博士学位论文

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Two case studies of oil-source correlation: Neo-Mesoproterozoic oil seeps and Paleogene oil pools in the north margin of the Bohai Gulf Basin

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摘　要

油源对比是基于有机质在不同沉积环境、埋藏条件下、不同物源条件下烃源岩有机质或有机质在不同的热演化阶段生成的油气地球化学特征存在一定差异，即具有各自的特殊性，而来源于相同或相似的源岩相的原油之间或原油与源岩之间的一些地球化学特性存在着相似性，通过这些差异性与相似性的比较就可以判断油-油、油-岩的关系以及提供原油运移的可能路径，从而指导勘探。目前生物标志化合物是油源对比的重要方法。然而对于前寒武系有机质，面临着有机质处于高热演化阶段、很少的地化信息和混染等问题。而对处于高成熟复杂构造勘探区来说，如何客观采用庞大地化数据库分析原油成因类型（油-油对比），如何更为精确的评价烃源岩并进行精细油源对比成为迫切解决的问题。在本文中，选用燕山地区中新元古界沉积物和辽河西部凹陷成熟探区两个典型实例具体研究解决油源对比的难题。

第一个实例主要以燕山地区中新元古界海相地层为研究对象，该区油苗和油气显示主要出现在下马岭组、铁岭组和雾迷山组储层中，经前人分析它们很可能来源于洪水庄组和/或高于庄组烃源岩。其中洪水庄组烃源岩有机碳（TOC）达到 5.5%，计算 *R*o 约为 1.7%，另一套潜在烃源岩高于庄组的 TOC 较低，约 2.7%，而成熟度较高，计算的 *R*o 达到 2.2%。本次对烃源岩的研究除了对岩心露头样品的有机质抽提物进行研究外，还选取 3 个露头样品进行干酪根催化加氢实验（HyPy），以从高成熟热演化样品中提取更多的地化信息。而对于原油的研究，考虑到油苗遭受降解或混染而导致抽提物结果失真，因此还选取富含含油包裹体的下马岭组沥青砂岩和铁岭组灰岩样品进行包裹体成分分析（MCI），此外还在储集岩中选择 20 个样品进行程序抽提，用以辅助 MCI 进行原油地化特征及演化的研究。

基于实验数据，藿烷、三环萜烷和二环倍半萜在包裹体和大多数储集岩抽提物（EOM2~EOM3）中都很富集，特别是较低的 Pr/Ph、伽马蜡烷指数和高含量的 C_{24} 四环萜烷和 C_{14} 二环倍半萜烷，认为该原油来源于深水还原环境下厌氧细菌生源的有机质，然而甾烷在这些原油中却低于可检测范围，这与厌氧条件下沉积的洪水庄组烃源岩相一致。此外这些原油的甲基烷烃同系物的分布形式也与洪水庄组烃源岩相似，而与高于庄组截然不同。基于生物标志化合物和芳烃组分所计算的成熟度参数反映了包裹体原油和大多数储层抽提物（EOM2~EOM3）为源岩在生油窗范围内的产物，从而揭示洪水庄组为该区的主力烃源岩，另外特殊化合物 13α 三环萜烷仅在这些储集岩抽提物和洪水庄组烃源岩有所检测有效支持了上述推断。其它储集岩抽提物（EOM-1）却表现为不同的地

化特征，如较高含量的 2α 甲基藿烷，少量的 3β 甲基藿烷和完整的甾烷系列反映为蓝藻等，结合较高 Pr/Ph、伽马蜡烷指数，以及成熟度参数反映该原油来源于浅水还原环境下高成熟度的高于庄组烃源岩。在油源研究的基础上重建油气成藏史，指出本区主要发生两次大规模油气充注，一是高于庄组烃源岩在 ca.1327Ma 前的一次充注，二是洪水庄组烃源岩在燕山期时达到生油高峰，在当时强烈的构造运动作用下发生第二次大规模油气充注并对第一次充注古油藏的调整改造，形成现今油气分布形式。

