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川中侏罗系自流井组大安寨段二亚段 页岩油赋存特征

张晨雨¹, 刘子驿^{1,2}, 王斌¹, 单帅强¹, 陆建林¹, 王保华¹, 左宗鑫¹

1. 中国石化石油勘探开发研究院 无锡石油地质研究所, 江苏 无锡 214126;

2. 中国石化油气成藏重点实验室, 江苏 无锡 214126

摘要:我国湖相页岩油资源丰富,但开采过程具有一定难度。揭示页岩油不同赋存状态在页岩储层中的赋存情况有助于页岩油资源的勘探与开发。以川中地区侏罗系自流井组大安寨段二亚段(以下简称大二亚段)页岩为研究对象,通过多温阶热解实验的实施、扫描电镜孔隙发育特征的观察以及洗油前后孔径分布的分析,揭示了页岩油不同状态在各介质孔隙中的赋存方式。川中地区大二亚段页岩中热模拟恢复后的页岩油以游离态为主(0.42~10.88 mg/g),吸附态次之(0.30~1.95 mg/g)。页岩发育的储集空间主要为有机质孔(孔径 2~600 nm)、黄铁矿粒间孔(孔径 10~700 nm)、介壳粒内孔(孔径 20~1 000 nm)、石英/长石粒间孔(孔径 4~500 nm)以及黏土矿物晶间孔(孔径 4~500 nm)。洗油后氮气吸附-高压压汞结果显示,页岩中孔径在 2~30 nm 以及 60~1 000 nm 的孔隙明显增多,页岩油主要赋存于此孔径范围的孔隙之中。同时建立了页岩油赋存状态与岩石中各介质间的关系热图,阐明了大二亚段页岩油主要赋存于有机质和黄铁矿之中。最终采用页岩油各赋存状态含量与洗油前后获取的含油体积拟合的方法,指明了研究区不同状态页岩油聚集的孔径范围。大二亚段页岩油游离态主要聚集于孔径 60~700 nm 的有机质和黄铁矿孔隙之中,吸附态主要聚集于孔径 2~6 nm 的有机质孔隙之中。对页岩油赋存特征进行深入剖析,有助于川中地区大二亚段页岩油开采突破。

关键词:页岩油;赋存状态;赋存空间;赋存方式;大安寨段二亚段;侏罗系;四川盆地

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Occurrence characteristics of shale oil in the second submember of Da'anzhai Member of Jurassic Ziliujing Formation, central Sichuan Basin

ZHANG Chenyu¹, LIU Ziyi^{1,2}, WANG Bin¹, SHAN Shuaiqiang¹, LU Jianlin¹, WANG Baohua¹, ZUO Zongxin¹

1. Wuxi Research Institute of Petroleum Geology, SINOPEC, Wuxi, Jiangsu 214126, China;

2. SINOPEC Key Laboratory of Hydrocarbon Accumulation, Wuxi, Jiangsu 214126, China

Abstract: Although China has abundant lacustrine shale oil resources, their exploitation is challenging. Investigating the various occurrence states of shale oil in shale reservoirs provides value for the exploration and development of shale oil resources. With the shale in the second submember of Da'anzhai Member of Jurassic Ziliujing Formation of the central Sichuan Basin (the Da2 submember) as the research object, the study reveals the occurrence modes of shale oil under different states in various medium pores, through the implementation of the multi-temperature pyrolysis experiment, the observation of pore development characteristics under the scanning electron microscope and the analysis of the pore size distribution before and after oil washing. In the Da2 submember, the shale oil is mainly in the free state (0.42 to 10.88 mg/g), followed by the adsorption state (0.30 to 1.95 mg/g), as revealed by thermal simulation recovery. The reservoir space of shale includes organic pores (pore size: 2 to 600 nm),

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作者简介:张晨雨(1993—),女,博士,主要从事含油气盆地分析工作。E-mail:zhangchenyu.syky@sinopec.com.

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pyrite intergranular pores (pore size: 10 to 700 nm), shell pores (pore size: 20 to 1 000 nm), quartz/feldspar intergranular pores (pore size: 4 to 500 nm) and clay mineral intergranular pores (pore size: 4 to 500 nm). After oil washing, the results of nitrogen adsorption and high pressure mercury injection demonstrated a significant increase in pores with sizes of 2 to 30 nm and 60 to 1 000 nm, where most of shale oil is stored. Meanwhile, it was demonstrated that the shale oil in the Da2 submember mainly occurs in organic matter and pyrite by establishing a heat map of the relationship between the occurrence state of shale oil and the medium in the rock. Lastly, by fitting the content of shale oil in different occurrence states with the oil volume obtained before and after oil washing, the pore size range for shale oil accumulation in the study area was determined. The free state of shale oil in the Da2 submember primarily accumulates in pores of organic matter and pyrite with pore size of 60 to 700 nm, and the adsorbed state of shale oil mainly accumulates in the organic matter pores with pore size of 2 to 6 nm. In conclusion, this study presents a thorough examination of the occurrence characteristics of shale oil in Da2 submember, and it will support shale oil exploitation efforts in the area.

