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沉积盆地超深层有机-无机复合生烃机理及地质模式

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内容提要：全球范围内超深层油气的不断发现，对经典的生烃理论提出了挑战，外源氢加入的有机-无机复合生烃过程引起了广泛关注。基于地质观察统计数据，分子氢在沉积盆地中分布广泛，形成机制复杂。在地质环境中，水和水-岩反应、深部流体等途径产生的无机氢是最主要的外部氢源。可控加氢模拟实验揭示了沉积盆地的氢逸度水平是调控烃类产物生成的重要因素之一，并且干酪根的加氢裂解是沉积盆地中易于发生的生烃过程。外源氢介入生烃过程的前提是环境氢逸度大于沉积有机质本身的氢逸度，其有效范围受生烃母质化学组成和结构的制约，约起始于生油高峰之后，约终止于沉积有机质 H/C＝0.3 之时。亦即，有机-无机复合生烃作用是沉积盆地超深层生烃的有效途径。在其有效发生的范围内，油气资源类型依然由生烃母质类型(化学组成和结构)、成熟度和受热历史等因素决定，具有明显的阶段性和不同于经典理论的生烃模式。外源氢的参与，在成熟阶段可小幅度提升生油产率；在高—过成熟阶段可显著增加天然气产率；在高成熟阶段，加氢脱烷基作用最大可增加 50％的轻质油/凝析油产率；在过成熟阶段，加氢脱甲基-开环作用最大可增加约 5 倍甲烷产率。有机-无机复合生烃模式的确立，丰富了传统生烃理论的内涵，奠定了超深层油气生成的理论基础，拓展了油气勘探的视野。

关键词：超深层；氢逸度；有机-无机复合生烃机理；判识标志；生烃模式

当前油气勘探领域不断向盆地深部拓展，6000 m 以下超深层的工业性油田数量随时间的推移而逐步增加(Bai，2014)。例如，国外的墨西哥湾 Tiber field 深达 8740 m 的油气藏；国内的塔里木盆地深达 7800 m 顺北油气藏和 8882 m 的轮探 1 井(Yang et al.，2020)；四川盆地深达 6500 m 的元坝气田和深度超过 8000 m 的马深 1 井、川深 1 井和角探 1 井三口风险探井(Liang et al.，2021)。可见，随着开发技术的进步，超深层现已成为油气勘探重要的接替领域。然而，因为超深层的温压条件已经超出了传统理论所预测的油气生成及保存的温度区间，所以对传统生油理论形成了一定的挑战。

干酪根晚期生烃理论是目前指导油气勘探最成熟的成烃理论(图 1a)(Tissot et al.，1974)。沉积有机质热演化产物的生成规律表明该过程发生了歧化反应(Helgeson et al.，2009)。随着地层埋深、热应力增加，沉积有机质中一部分官能团发生脱氢氧化反应，通过成环或交联反应形成更加贫氢的大分子，另一部分发生加氢还原反应，断裂成一些短链化合物(图 1b)(吴治君等，1995；Lewan，1997；Amrani，2014；刘佳宜等，2019)。在传统生烃理论框架内，沉积有机质生烃过程中发生的裂解反应所需的 H 均来自生烃母质，是一个有机质内部氢转移的过程，不存在外部氢源的补充。

由于油气多是从深往浅运移，对应的烃源岩很可能处于更深的地层，其温压条件大幅高于沉积盆

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Wu Jia, He Kun, Meng Qingqiang, Lu Hong, Zhong Ningning, Fang Peng, Wang Yuan, Ji Fujia, Yang Ya'nan, Huang Xiaowei, Li Kang, Zhao Zhongfeng. 2023. Hydrocarbon generation mechanism via the organic-inorganic interaction pathway and its geological pattern in ultra-deep sedimentary basins. Acta Geologica Sinica, 97(3): 961～972.