第二个实例是针对高成熟探区的精细油源对比问题，本论文选择了辽河西部凹陷这一典型复杂构造区带，对其烃源岩在层序地层格架下进行有机质丰度、类型和抽提物地球化学特征的研究，主要从显微组分特征及组成、碳同位素组成、饱和烃色谱面貌、生物标志物分布以及芳烃分子标记物分布特征等方面，揭示了西部凹陷沙河街组下部层序烃源岩主要形成于咸化-强还原沉积环境下以菌藻类生源输入为主；上部层序烃源岩则是在淡水弱还原环境下沉积，具有以藻类为主、兼有高等植物输入的特征。而对该区的原油，主要对 1000 余个原油样品地化数据进行统计分析（Pirouette 软件），基于反映原油母岩沉积环境、生源输入、成熟度和原油次生蚀变的参数，把西部凹陷原油的成因类型划分为成 3 大类 9 个亚类，并进行精细油源对比，其结果为：对第Ⅰ类高盐还原环境下生成的菌藻类生源的原油来说，主要分布于凹陷的北部，其中第$Ⅰ_A$型原油主要来源于牛心坨洼陷的 SQ_1 未熟烃源岩；第$Ⅰ_B$型原油来源于台安洼陷 SQ_2 的成熟烃源岩；第$Ⅰ_C$型原油为$Ⅰ_A$和$Ⅰ_B$型原油的混合。对第Ⅱ类咸化还原环境下双重生源的原油来说，主要分布于凹陷的中南段，其中第$Ⅱ_A$型原油来源于盘山-陈家洼陷 SQ_3 的低熟烃源岩；第$Ⅱ_B$型原油主要来源于盘山-陈家洼陷 SQ_4 成熟烃源岩；第$Ⅱ_C$型原油为$Ⅱ_A$和$Ⅱ_B$型原油的混合。而对第Ⅲ类淡水弱还原环境下以藻类生源为主的原油来说，主要分布于凹陷西斜坡的南段，其中第$Ⅲ_A$型原油主要来源于清水洼陷 SQ_6 的低熟烃源岩；第$Ⅲ_B$型原油来源于清水洼陷的 SQ_4 烃源岩；第$Ⅲ_C$型原油为$Ⅲ_A$和$Ⅲ_B$型原油的混合。从而确定了西部凹陷主要含油气区带油气与沙河街组具体的三级层序烃源岩的成因关系，这将为高成熟探区的油气资源评价提供了重要的依据。

关键词：燕山地区；中新元古界；含油包裹体成分分析；辽河西部凹陷；下第三系；油源对比

Two cases study of oil-source correlation: Neo-Mesoproterozoic oil seeps and Paleogene oil pools in the north margin of the Bohai Gulf Basin

ABSTRACT

Oil-source correlations are based on the concept that certain compositional parameters of migrated oil do not differ significantly from those of bitumen remaining in the source rocks. This similarity though heritage can range from bulk properties, such as stable carbon isotope compositions, to individual compound ratios. Detailed oil-source rock correlations provide important information on the origin and possible paths of migration of oils that lead to additional exploration plays, and are helpful for reconstructing petroleum reservoir accumulation histories and fuel resource assessments. Biomarkers play a critical role in geochemical correlations. However, for Precambrian organic matter, there are significant difficulties doing oil-source rock correlations because of the likely high thermal maturity of the sedimentary organic matter, the sometimes low organic matter abundance, the small amount of geochemical information, and problems of contamination and over-printing. For highly mature exploration areas, attempts to objectively analyse the geochemical characteristics of crude oils based on a large geochemical data set, and how to evaluate source rocks more accurately, so as to improve the understanding of reservoir relationships and predicting petroleum resource are becoming more urgent problems at the moment. In this thesis, two representative fields were selected, the Neo-Mesoproterozoic sequence of the Yanshan Region and the highly mature exploration area of the Western Depression of the Liaohe Basin, in order to specifically answer correlation and other geochemical problems.