Key words: shale oil; occurrence state; occurrence space; occurrence mode; second submember of Da'anzhai Member; Jurassic; Sichuan Basin

四川盆地湖相页岩油资源丰富,其中侏罗系自流井组大安寨段的测试产能高,资源潜力大,是页岩油勘探开发的主要目标层段^[1-6]。目前川中大安寨段的 LA1 井页岩层段改造后估算日产油 1.76 t, RA1 井页岩排液估算日产油 1.96 t。川中大安寨段页岩油资源潜力还需进一步研究与挖掘。

页岩油常以游离态和吸附—互溶态存在于页岩之中^[7-14],其组成主要为游离油和吸附油。其中游离油常赋存于页岩的微裂缝和较大孔隙中,而吸附油主要吸附于小孔隙中和矿物、干酪根表面^[7]。前人已通过 NMR 实验、分子动力学以及数学拟合的手段,发现孔径小于 4 nm 的孔隙中主要赋存吸附油^[15-16],而游离油主要赋存于较大孔隙中。通常游离油的含量影响着页岩油井的产能,因此有必要揭示页岩层系中页岩油的赋存状态和赋存方式,以指导后期页岩油资源的勘探与开发。

前人通过荧光、扫描电镜观察、激光共聚焦和核磁共振的实验手段,发现不同页岩岩相中页岩油的赋存特征具有一定差异,主要体现在页岩油在各孔缝中的赋存差异以及与矿物间的不同接触关系^[17-20]。此外,利用分子动力学模拟,可以分析孔隙尺寸、有机质热成熟度、烷烃特征等因素对原油赋存状态的影响^[15,21-23]。除了以上定性分析页岩油赋存状态外,岩石热解和氯仿沥青“A”测量可以定量地获取不同状态页岩油量^[24-25]。然而,传统的岩石热解所获取的热解参数 S_1 可能并不能完全代表游离油量,可能含有少量吸附油;热解参数 S_2 也不完全是干酪根降解生烃潜量,其中可能包含少量的游离油和全部的吸附油^[7,24,26-27]。为了解决这些问题,前人也尝试用分级萃取和多温阶热解的

方法,来获取页岩油不同赋存状态的含量^[7-8,28-29]。分级萃取是通过对样品进行不同程度的研磨,并选择不同极性的溶剂,利用不同的萃取方法来研究岩石中页岩油的赋存状态及组分^[8,28]。多温阶热解是通过设置合理的加热实验方案,来对岩石中页岩油的不同赋存状态进行定量表征^[7,29]。相对于分级萃取的方法,多温阶热解方法的优点在于简便易行,且实验方法相对统一。川中地区大安寨段页岩中具有一定的滞留烃量^[1],据中国石油西南油气田分公司 2019 年统计数据可知,大安寨段页岩热解参数 S_1 主要在 1.0~2.0 mg/g 范围,氯仿沥青“A”测量的滞留烃量主要为 2.0~3.0 mg/g。然而研究区页岩中油的荧光显示不明显^[30],究其原因是对研究区页岩油的赋存状态和赋存方式尚未澄清,导致所用的技术手段未达预期效果。

为揭示川中地区侏罗系自流井组大安寨段二亚段(以下简称大二亚段)页岩油赋存特征,利用多温阶热解和热模拟恢复的方法,定量研究该区页岩油不同赋存状态。通过扫描电镜观察和氮气吸附—高压压汞实验,分析页岩中发育的孔隙特征,并获得样品孔隙中含油体积。根据数学拟合页岩油各赋存状态含量与含油体积的方法,确定研究区介质孔隙中的页岩油赋存方式。

1 区域概况

四川盆地侏罗系致密油的勘探开发主要集中在川中地区,已发现 5 个油气田、18 个含油区块,探明石油储量 $8\ 118.38 \times 10^4$ t、累计生产原油 526.72×10^4 t、凝析油 164.50×10^4 t(图 1a)^[31]。以往大安寨段油气勘探开发目标是致密介壳灰岩层,油气田

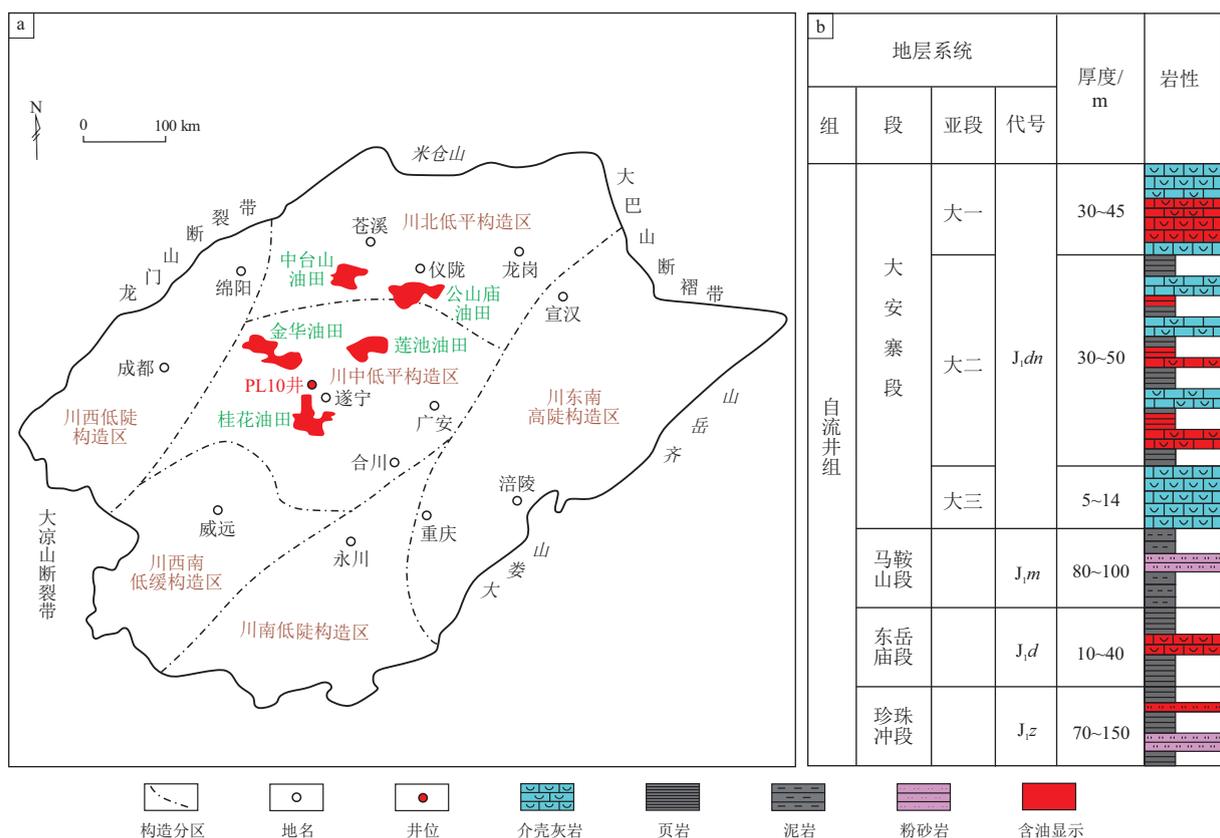


图1 四川盆地构造分区(a)及侏罗系自流井组地层柱状图(b)