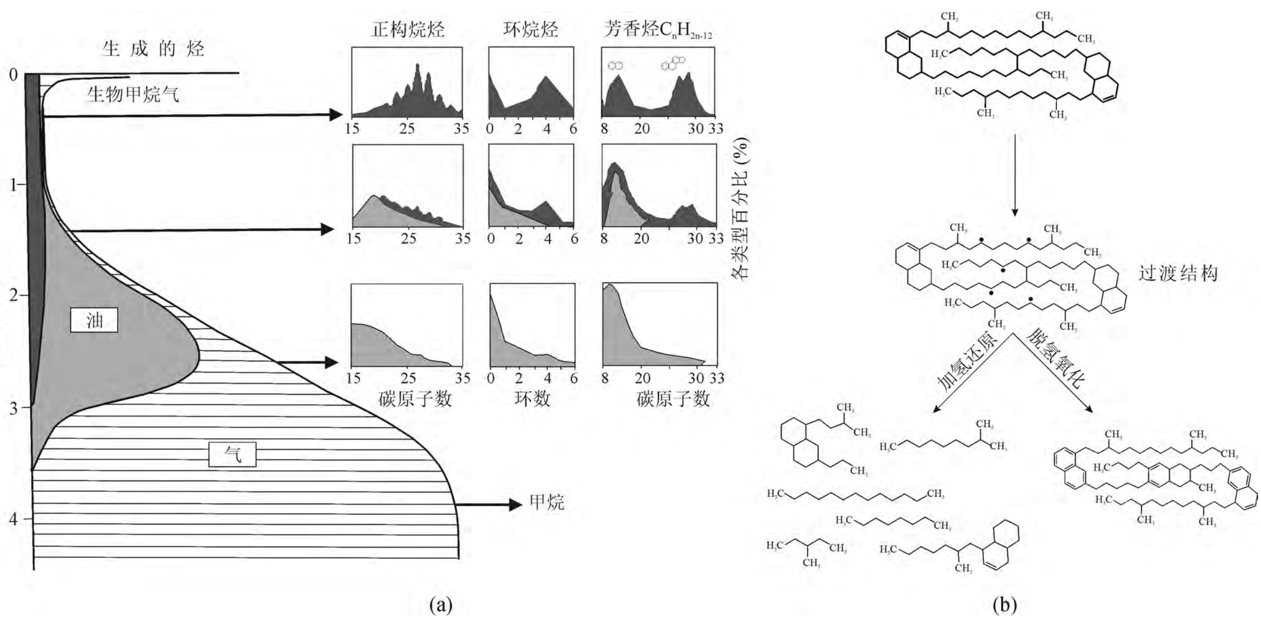

图 1 经典生烃理论模式(a)(据 Tissot et al.，1974)和干酪根热降解过程的歧化反应模式(b)(据 Lewan，1997)

Fig. 1 Classic pattern of hydrocarbon generation theory (a) (after Tissot et al.，1974) and the pattern of disproportionation reaction during the thermal decomposition process of kerogen (b) (after Lewan，1997)

地中浅层。以往认为，超深地层所经历的埋藏史热应力会导致其成熟度过高，从而失去生烃潜力。因此，在沉积盆地超深层相对高温、高压和复杂流体介质的环境下，是否存在无机介质中外部氢源加入的有机质生烃反应，是不可回避的理论和现实问题。

人工热模拟实验已证明外部氢源，特别是氢气，可以促进沉积有机质的热分解(Love et al.，1997；Jin et al.，2004；Speight，2004；Sahu et al.，2015)。另外，研究表明在特定的地质体条件下，由水-岩反应产生的氢能够促使无机成因的甲烷生成(Milesi et al.，2015，2016；Klein et al.，2019)。然而，地球岩石圈中远低于人工体系的氢逸度水平，是否能够介入还原性较强的富沉积有机质地层，并促使生烃尚无定论。

为了揭示沉积盆地超深层的地球化学环境是否具备有效氢源、加氢裂解反应的临界条件及制约因素等科学问题，本文综合热模拟实验和地质观察证据，明确了沉积盆地超深层的生烃机理是以沉积有机质(高熟干酪根、原油、储层沥青等)为主要反应物，在外部氢源加成下的有机-无机复合生烃过程。换言之，尽管有机-无机复合生烃的可能反应途径有很多种，但是，以水 H 作为外部氢源与生烃母质的反应，才是有效的有机-无机复合生烃作用过程。

1 沉积盆地存在多种无机供氢途径

沉积盆地中，氢气大多以游离氢或水溶气的形式存在(Arnórsson，1985；Smith，2002；Lin et al.，2005；孟庆强等，2014，2021；Lollar et al.，2014；Truche et al.，2020；Zgonnik，2020；韩双彪等，2021；Boreham et al.，2021；Moretti et al.，2021)。不同地质体中因氢气来源和赋存条件的不同，氢气含量迥异，从远小于 1%到几乎纯氢气都有分布(表 1)。

土耳其 Chimaera 的一个气苗已经活跃 2500 a，至今仍含有 7.5%～11.3%的氢气(Zgonnik，2020)。来自俄罗斯科拉半岛的一处碱性火山岩复合体气体中，氢气含量为 2.8%～3.8%且在三年的时间中氢气的含量没有明显的变化(Hawkes，1972)。中国科研钻井松科 2 井中也检测到大段连续的氢气测气异常(韩双彪等，2021)。当前世界上最深的科拉超深钻井 SG-3 钻深 12263 m，其钻井冲洗液的气体分析结果表明，在其 5000 m 以深多个层段均有异常 H_2 含量显示，钻出岩石中 H_2 含量在 4.9～32.5 m^3/m^3 rock，而且 SG-3、SG-4、SG-8 和 Gravberg-1 都显示钻井深部具有比浅部更高的氢气含量(Zgonnik，2020)。这是因为盆地超深层环境比浅层更接近前寒武纪结晶基底和地球深部，具有更强烈的变质和热液活动，因而比浅层环境具有更高的氢逸度。