The first of these case studies involves the marine sediments of the Yanshan Region which are some of the least deformed and least thermally mature hydrocarbon-bearing Neo-Mesoproterozoic sequences in China. The oil shows and seeps are mainly distributed in the reservoir sequences of the Xiamaling Formation (ca. 1368 Ma), Tieling Formation and Wumishan Formaiton, which are probably derived either from the underlying organic-rich Hongshuizhuang Formaiton, or from kerogen within the Gaoyuzhuang Formation, as there are no known source rocks in the section. The 27 m thick mudstone of the Hongshuizhuang Formation has total organic carbon (TOC) levels of up to 5.5% and eq$R_{o_{marine}}$ of about 1.7%. The other potential source rock (dolomite from the Gaoyuzhuang Formation) has TOC levels

around 2.7% with 2.2% eqRo_{marine}. Three outcrop source rocks were sampled from these two sequences and kerogen catalytic hydrogenation was performed in order to get more geochemical information on these high thermal maturity samples. Another two source rocks from drilling cores using standard solvent extraction have been analysed by gas chromatography-mass spectrometry (GC-MS). As for the either contaminated or biodegraded oil seeps, two samples rich in oil-bearing fluid inclusions (FI), (1) a limestone sample from the Tieling Formation, and (2) a bitumen sandstone from the Xiamaling Formation, were chosen for detailed analyses by the Molecular Composition of Inclusions (MCI) protocols. In addition, twenty samples from the reservoirs have been sequentially extracted as a supplement to the MCI analysis.

Hopanes, tricyclic terpanes and bicyclic sesquiterpanes are abundant in the FI oils and most samples from reservoir sequences, and their ratios，such as lower Pr/Ph ratio, higher Gammacerane Index and higher C_{24} tetracyclic terpane and C_{14} biocyclic terpane suggest dominantly microbial input under a reductive deep water environment. However, steranes were below detection limit in the FI oils, and also in the source rocks of the Hongshuizhuang Formation which was deposited under anoxic conditions. The distribution of monomethylalkanes in the reservoir sequence FI oils and most reservoir extracts correlate well with the organic-rich marine Hongshuizhuang Formation and is different from the Gaoyuzhuang Formation. Maturity parameters based on biomarkers, alkanes and aromatic hydrocarbons indicate that the FI oils and most reservoir sequential extracts have reached the peak stage of the oil generation window, indicating that the Hongshuizhuang Formation is the main source rock of this area. Furthermore, the particular 13α(H)-tricyclic terpanes only detected in the FI oils, most reservoir extracts and the Hongshuizhuang Formation also supports this deduction. However, some reservoir sequential extracts contain different geochemical signatures, including higher 2α(H)-methylhopanes, less abundant 3β-methylhopanes and rich steranes, which indicate cyanobacterial and algal input. Associated with other parameters, such as lower Gammacerane Index, lower ratio of Pr/Pr, higher *R*c(%) (based on MPI_1) and C_{30} αβ/(αβ+βα) ratios, these data suggest that these extracts are derived from the Gaoyuzhuang Formation, which was deposited in a shallow water oxic environment and which had experienced high thermal evolution. Following these oil-source correlations, and combined with geological background, the history of this

palaeo-oil reservoir accumulation has been reconstructed. In particular, the region received early petroleum charge that was possibly from the Gaoyuzhuang Formation source rock before dolerite intrusion (ca. 1327Ma). A late oil charge was happened during Yanshan movement when the Hongshuizhuang Formation source rock generated mature oil and expelled. This has more significant oil contribution in terms of large oil generation potential and tectonic dynamic.

The second case study was on Paleogene age sediments of the Western Depression of the Liaohe Basin, which are currently in mature production. The objective of this case is systematically and objectively to interpret large volumes of multivariate geochemical data and correlate crude oils and source rocks. A suite of samples consisting of seventy-five crude oils and fifty-six reservoir sandstones, thus have been analysed for biological marker compounds by GC-MS, and twenty-nine of these samples were also selected for stable carbon isotopic analysis. Combined with the former geochemical database (~220 samples), crude oils were correlated into three genetic families (Ⅰ, Ⅱ, Ⅲ), mainly based on the Gammacerane Index, Pr/Ph, C_{24} tetracyclic terpane/tricyclics terpanes and ααα20*R* C_{28}/C_{29} sterane ratios. These samples were then subdivided them into three groups (A, B, C) based on thermal maturity (αααC_{29} 20*S/(*20*S*+20*R*) steranes) and level of biodegradation (25-norhopanes).