Fig.1 Tectonic subdivision of Sichuan Basin (a) and stratigraphic column of Jurassic Ziliujing Formation (b)

中致密油井累计产油量约为 $(1.05 \sim 2.50) \times 10^4$ t、累计产气量约为 $(41.6 \sim 3187.2) \times 10^4$ m³。然而大安寨段中页岩层的储集物性明显好于介壳灰岩层的储集物性,应具有更好的油气勘探前景^[32]。川中地区LQ2井大安寨段页岩储层黑色页岩厚度可达56 m、钻探测试日产量2659 m³,明显好于介壳灰岩储层(厚度3~13 m、钻探测试日产量150 m³)^[32]。研究区大安寨段自上而下可划分为大一亚段、大二亚段和大三亚段(图1b)。其中大二亚段是大安寨段页岩油富集的主要层段,且该层段主要发育富含介壳的页岩,而大一和大三亚段主要发育灰岩。大二亚段页岩的 VR_o 介于0.74%~2.34%,且大部分 VR_o 大于1.00%,有机质主要处于成熟—高成熟阶段^[33]。

2 样品与实验

2.1 样品信息

本次研究所用样品主要来自川中地区PL10井大二亚段,获取的15个页岩样品进行了总有机碳(TOC)含量、XRD分析、多温阶热解实验,挑选其中3个富有机质(总有机碳含量高于2.0%)和3个贫有机质(总有机碳含量低于1.0%)的页岩样品,分析其孔缝类型和相关孔隙发育属性(包含孔隙

度、比表面积)(表1)。最终分析了样品中页岩油在不同介质、孔径下的赋存状态。本次研究未能第一时间获取钻井岩心并液氮封存,因此岩心中的轻质油成分可能有较大程度的散失。

2.2 TOC、XRD与 VR_o

岩心样品的总有机碳含量使用中国石油大学(北京)的LECO CS-230碳分析仪测定。为了去除无机碳,将岩心样品压碎并用80目筛过筛,然后与10%(体积分数)HCl溶液反应2 h以上,至反应完全为止。测量精度估计为测量值的0.45%。

利用有机质镜质体反射率($\%VR_o$,即随机反射率)来反映有机质成熟度的标志,对于含镜质体的页岩,按照中国石油天然气行业标准《沉积岩中镜质体反射率测定方法:SY/T 5124—2012》,测量样品中镜质体的平均随机反射率,以确定其有机质成熟度^[34]。

本次研究使用Bruker D8 Discover X射线衍射仪来测定全岩矿物含量。操作参数和数据处理符合中国石油天然气行业标准《沉积岩中黏土矿物和常见非黏土矿物X射线衍射分析方法:SY/T 5163—2010》。首先将岩心样品粉碎并离心分离至粒径小于10 μm,随后分析粉状样品的成分组成以确定

表 1 选取样品基本信息

Table 1 Basic information of selected samples

样品 编号	深度/ m	$\omega(\text{TOC})$ / %	VR_0 / %	主要矿物成分/%				S_{1-1} / (mg/g)	S_{1-2} / (mg/g)	S_{2-1} / (mg/g)	S_{BET} / (m^2/g)	孔隙度/ %
				长英质	碳酸盐	黏土矿物	黄铁矿					
PL10-1	1 983.1	1.60	1.00	49.9	15.1	29.8	5.2	0.01	0.93	0.98		
PL10-2	1 993.4	1.07	1.00	22.3	63.3	13.0	1.4	0.00	1.03	0.41		
PL10-3	1 997.4	2.25	1.03	49.5	22.6	24.1	3.8	0.06	1.62	1.95	4.21	2.69
PL10-4	2 006.0	2.60	0.96	54.5	4.4	35.9	5.1	0.09	1.76	1.26	11.56	3.95
PL10-5	2 011.8	1.82	1.00	60.3	5.3	32.1	2.3	0.04	1.64	1.87		
PL10-6	2 014.3	2.40	1.03	58.1	8.1	26.8	7.0	0.04	0.86	0.78	21.80	3.61
PL10-7	2 015.2	1.14	1.03	60.8	11.2	28.0	0.0	0.02	0.75	0.73		
PL10-8	2 019.1	1.41	1.04	40.1	39.9	16.6	3.5	0.01	0.67	0.88		
PL10-9	2 020.1	0.45	1.11	45.2	31.0	23.7	0.0	0.02	0.61	0.34	1.80	1.24
PL10-10	2 022.5	0.68	1.06	58.1	7.3	32.6	1.4	0.00	0.25	0.36	3.65	2.76
PL10-11	2 022.7	0.73	1.12	45.7	33.5	18.9	2.0	0.02	0.79	0.61		
PL10-12	2 025.8	0.84	1.16	54.8	34.5	9.4	1.4	0.00	0.21	0.30		
PL10-13	2 026.2	0.91	1.19	54.5	15.3	28.5	1.2	0.00	0.28	0.31	2.76	1.95
PL10-14	2 028.5	0.66	1.11	59.2	11.2	29.6	0.0	0.00	0.29	0.49		
PL10-15	2 029.8	0.60	1.17	55.1	16.2	26.4	2.3	0.00	0.14	0.31		