从形成机理方面看，在沉积盆地超深层环境下，存在水-矿物反应、深部流体直接携带输入以及放射

表 1　不同地质体中氢气含量统计表

Table 1　A summery of hydrogen abundances in various geological bodies

构造		H_2(%)	通量($\times 10^9$ m^3/a)	来源
沉积盆地	油气藏区	大多<1;富氢气藏 6～95.2	—	深部来源、断裂活动、水岩相互作用、放射性作用、生物来源(Rogers, 1921; Headlee, 1962; Wood, 1972; Angino et al., 1984; Coveney Jr et al., 1987; Moore et al., 1987; Levshounova, 1991; Осика et al., 2002; Smith et al., 2005; Briere et al., 2016; Gueélard, 2016; Deville et al., 2017; Prinzhofer et al., 2018)
	沉积岩区	4.2～98		
蛇绿岩带		7.5～99.0	2～4	主要与蛇纹石化作用有关,含量多在 30% 以上(Sano et al., 1993; Hosgormez et al., 2008; Etiope et al., 2011; Vacquand, 2011; Boulart et al., 2013; Morrill et al., 2013; Lollar et al., 2014; Yuce et al., 2014; Deville et al., 2016; Vacquand et al., 2018; Zgonnik et al., 2019)
断裂带		9.4～70	—	水与岩石破碎表面的反应(Wakita et al., 1980; Sugisaki et al., 1983; Ware et al., 1984; Shcherbakov et al., 1986; Wiersberg et al., 2008)
火山岩		0.002～93	108±81	H_2S 与水的反应、深部来源、水岩相互作用(Zinger, 1962; Sigvaldason, 1966; Hawkes, 1972; Huntingdon, 1973; Evans et al., 1981; Angino et al., 1984; Башта et al., 1991; Ikorsky, 1999; Symonds et al., 2003; Potter et al., 2004; Gilat et al., 2005; Canfield et al., 2006; Fiebig et al., 2015)
温泉、热液系统		2.4～51.4		深部来源、水岩相互作用(Kiyosu, 1983; Shcherbakov et al., 1986; Blavoux et al., 1990; Proskurowski et al., 2006; Petersen et al., 2011; Tassi et al., 2012; Suda et al., 2014; Etiope et al., 2017; Hao et al., 2020)
矿体		1.4～98.5	—	深部来源、水岩相互作用、放射性作用、混源(Dubessy et al., 1988; Melcher et al., 1997; Smith, 2002; Nivin et al., 2005; Nivin, 2016; Boreham et al., 2021)
结晶基底		12.8～91.8	0.45～4.3	水岩相互作用、放射性作用、混源(Petersilie et al., 1970; Goebel et al., 1983; Angino et al., 1990; Lollar et al., 1993a, 1993b, 2006, 2014; Newell et al., 2007; Sherwood Lollar et al., 2007; Guélard et al., 2017)

性作用促进无机流体分解生成 H_2 等多种供氢途径。在自然界,橄榄岩蛇纹石化反应是形成 H_2 较为熟知的方式。较高的温度和含水体系有利于蛇纹石化作用的发生。该过程形成的气体产物中,氢气的含量可高达 90%以上(Klein et al., 2019)。高温条件下还原性含铁矿物(如菱铁矿,磁铁矿等)能与水发生氧化还原反应生成 H_2,可参与烃类有机质的生成(Seewald, 2001; Jin et al., 2004; Milesi et al., 2016; He et al., 2019)。

深源岩浆是氢气由地球深处向上运移的极好载体,碱性岩内的氢气丰度为 3 cm^3/kg,基性—超基性岩的则高达 26.8 cm^3/kg,二者均具备较强的输氢能力(Newell et al., 2007)。来源于深处的液相流体也可以溶解大量氢气。1 kg 水从地下 15 km 运移至地表,能释放出 12 L 的 H_2(郭占谦, 2001)。此外,南非 Witwaterand 盆地和加拿大 Timmins 盆地深部裂缝水中的高浓度 H_2 是辐射分解 H_2O 形成的(Lin et al., 2005; 刘池洋, 2013; Lollar et al., 2014)。

2　沉积有机质裂解生烃受地层氢逸度水平的调控

随着油气形成的有机-无机相互作用理论的提出和发展,无机环境在有机质生烃演化中的作用越来越受到关注,而 H 是生烃过程中最重要的限制性因素。基于歧化反应的化学本质,在热演化过程中,生烃体系中氧化还原条件会受到氢逸度的调控。当有来自于沉积有机质体系外的氢源介入时,不仅会对体系进行物质补充,也会影响体系的氧化还原条件,进而改变生烃反应的方向、效率与动力学过程。

在地质体中,无论在前寒武纪地层还是新生代地层中,均有含量丰富的 H_2 存在(Lollar et al., 2014)。当 H_2 与沉积岩相遇时,易于被沉积岩中的黏土矿物和有机质吸附而参与烃源岩的生烃演化(Jin et al., 2004)。在干酪根的热演化过程中,生烃潜力逐渐减小,并伴随着有机质结构的缩合,对于高演化的干酪根而言,生烃已近终止,元素组成极富碳贫氢。因此只有在额外氢源供应的情况下,高演