The source rocks (one hundred sixty-eight samples) were analysed using a series of geochemical and petrological experiments. The geochemical signatures were then evaluated in the sequence stratigraphic framework and compared with the oil types respectively. Generally, Family Ⅰ oils were sourced from rocks containing algal and bacterial input under reducing and probably hypersaline environments, and are mainly distributed in the north of the depression (SQ_1, SQ_2). The Family Ⅱ oils were sourced from rocks containing algal and higher plant input under reducing and brackish conditions, and are distributed in the mid-south of the depression (SQ_3, SQ_4). The Family Ⅲ oils were sourced from rocks containing mainly alga input deposited under reducing, freshwater environments, and are distributed on the southwest of the depression (SQ_4, SQ_6). This information on the correlation of oil groups and source rocks will be crucial in understanding the Western Depression petroleum system and for guiding petroleum resource assessment and future oil exploration.

Key Words： Yanshan Region; Neo-Mesoproterozoic; Molecular Composition of Inclusion; Paleogene; Western Depression of the Liaohe Basin; oil-source correlation

创 新 点

1．深度挖掘可靠的前寒武系地化信息

在高、过成熟沉积有机质地球化学信息挖掘方面，重点开发加氢催化提取可溶有机质的技术，深度挖掘高过成熟沉积有机质的地球化学信息，充分认识中新元古界有机质热演化特征，并探讨各种理化分析参数对有机质热演化的表征能力；另外鉴于包裹体在地质时期具有很强的抗高温、高压的能力，因此在获取可靠油气地化信息方面，主要提取有机包裹体成分进行分析，辅以程序抽提的方法研究原油的演化特征，从而进行有效油源对比。

2．深刻剖析燕山地区中新元古界生物标志化合物

通过系统分析地化特征和对特殊生物标志化合物的定量分析，明确提出中新元古界洪水庄组和高于庄组两套潜在烃源岩地化特征的不同：1) 13α 三环萜烷系列化合物仅在洪水庄组烃源岩中检测到，另外洪水庄组还检测到高含量的新藿烷和重排藿烷，认为是由藿烷衍生而来，这与该烃源岩三环萜烷/藿烷比值很高相一致，结合高伽马蜡烷、高 C_{24} 四环萜烷、高 C_{14} 二环倍半萜烷和低 Pr/Ph 比值共同反映洪水庄组为高盐深水强还原环境下以厌氧细菌为主要生源贡献的烃源岩；2) 甾烷仅出现在高于庄组烃源岩，且以完整系列分布，还在该套烃源岩中检测到少量的 2α 甲基藿烷和 3β 甲基藿烷，结合低伽马蜡烷、C_{14} 向 C_{15} 二环倍半萜的转换和较低 Pr/Ph 比值共同反映高于庄组为浅水还原环境下以蓝藻或无氧光合作用变形杆菌等为主要生源的烃源岩。另外在成熟度方面还提取出两个适于评价高、过成熟沉积有机质的地化参数：C_{30} αβ/(αβ+βα) 藿烷和基于 MPI_1 计算的 *R*c。从而为今后前寒武系地层的研究提供重要的借鉴意义。

3．地质与地化相结合进行精细油源对比

对高勘探程度地区庞大地化数据库，本着样品验证和补充以及紧随勘探进展的原则，进行采样实验分析。对该区原油的研究，主要基于 Pirouette 统计分类软件对原油成因类型进行客观有效的划分；对烃源岩主要是在三级层序格架下进行烃源岩的有机质丰度、类型和抽提物地球化学特征的研究。在此基础上，首次将各类原油对比到三级层序下的烃源岩，达到了对高成熟勘探区的精细油源对比的目的。

目　录