注:表中 S_{BET} 代表比表面积。

总黏土含量,最后更细的馏分样品被分析以确定其他矿物含量^[35-36]。实验分析误差一般小于 5%。

2.3 多温阶热解

本次研究是通过多温阶热解实验来获取样品中页岩油的赋存状态。采用中国石化石油勘探开发研究院无锡石油地质研究所改进后的 Rock-Eval 6 热解仪进行实验分析,在 200 °C 恒温 1 min 测得 S_{1-1} (轻质油组分),随后以 25 °C/min 速率升温至 350 °C,并恒温 1 min 测得 S_{1-2} (轻—中质油组分),再以 25 °C/min 速率升温至 450 °C,并恒温 1 min 测得 S_{2-1} (重烃、胶质沥青质组分),最后以同样的速率升温至 600 °C,测得 S_{2-2} (干酪根热解烃)^[7]。

2.4 扫描电镜

在进行扫描电镜观察之前,用氩离子抛光机将样品抛光至厚 0.1 mm,以创建适用于二次电子(SE)高分辨率图像的无伪影表面。采用中国石油大学(北京)SU8010 冷场发射扫描电镜来观察样品中发育的孔缝类型以及矿物形貌。

2.5 洗油处理

为了分析页岩油在不同介质、孔径下的赋存状态,本次研究进行了洗油前后样品氮气吸附、高压压汞实验结果的对比分析。洗油是为去除样品中的可溶有机质,将经过氮气吸附实验后的样品进行回收,用二氯甲烷与甲醇的混合溶剂(体积比 93:7)索氏抽提 72 h,至提取液无明显油斑为止,保留抽提后的样品,并放入烘箱(110 °C)脱水 3 h,最后再将烘干后的样品进行氮气吸附实验。其中氮气吸

附实验是将岩石碎样研磨至 80 目,使用 Quantachrome Quadrasorb SI 仪器进行实验,氮气吸附等温线测量在温度为 77 K 条件下进行,相对压力(P/P_0)范围控制在 0.010~0.995,并利用 BJH 模型分析样品中的孔径分布特征。利用 BET 模型分析样品孔隙的比表面积(S_{BET}),其吸附模型曲线是基于相对压力范围为 0.05~0.35 下的吸附体积。不同于氮气吸附实验后的样品,经过高压压汞实验后的样品因受汞污染,不能回收再利用,因此只能利用未经过高压压汞实验的同一样品,经过研磨、洗油后再进行高压压汞实验,以获取含油孔径分布。高压压汞实验利用 Pore Master 60 压汞仪器进行,汞首先在高达 20 psi 的压力下进入膨胀计,使汞充满岩石碎片之间的空隙。然后,将膨胀计转移到高压站,使得汞侵入样品中,最大压力可达 35 000 psi。利用 Washburn 方程将实验压力转换为孔喉直径,其中汞表面张力为 0.485 N/m,接触角为 140°。

2.6 孔隙度

岩心样品孔隙度测定符合中国石油天然气行业标准《岩心常规分析方法:SY/T 5336—1996》。使用 Ultrapore-200A 氮孔隙仪,通过氦气膨胀原理测量颗粒和气体体积,以计算孔隙率,其体积(包括微孔的体积)范围为 0.01%~40.00%。

3 大二亚段页岩油赋存状态

岩石中页岩油的赋存状态可以由多温阶热解实验数据来表征,实验获取的 S_{1-1} 为可动油量, S_{1-2}

和 S_{1-1} 共为游离油量, S_{2-1} 为吸附油量^[7,16,37]。

由于所获取的岩心中轻质油成分可能较大程度散失,样品中残留的可动油极少 (S_{1-1} 为 0.00~0.09 mg/g),多温阶热解实验的结果表现出吸附油量 (S_{2-1} 为 0.30~1.95 mg/g) 高于游离油量 ($S_{1-1} + S_{1-2}$ 为 0.14~1.85 mg/g) (图 2a)。为预测研究区样品中散失的轻质油部分,本次研究采用岩石生烃热模拟数据来恢复可动油量。根据前人数据(表 2)^[33,38],对研究区岩石滞留油产率进行拟合预测(图 3a),预测的滞留油产率与真实值较为吻合(图 3b),进而计算岩石中的可动油量。其中阙永泉等^[39]发现热模拟实验残渣测得的 VR_0 值会出现偏高的现象,并提出校正公式进行 VR_0 校正,校正适用范围为大于 1.46% 的 VR_0 。研究区利用生烃热模拟和多温

阶热解实验获取可动油量的公式如下:

$$Q_m = y_{ROGR} \times \omega(\text{TOC}) - Q_R + S_{1-1} \quad (1)$$

式中: Q_m 为可动油量,单位 mg/g; y_{ROGR} 为滞留油产率,单位 mg/g; Q_R 为多温阶热解总油量,单位 mg/g; S_{1-1} 为多温阶热解可动油量,单位 mg/g。倘若 $y_{ROGR} \times \omega(\text{TOC}) - Q_R$ 为负值,说明岩石中有外界油的流入,此时将 $y_{ROGR} \times \omega(\text{TOC}) - Q_R$ 取值为 0。

采用岩石生烃热模拟数据恢复可动油量后, S_{1-1} 可达 0.02~9.12 mg/g, $S_{1-1} + S_{1-2}$ 可达 0.42~10.88 mg/g(图 2b)。恢复后的游离油量是恢复前的 1~8 倍,可知未用液氮封存获取的岩心中轻质油较大程度散失。同时恢复后游离油量明显高于吸附油量,这与大二亚段页岩有机质主要处于成