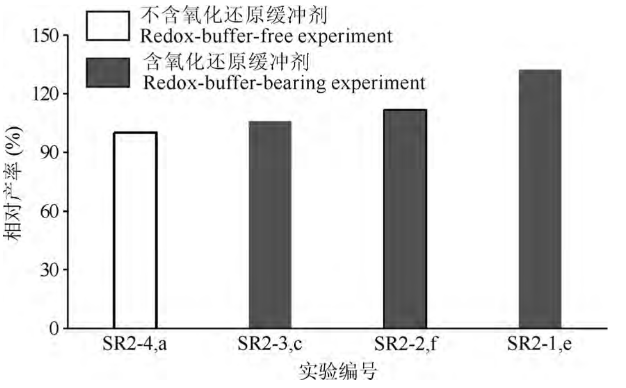

图 2 还原性增加对低熟烃源岩生油产率的影响(空心柱为对照组,未加入氧化还原缓冲剂)(据 Wu et al.,2021)

Fig. 2 Influences of higher reduced condtions on the hydrocarbon yields of low-maturity source rock (empty collum is the control experiment without redox buffer) (after Wu et al., 2021)

化干酪根才可能继续生烃。

李亢等(2022)以高成熟寒武系玉尔吐斯和奥陶系萨尔干干酪根为反应物,研究了金属催化和供氢剂对高演化干酪根再活化生烃的影响。由于 $NaBH_4$ 受热会分解出 H_2,在反应体系中提供外源氢,在气态产物中检测出了高产率的 H_2。对比研究表明,金属催化效应对干酪根热解气态烃总产率无显著影响,而供氢剂 $NaBH_4$ 的加入显著促进了高演化干酪根的生烃产率(9.4～12.8 倍)。因此,充足的氢源供应能够使高演化干酪根再次活化生烃。

然而在实际地质体中,外源氢存在形式和丰度远低于人工体系中氢气的纯度和逸度。因此,必须真实模拟沉积盆地中氢逸度水平,探究外源氢能否参与有机质的裂解生烃。氢气虽然在沉积盆地环境中普遍存在,但是油气田区地层中的含量往往低于周边岩石地区,气藏中的氢气浓度仅为气藏外氢气浓度的 4%(Levshounova, 1991; Yuce et al., 2014; Boreham et al., 2021),而且地层中氢气浓度随着与油气藏距离的减小发生指数型降低(Levshounova, 1991)。由于水热体系氢逸度主要受温度和压力的影响,基于不同温压条件下的氢逸度系数(Shaw et al., 1964),可以通过天然气氢含量计算对应的氢逸度。例如,在沉积盆地 7 km 的深部,天然气样品中的氢逸度范围在 10^3～10^6 Pa 之间。水热体系中,磁铁矿-赤铁矿(MH)和钴-氧化钴(CoCoO)氧化还原缓冲对在 450～600℃,70 MPa 时的氢逸度范围分别为 1.09×10^4～1.38×10^4 Pa 和 1.27×10^6～2.19×10^6 Pa。因此,生烃模拟实验用 MH 和 CoCoO 氧化还原缓冲对控制氢逸度可较为准确的还原沉积盆地的氢逸度条件。

在水热条件下,通过氧化还原矿物缓冲剂可限定封闭体系内的氢逸度水平。利用该技术可实现在沉积盆地氢逸度范围内对干酪根生烃过程进行实验。实验结果表明,沉积盆地的氢逸度水平条件下促进了可溶有机质的生成,增量可达 30%(图 2)(Wu et al., 2021)。根据 Alum Shale 低熟干酪根可控加氢模拟实验中 CO_2 产率、烃类气体干燥系数和 $\delta^{13}C$ 值的变化规律,可以确定导致生烃产率升高的反应机理主要为加氢裂解。同时,在设置沉积有机质过量的实验体系中,生烃产率降低。这是由于体系初始氢逸度高于 MH 限定的氢逸度平衡值,发生了 MH 消耗初始氢的反应。这表明沉积有机质生烃本身的氢转移过程是依托 H_2 作为中间体完成的(Wu et al., 2021)。因此,沉积有机质在热应力作用下发生分解的时候,无论 H_2 是来自有机质本身还是外源氢,其基元反应类型是相同的,均为加氢(H_2)裂解反应。

除此之外,在外源氢条件下,高—过成熟干酪根热模拟实验产物主要为甲烷,伴随少量乙烷,其中甲烷产率可增长 4～6 倍(Yang et al., 2022)。综上,整个生烃过程中,干酪根裂解生烃机理都是可以看作为加氢裂解为主,氢源既可来自干酪根自身,也可来自外部无机环境,拓展了传统生烃理论中对生烃过程制约条件元素 H 供给方式的理解。

3 有机-无机复合生烃的临界条件

外部氢源加成所引发的有机-无机复合生烃作用,受到沉积有机质及其外部环境(沉积盆地无机环境)氢逸度的制约。复合生烃反应发生的前提是环境氢逸度大于沉积有机质本身提供的氢逸度,即 f_{H_2}(环境)$>f_{H_2}$(有机质)。

