服白云石形成的动力学障碍，形成低温下的白云石矿物（Wright，1999；Wacey，2002；Wright and Wacey，2004）。

3　微生物成因白云石在古温度恢复中的应用

随着 McCrea（1950）对方解石-水体系的温度所控制的氧同位素分馏的确立，研究者对更多的碳酸盐矿物的稳定同位素组成进行了分析，并提出许多关于矿物成因方面的论证（Emiliani，1955；Epstein *et al*.，1963；Anderson *et al*.，1971；Clayton，1986）。由于白云石沉淀发生在水体环境中，故其氧同位素组成仍受流体氧同位素组成和沉淀温度的控制（Schmidt *et al*.，2005）。因此，白云石氧同位素可以作为指示白云石沉淀时期环境的良好替代指标，可以被用来重建白云石形成时期水体的氧同位素组成以及当时的温度状况（Vasconcelos *et al*.，2005）。以往在低温条件下无法重建白云石形成的时期，一方面，只能通过高温白云石-水之间的同位素分馏方程外推（Northrop and Clayton，1966；Matthews and Katz，1977），而这在当时是无法通过实验进行验证的；另一方面，从理论上来讲，如果共生的方解石和白云石是在同样的温度下，且均与水达到平衡的情况下沉淀下来，那么，白云石-方解石氧同位素差值应该是个常数，而方解石-水分馏系数是可知的，白云石-方解石氧同位素差值又可以测量，那么白云石-水体系的氧同位素分馏系数就可能间接得到，但事实上，方解石-白云石对的同位素研究结果表现出很大的分散性（Clayton and Epstein，1958；Engel *et al*.，1958；Sheppard and Schwarz，1970），所以推导出来的白云石-水体系的氧同位素分馏仍是不确定的。随着微生物诱导白云石的发现和实验室内低温条件下白云石的成功沉淀，使得直接构建低温条件下白云石-水之间的氧同位素分馏方程成为可能（Vasconcelos *et al*.，2005）。因此，低温白云石的氧同位素也可以被用来作为全球气候研究的替代指标，恢复白云石沉淀时期的温度，进而作为古温度恢复的一个间接手段。

4　结语

“白云岩问题”是一个涉及地质学、动力学、热力学及微生物化学等领域的复杂问题。微生物的诱导作用克服了白云石低温条件形成的动力学障碍，使得形成于地表温压条件下的白云石成为可能，这对认识“白云岩问题”具有突破性的贡献，这也会带动白云岩相关方向研究的不断深入。目前发现的能够诱导形成低温条件白云石的微生物/细菌主要是硫酸盐还原菌和甲烷古菌（Roberts *et al*.，2004；Kenward *et al*.，2007，2009），最近又发现适盐需氧细菌在硫酸根存在的情况下也可以沉淀出白云石（Sanchez-Roman *et al*.，2009），除此之外其他低温白云石诱导微生物种类的研究还需要进一步探索研究。伴随微生物成因白云石形成模式不断完善，低温条件下白云石-水之间氧同位素分馏方程将为今后古气候研究提供新的途径。另外，随着诸如精细同位素定年技术、地球化学同位素示踪技术以及微区分析方法的不断发展，白云岩成因研究将会在不久的将来取得新的突破，也将为石油学家关心的白云岩储层问题提供新的理论基础和研究思路。

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