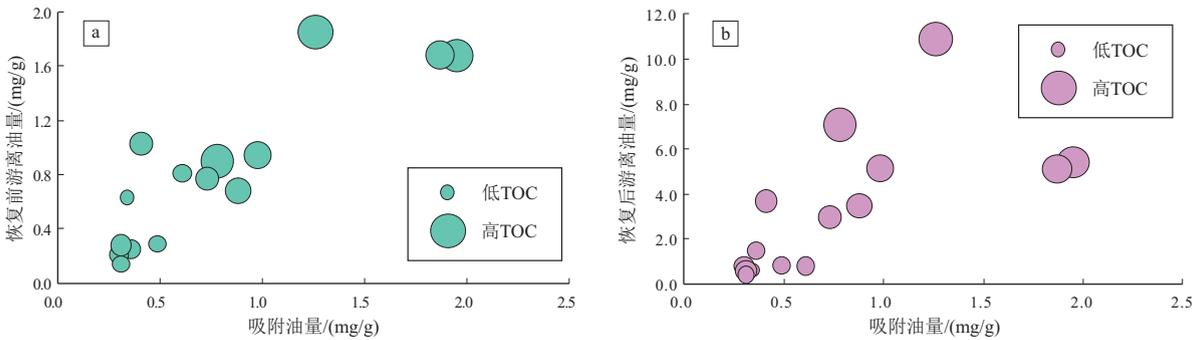


图 2 川中侏罗系自流井组大安寨段二亚段页岩油不同赋存状态的含量
Fig.2 Content of shale oil in different occurrence states in second submember of Da'anzhai Member of Jurassic Ziliujing Formation, central Sichuan Basin

表 2 川中侏罗系自流井组大安寨段页岩热模拟生排油参数^[33,38]

Table 2 Parameters of oil generation and expulsion during shale thermal simulation in Da'anzhai Member of Jurassic Ziliujing Formation, central Sichuan Basin

样品信息	热模拟实验结果							
	温度/ ℃	VR_0 / %	校正 VR_0 / %	总油产率/ (mg/g)	排出油产率/ (mg/g)	滞留油产率/ (mg/g)	排油效率/ %	预测滞留油产率/ (mg/g)
M030-H31, $\omega(\text{TOC}) = 1.83\%$, $VR_0 = 0.97\%$, 据文献[33]	250	1.15		84.47	11.15	73.32	13.20	
	300	1.49	1.12	157.80	25.59	132.21	16.22	180.12
	350	1.63	1.19	200.76	110.24	90.52	54.91	102.61
	365	1.74	1.24	178.00	125.20	52.80	70.34	57.17
	380	1.84	1.28	88.83	78.71	10.12	88.61	26.73
	400	1.86	1.29	78.37	69.94	8.43	89.24	21.83
Xi20, $\omega(\text{TOC}) = 2.25\%$, $VR_0 = 1.0\%$, 据文献[38]	450	1.97	1.33	31.77	29.41	2.36	92.57	1.56
	250			198.72	31.80	166.93	16.00	
	300			290.50	53.07	237.43	18.27	
	325			293.32	65.95	227.37	22.48	
	350			292.69	81.53	211.16	27.86	
	375	1.54	1.15	311.50	96.87	214.64	31.10	144.55
	400	1.79	1.26	166.16	110.03	56.12	66.22	39.16
	450	1.93	1.32	93.01	83.45	9.56	89.72	6.80
	500	2.28	1.46	51.48	48.25	3.23	93.73	0.26

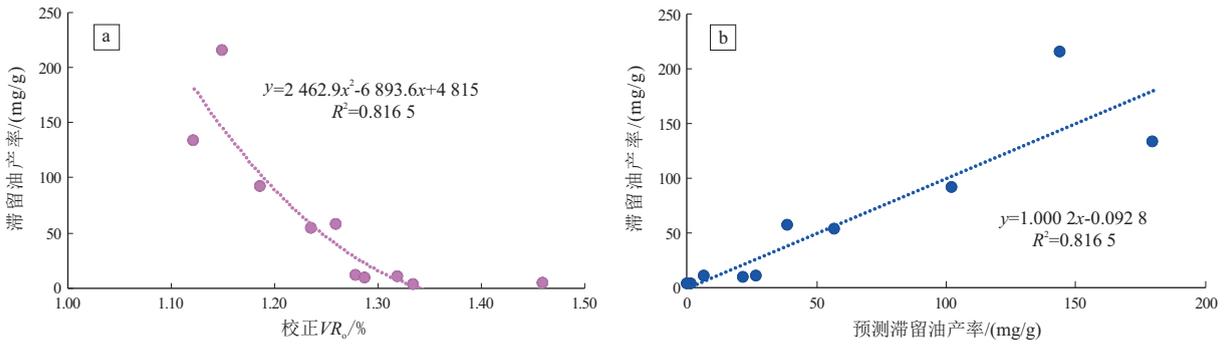


图 3 川中侏罗系自流井组大安寨段岩石中滞留油产率预测

Fig.3 Prediction of residual oil yield in Da'anzhai Member of Jurassic Ziliujing Formation, central Sichuan Basin

熟—高成熟阶段相符合。

4 大二亚段页岩油赋存空间

大二亚段页岩中主要发育有机质孔、黄铁矿粒间孔、介壳粒内孔、石英/长石粒间孔以及黏土矿物晶间孔(表 3)。利用 ImageJ 图像孔隙智能识别技术,对样品扫描电镜照片分析可知(表 3),有机质孔从介孔(孔径 2~50 nm)到宏孔(孔径大于 50 nm)级别均有分布,介孔孔径可达 10 nm 以下,宏孔孔径可达 500~600 nm,孔径分布具双峰特点,峰值主要分布在 10~20 nm 和 100~200 nm;石英/长石粒间孔和黏土矿物晶间孔孔径较小,孔径分布具单峰特点,孔径峰值在 10~20 nm 范围;相比前者,黄铁矿粒间孔和介壳粒内孔的孔径较大,孔径主要分布