在沉积盆地氢逸度水平下,沉积有机质生烃过程中会有一部分化合物处于亚稳态热力学平衡,比如同碳数的烯烃和烷烃会形成烯-烷平衡(Seewald, 2003)。热模拟实验也已证明,短链烯-烷平衡与体系的氢逸度水平直接相关(Seewald, 1994, 1996),故烯-烷比值可以用于推测体系的氢逸度水平。原油或烃源岩体系中的沥青质作为一类地质大分子,其网状分子结构可以包裹一些小分子烃类(Cheng et al., 2017)。利用分散固相吸附分离法可以无损定量分离沥青质包裹烃,可算出包裹烃里同碳数烯-烷比值,可计算出体系对应的 f_{H_2}(环境)。对应条

件下生烃母质的 f_{H_2}(有机质)则可在同样的理论框架中计算得到。

基于塔里木盆地深层-超深层的原油和烃源岩样品，获得对应温压条件下烷-烯等效氢逸度、沉积有机质自身的氢逸度及水-岩作用限制的生烃环境的氢逸度，发现随着地层深度的增加，计算得到的等效氢逸度数值呈现指数级上升的趋势。塔里木沉积盆地中水-岩反应 f_{H_2}(环境)＞f_{H_2}(有机质)的界限大约为 0.1 Pa，对应温压条件预计在 130℃左右，近似在沉积有机质生烃高峰附近。据此，可推测在生油高峰之前，沉积有机质热降解生烃以其自身的氢供给为主，外源氢无法有效促进生烃产率提升，而有机-无机复合生烃的有效发生始于生烃高峰之后。

另一方面，外源氢加成的有机-无机复合生烃作用的发生，受生烃母质化学组成和结构(成熟度)的制约。理论上，尽管随着地层加深，环境氢逸度随之增加，但生烃产率并非持续升高。到了变生作用阶段，高—过成熟沉积有机质成烃以脱甲基作用为主。因此，当沉积有机质分子结构中甲基基团的比例低于阈值时，加氢脱甲基反应则会停滞，烃类气体产率不再增加。以牛蹄塘组高熟烃源岩为例，即使在高氢逸度条件下，其生烃量也没有任何增加，气态烃总产率均在 0.1 mg/gTOC 左右(Yang et al.，2022)。

4　有机-无机复合生烃的判识标志

判断有机-无机复合生烃反应的理论基础是 f_{H_2}(环境)＞f_{H_2}(有机质)。然而，在实际沉积盆地中，该判识方法的应用主要有两个制约因素。一方面，需要较新鲜的深部样品，且能够分离获得沥青质；另一方面，由于烯-烷平衡的达成比生烃更快，因此其对应的等效氢逸度往往反映的是当前地质条件下样品环境的氢逸度水平，无法直接反映生烃过程中的信息。基于此，在外源氢作用下，产物特征如出现甲烷 C、H 同位素异常分馏现象亦可作为判定依据。

4.1　甲烷 H 同位素分馏

高温水热体系模拟实验发现，水能通过加氢作用或氢的转移改变甲烷的氢同位素组成(Reeves et al.，2012；He et al.，2018)。深层页岩气和常规气中常见的同位素异常，比如甲烷氢同位素的反转现象，被归因于水-有机质生气反应或烃类气体水热反应(Zhang et al.，2018)。370℃下的含水(δD_{H_2O}＝－22‰)和无水热解实验，发现含水热解体系生成的甲烷氢同位素明显偏轻(Gao et al.，2014)。但似乎未能观察到相对低温(60～100℃)条件下有机质的含水热解甲烷氢同位素的显著变化(Wei et al.，2018)。导致不同实验结果差异的原因很可能由于水-有机质加氢生气过程中的同位素分馏受控于动力学(KIE)和热力学平衡效应(EIE)的共同控制(He et al.，2021)。对于 EIE，甲烷氢同位素组成(δ^2H_1)受控于水的氢同位素(δ^2H_w)和特定温度条件下的分馏系数或平衡常数(αEIE)(Horibe et al.，1995)。对于 KIE，δ^2H_1 受控于水中的氢向甲烷转移的速率，后者与实验温度相关(Sessions et al.，2004；Reeves et al.，2012)。

基于不同水-岩-烃体系下的模拟实验和理论计算，通过研究水-有机质加氢生气过程中 H 同位素分馏的 KIE 效应，得到加氢生气过程中水-甲烷间氢转移速率与温度的相关关系。同时根据动力学推演得到不同温度条件 H 转移达到平衡(EIE)所需时间，发现在大于 200℃地质条件下，H 转移达到近似平衡(f＝0.99)所需要的时间仅为 4.8 Ma。在此基础上，结合原油裂解生气过程中甲烷 C/H 同位素分馏动力学模型和 EIE 分馏模型，通过数值计算建立了基于甲烷 C/H 同位素演化的水加氢生气贡献判识图版(图 3)。对于经历了较高热演化史的四川盆地志留系—震旦系而言，最大地温普遍超过 200℃，水-烃加氢生气作用对常规气和页岩气的贡献分别为 30%～60%和 30%～80%。通过该图版能够评价天然气中水加氢生气的贡献，并可作为有机-无机复合生烃反应有效发生的依据之一(He et al.，2021)。