在 30~400 nm,孔径峰值在 100~200 nm 范围。孔径分布较宽的有机质孔更有可能成为页岩油赋存的主力场所,而孔径较小的石英/长石粒间孔和黏土矿物晶间孔可能主要赋存吸附态页岩油,孔径较大的黄铁矿粒间孔和介壳粒内孔则可能主要赋存游离态页岩油。

对比洗油前后样品中孔径分布的变化可知,洗油后孔径在 30 nm 以下以及 60~1 000 nm 的孔隙明显增多(图 4),说明介孔中的滞留油大多聚集于 30 nm 孔径范围内的孔隙之中,宏孔中的滞留油大多聚集于 60~1 000 nm 孔径的孔隙之中。大二亚段页岩样品中黄铁矿粒间孔和介壳粒内孔的孔径峰值在 100~200 nm 范围,两者可能提供了页岩油赋存于宏孔中的储集空间。而石英/长石粒间孔和

表 3 川中侏罗系自流井组大安寨段二亚段页岩孔隙发育特征

Table 3 Characteristics of shale pores in second submember of Da'anzhai Member of Jurassic Ziliujing Formation, central Sichuan Basin

类型	孔隙识别图片				孔径分布
有机质孔					
黄铁矿粒间孔					
介壳粒内孔					
其他孔					

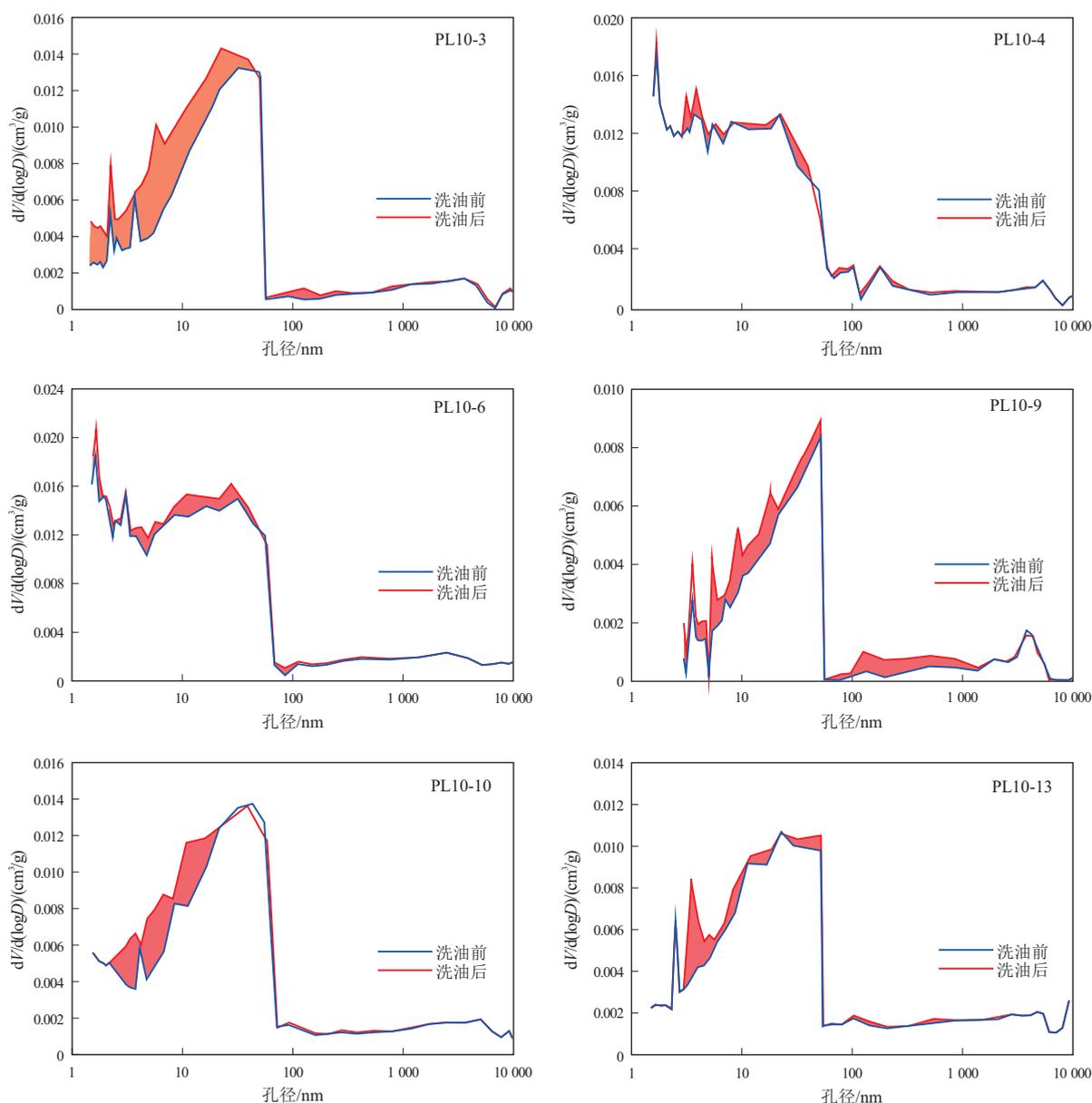


图4 洗油前后氮气吸附—高压压汞孔径分布

Fig.4 Pore size distribution with nitrogen adsorption and high pressure mercury injection before and after washing

黏土矿物晶间孔孔径较小,孔径峰值在10~20 nm范围,可以作为页岩油赋存于介孔中的储集空间。此外介孔到宏孔级别均有有机质孔分布,可以同时作为页岩油赋存于介孔和宏孔中的储集空间。

5 大二亚段页岩油赋存方式

5.1 不同介质中的赋存方式

受储集空间、介质润湿性、介质与烃类间作用力等的影响,页岩油在岩石中不同介质内的赋存方式不尽相同。通过建立大二亚段页岩油赋存状态与岩石中各介质间的关系热图(图5),可知石英、长石以及黏土矿物之间相关性好,表明它们都来自同一物源。页岩油各赋存状态与石英、长石以及黏

土矿物具有较弱的正相关关系,说明它们并不是岩石中页岩油的主要赋存场所。碳酸盐矿物与其他介质之间均表现出负相关关系,说明与其他介质不属于同一来源,具有此消彼长的特点,这点符合研究区页岩中的碳酸盐介壳来自风暴沉积的认识^[40]。此外,负相关关系也说明碳酸盐矿物中也并非页岩油的主要赋存场所。然而有机质与黄铁矿,以及它们与页岩油各赋存状态之间具有较强的正相关关系,一方面说明大二亚段中的黄铁矿多为同沉积黄铁矿,这与同沉积黄铁矿的成因有关^[41];另一方面说明有机质与黄铁矿主要提供了页岩油的赋存场所。尤其是有机质与页岩油含量具有强正相关关系(图5),在图3中也表现出随着总有机

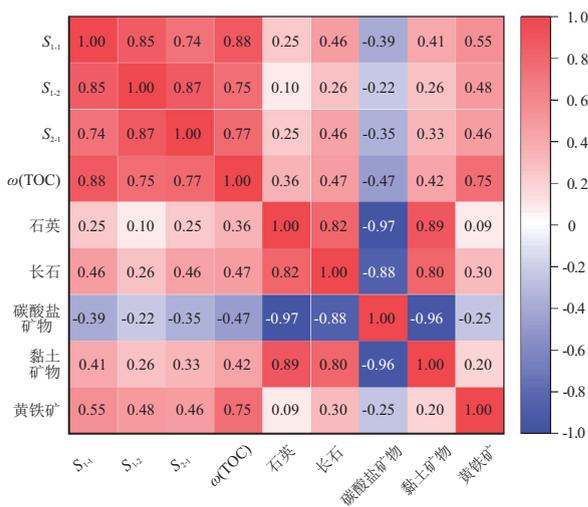


图 5 川中侏罗系自流井组大安寨段二亚段页岩油赋存状态与岩石中各介质间的关系热图

Fig.5 Heat map of relationship between shale oil occurrence states and various media within rock in second submember of Da'anzhai Member of Jurassic Ziliujing Formation, central Sichuan Basin

碳含量增加,吸附油和游离油量增加的特点。此外,随着研究区岩石孔隙度的增加,岩石中的吸附油和游离油含量也随之增加(图 6a),然而吸附油和游离油含量与岩石比表面之间的关系并不明显(图 6b),因此岩石中的孔隙主要提供了页岩油的赋存空间。综合不同介质对页岩油赋存的影响,页岩油主要赋存于有机质的介孔—宏孔和黄铁矿的宏孔之中。

5.2 不同孔径下的赋存方式

为了分析不同孔径下页岩油的赋存方式,本次研究采用页岩油各赋存状态含量与含烃体积拟合的方法,来探索游离油和吸附油在孔隙不同孔径下的赋存情况。利用氮气吸附和高压压汞实验洗油后减去洗油前的累积 $dV/d(\log D)$ 数据来表示样品中不同孔径的累积含油体积(图 2)。然后将累积含油体积数据与游离油或吸附油量进行线性回归

拟合(图 7a-b),以确定不同孔径下页岩油赋存状态。在线性回归拟合的过程中,吸附油对应的累积 $dV/d(\log D)$ 值是从小孔隙向大孔隙累积计算(图 7c),而游离油对应的累积 $dV/d(\log D)$ 值则是从大孔隙向小孔隙累积计算(图 7d)。由线性回归拟合结果可知,与吸附油拟合效果好($R^2 > 0.5$)的累积含油体积所对应的孔隙孔径可达 6 nm(图 7c)。由于吸附油累积含油体积是从小孔隙向大孔隙累积计算,因此大二亚段页岩中孔径为 2~6 nm 的孔隙中主要赋存吸附油,这与 WANG 等^[42]通过分子动力学模拟得到的吸附态页岩油主要赋存于 4 nm 左右孔隙中的结论基本一致。与游离油拟合效果好的累积含油体积所对应的孔隙孔径为 60~100 nm(图 7d),由于游离油累积含油体积是从大孔隙向小孔隙累积计算,大二亚段页岩中孔径大于 60 nm 的孔隙中主要赋存游离油。

结合对页岩油赋存空间和介质中的赋存方式的研究,大二亚段页岩中游离态页岩油主要赋存于有机质和黄铁矿孔径为 60~700 nm 的孔隙之中,吸附态页岩油主要赋存于有机质孔径为 2~6 nm 的孔隙之中。

6 结论

(1)川中地区侏罗系自流井组大安寨段二亚段页岩中主要发育有机质孔、黄铁矿粒间孔、介壳粒内孔、石英/长石粒间孔以及黏土矿物晶间孔。黄铁矿粒间孔和介壳粒内孔的孔径主要大于 30 nm,而石英/长石粒间孔和黏土矿物晶间孔孔径较小,峰值在 10~20 nm 范围。此外,介孔到宏孔级别均有有机质孔的分布。