4.2　甲烷 C 同位素“倒挂”现象

在高—过成熟地层中，甲烷平均 $\delta^{13}C$ 值重于干酪根或者固体沥青的平均 $\delta^{13}C$ 值(甲烷 $\delta^{13}C$ 值“倒挂”现象)时有出现(魏国齐等，2015；秦胜飞等，2016；周国晓等，2016)。例如：中国四川盆地长宁地区五峰组—龙马溪组(张小龙，2015；张浩淼，2017；牛强等，2020)、华北盆地太康隆起二叠系(白斌等，2006；Liu et al.，2018)、鄂尔多斯盆地下古生界(腾格尔等，2006；Ni et al.，2018；赵晓阳等，2021)以及北美 Appalachian 盆地北部志留系和奥陶系(Jenden et al.，1993；Mastalerz et al.，2003；Burruss et al.，2010)都有相关报道。“倒挂”现象往往被认为异于常规生烃过程中同位素分馏行为，在气-源对比研究方面常常被当作反证来用(帅燕华等，2021)。同时，几乎未见热模拟实验重现这个现象。因此，目前对“倒挂”现象的形成机制仍有争议。

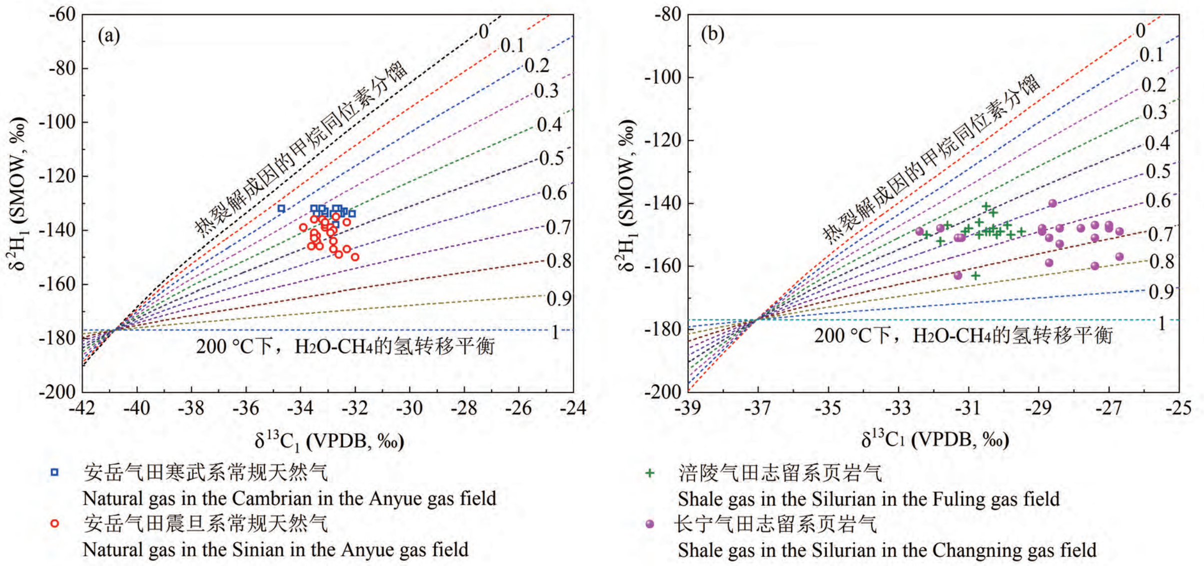

图 3 基于甲烷 C/H 同位素分馏模型的水-加氢生气贡献定量判识图版(据 He et al.，2021)

Fig. 3 C- and H-isotope fractionation of CH_4 with various contributions (x) from the H_2O-hydrocarbon reaction (after He et al.，2021)

(a)—震旦纪—寒武纪地层碳酸岩储层气体；(b)—志留纪地层页岩气；曲线上的 0～1 为水氢的贡献比例

(a)—Carbonate reservoir gases in the Sinian-Cambrian; (b)—shale gas in the Silurian; the value of 0～1 on the curves indicates the contribution proportion of H from water

通过在 420～450℃ 条件下，对高—过成熟 Alum Shale 干酪根进行可控加氢热模拟实验。实验结果表明，对于一定成熟度的高熟干酪根，可以重现产物甲烷碳 $\delta^{13}C$ 值重于残留干酪根碳 $\delta^{13}C$ 值的“倒挂”现象，而在更高温度条件下，“倒挂”现象消失(Yang et al.，2022)。这是因为由温度差异导致不同的同位素分馏效应——温度较低时反应速率较慢，导致同位素分馏更明显。这表明相对低温和外源氢是“倒挂”现象的必要条件。

催化加氢裂解实验等研究表明干酪根、固体沥青和沥青质等地质有机聚合体的内部包裹烃。基于固相沉积有机质的多层级分子结构特征，地质有机聚合体局部结构因空间位阻造成的限域效应和保护作用，使得其内部包裹烃或官能团的热演化行为较外层基团或者游离烃表现出一定的滞后性(Love et al.，1997)，其同位素分馏效应也会存在滞后现象，从而导致内部基团或包裹烃的 $\delta^{13}C$ 值偏低(Chen et al.，2020)。在加氢裂解过程中，固体沉积有机质外层基团会优先发生加氢裂解，该阶段生成甲烷的 $\delta^{13}C$ 值会重于对应母质的平均 $\delta^{13}C$ 值。

此外，同位素分馏效应建立在对应的化学反应之上。由于地质体中的氢逸度水平不足以导致高熟沉积有机质的多环芳香结构进行开环裂解，能够发生的化学反应及其同位素分馏效应仅限于脂肪碳官能团集合内。因此，用高熟沉积有机质的平均碳同位素变化趋势无法解释其烷烃产物的同位素分馏行为。

深层气藏中出现的甲烷 $\delta^{13}C$ 值重于干酪根或残余固体沥青 $\delta^{13}C$ 值的现象，是一种在外部氢源介入时由满足一定 H/C 比、官能团比例的高—过成熟固态沉积有机质在深层高温高压条件下发生脱甲基生气的过程。所以，天然气中甲烷碳同位素 $\delta^{13}C$ 值“倒挂”现象可以作为外源氢介入沉积有机质生烃过程的判识标志之一。

值得注意的是，在外源氢参与沉积有机质生烃过程的判识标志问题，依然存在很大的争议。比如，天然气 H 同位素受到多因素的影响，即使可以通过理论推导得到无机氢源的贡献量，但其中有一部分的贡献源自交换反应，真正的增量部分依然难以明确。这可能是因为仅从产物端的地球化学信息出发，信息量似乎不足以折射出整个反应过程的化学行为。因此，将反应物端的信息也作为研究对象，结合对应的产物信息，利用理论分析对整个反应体系进行系统性研究，可能是打破目前僵局的新策略。

5 超深层有机-无机复合生烃模式

沉积盆地超深层环境中，烃类的生成是一种有

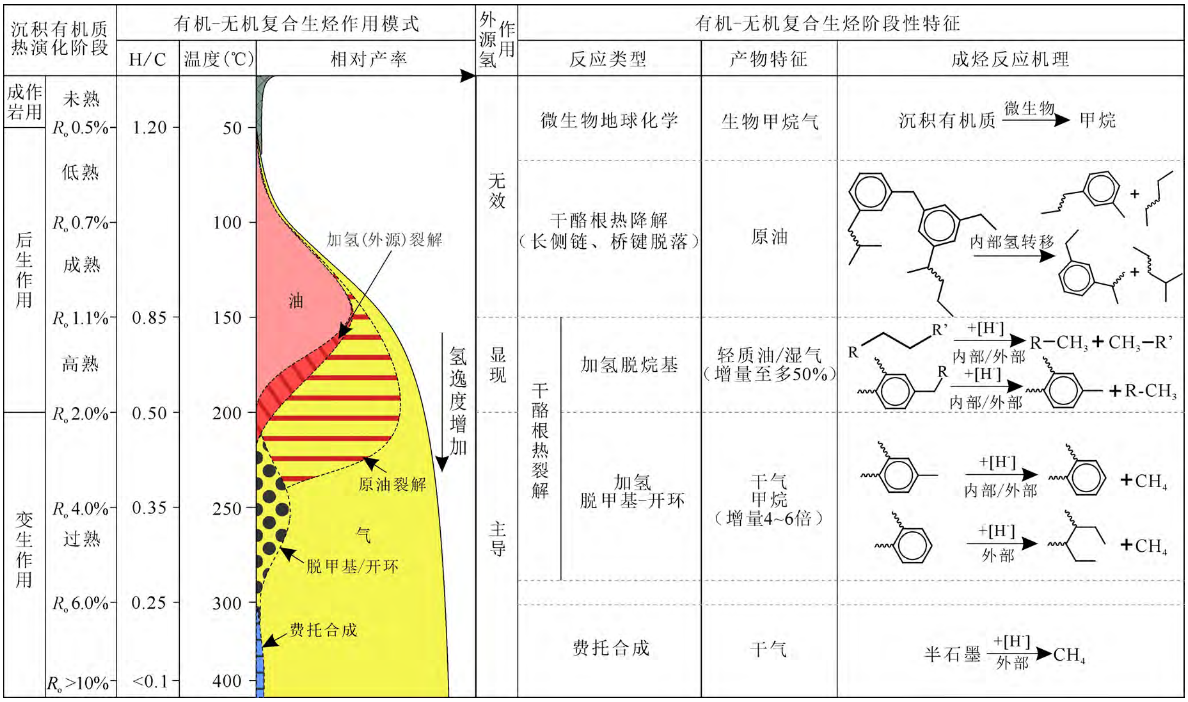

图 4　沉积盆地有机-无机复合生烃模式示意图

Fig. 4　The pattern schema of hydrocarbon generation mechanism via organic-inorganic interaction pathway

机-无机复合作用过程。有效的有机-无机复合生烃作用是在水-岩反应限定的还原条件下，以有机碳(干酪根、油气、固体沥青等)为碳源，水 H 为外部氢源的生烃反应，分为加氢脱烷基、加氢脱甲基-开环和费-托合成三个阶段(图 4)。生烃效率由沉积有机质的化学组成和结构与地质体氢逸度的耦合关系决定。与干酪根晚期成烃理论类似，在外源氢加成的有机-无机复合生烃作用有效发生的范围内，沉积有机质热演化存在明显的阶段性，在成熟阶段可小幅提升生油产率，在高—过成熟阶段可显著增加天然气产率。