(2)未用液氮封存获取的岩心中 S_{1-1} 存在较大的散失,热模拟恢复散失量可达残留量的 8 倍。大二亚段的页岩有机质主要处于成熟—高成熟阶段,

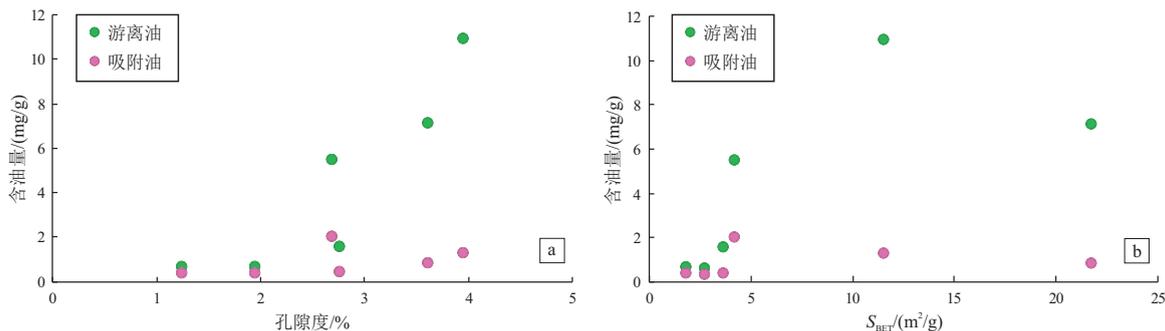


图 6 川中侏罗系自流井组大安寨段二亚段页岩油赋存状态与岩石孔隙度、比表面积关系

Fig.6 Relationship between shale oil occurrence states, porosity, and specific surface area (S_{BET}) in second submember of Da'anzhai Member of Jurassic Ziliujing Formation, central Sichuan Basin

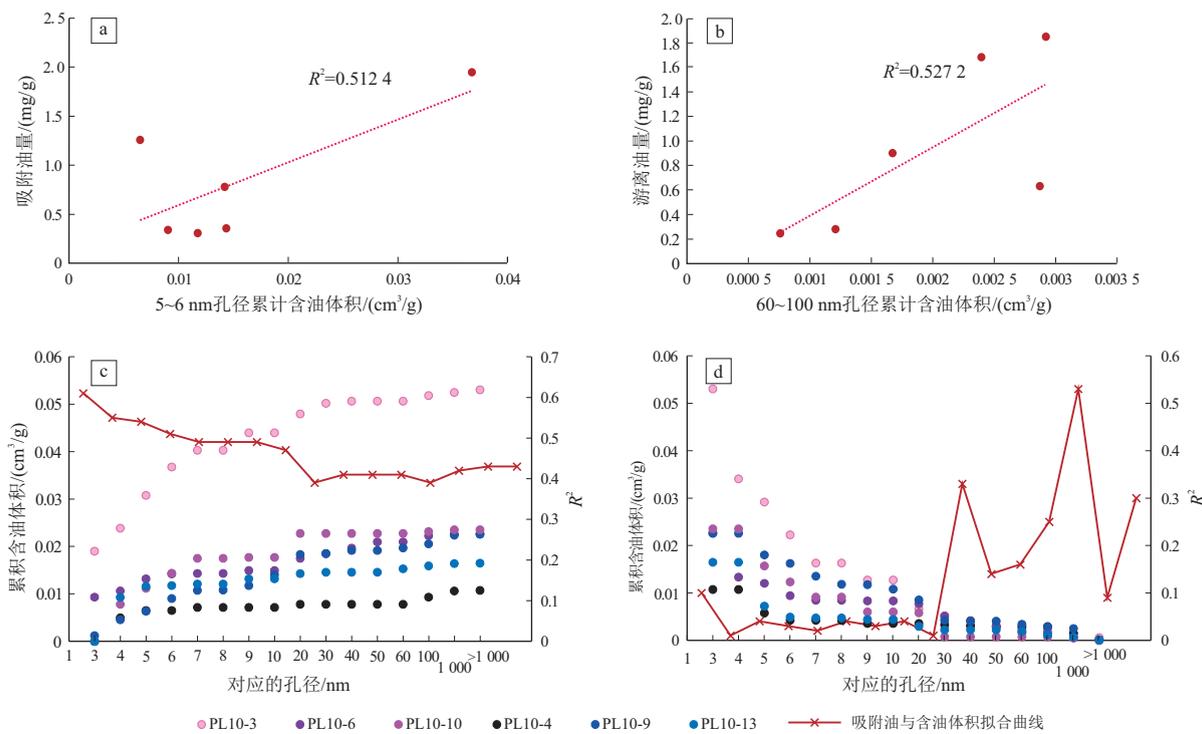


图7 川中侏罗系自流井组大安寨段二亚段不同孔径下的页岩油赋存状态

Fig.7 Shale oil occurrence in different pore sizes in second submember of Da'anzhai Member of Jurassic Ziliujing Formation, central Sichuan Basin

恢复后游离油量明显高于吸附油量。

(3)研究区大二亚段页岩油游离态主要聚集于孔径为60~700 nm的有机质和黄铁矿孔隙之中,吸附态主要聚集于孔径为2~6 nm的有机质孔隙之中。

利益冲突声明/Conflict of Interests

作者张晨雨、刘子驿、王斌、单帅强、陆建林、王保华、左宗鑫是本刊主办单位员工;单帅强是本刊青年编委会成员,均未参与本文的同行评审或决策。

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作者贡献/Authors' Contributions

张晨雨、刘子驿参与实验设计,并完成实验操作;张晨雨、刘子驿、王斌、单帅强、陆建林、王保华和左宗鑫均参与论文写作和修改。所有作者均阅读并同意最终稿件的提交。

The study was designed and the experimental operation was completed by ZHANG Chenyu and LIU Ziyi. The manuscript was drafted and revised by ZHANG Chenyu, LIU Ziyi, WANG Bin, SHAN Shuaiqiang, LU Jianlin, WANG Baohua, and ZUO Zongxin. All authors have read the last version of the paper and consented to its submission.

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