在沉积盆地中浅层(成熟阶段生油窗前期)，因为环境氢逸度较低，生烃母质自身的氢逸度(H/C)也较高，故外部氢源加成几乎不可能发生，或者仅起到略微提升生油产率的效果。在生油窗后期和湿气阶段，复合生烃作用的主要产物为可溶有机质，伴随少量气态烃。外部氢源促进了长链烷基均匀断裂，反应位点以烷基 C—C 键为主。

在盆地深层的高温-高压条件下，通常对应于干气阶段，环境氢逸度远高于生烃母质自身的氢逸度，使加氢作用的发生成为必然，并且可显著增加天然气产率。换言之，外源氢参与的有机-无机复合生烃作用能够使得超深层的高—过成熟生烃母质依然保持着较高的生烃潜力，反应位点以芳环甲基为主，反应类型以脱甲基反应为主，并可能存在极少量的芳烃开环反应。

如果成熟度持续增高，外源氢作用的效率将出现反转，当外部氢源仅能作用于芳香结构开环裂解生气时，效率变得很低。实验和地质观察证明，当沉积有机质 H/C<0.3 时，生烃母质将难以被外源氢有效活化生烃。不过，模拟实验揭示了在盆地的更深部，可能存在以有机碳为碳源的费托合成反应，使沉积盆地的生烃作用范围进一步向下延伸(图 4)。

6　结论

本文综合了沉积盆地中氢气来源、分布特征、氢逸度水平和对生烃影响等几个方面的信息，并结合本团队近期的研究进展，总结出对沉积盆地有机-无机复合生烃模式的新认识：

(1)沉积盆地超深层环境，有效的有机-无机复合生烃作用是在水-岩反应限定的还原条件下，以水 H 为外部氢源，与生烃母质的加氢裂解反应。

(2)初步确定外界氢源介入生烃过程起始于生烃高峰之后。生烃母质的化学组成和结构将有机-无机复合再活化生烃下限限定在 H/C=0.3 之前。

(3)提出了 3 条有机-无机复合生烃的判识标志：环境氢逸度大于沉积有机质自身氢逸度；基于甲烷 C/H 同位素分馏的水-烃加氢生气贡献图版；甲

烷C同位素重于初始干酪根或储层固体沥青C同位素的“倒挂”现象。

(4)建立了有机-无机复合生烃模型，对传统晚期干酪根生烃理论进行了完善。在该模型框架下，沉积有机质热演化存在明显的阶段性，油气资源类型依然由生烃母质类型(化学组成和结构)、热史和成熟度等因素决定。

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Hydrocarbon generation mechanism via the organic-inorganic interaction pathway and its geological pattern in ultra-deep sedimentary basins

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Abstract

The continuous discovery of ultra-deep oil and gas around the world challenges the classical theory of hydrocarbon generation. The hydrocarbon generation process with exogenous hydrogen from organic-inorganic interactions has attracted wide attention. Based on the statistical data of geological observations, molecular hydrogen is widely distributed in sedimentary basins and its formation mechanism is complex. In geological environments, inorganic hydrogen derived from water, water-rock reactions and deep fluids is the main external source. Controlled hydrogenation simulation experiments reveal that the level of hydrogen fugacity in sedimentary basins is one of the essential factors regulating hydrocarbon generation, and the hydrocracking of kerogen is a preferential pathway for the hydrocarbon generation process in sedimentary basins. The premise of exogenous hydrogen participating in hydrocarbon generation is that the environmental hydrogen fugacity is greater than that of sedimentary organic matter. The range of this effect is constrained by the chemical composition and the structure of kerogen, and it probably starts after the peak of oil generation and ends approximately when the H/C of sedimentary organic matter is less than 0.3. This demonstrates that hydrocarbon generation via organic-inorganic interactions is an effective pathway for hydrocarbon generation in ultra-deep strata of sedimentary basins. Within the effective range, the types of oil and gas resources are still determined by factors such as the types of kerogen (chemical composition and structure), maturity and heating history, with obvious stages and hydrocarbon generation modes different from the classical theory. With the participation of exogenous hydrogen, the oil generation yield can be slightly promoted in the mature stage and be significantly enhanced in the high-over maturity stage. Moreover, in the high-maturity stage, the hydrodealkylation reaction can increase the yield of light/condensate oil up to 50%, and in the over-maturity stage, the demethylation-ring opening reaction can increase the methane yield by approximately 5-fold. The new hydrocarbon generation model via the organic-inorganic interaction pathway expands the connotation of traditional hydrocarbon generation theory, establishes the theoretical foundation for ultra-deep oil and gas generation, and expands the vision of oil and gas exploration.

Key words: ultra-deep strata; hydrogen fugacity; organic-inorganic interactions; identification index; hydrocarbon generation pattern