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厦门大学

博 士 学 位 论 文

南海北部天然气水合物潜在区源岩沉积有机地球化学研究

Sedimentary organic geochemistry research of source rocks of the potential gas hydrate-bearing areas in the northern South China Sea

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专业术语汇总表

简写	含义	
BSR	似海底反射层	bottom simulating reflector
GHSZ	天然气水合物稳定带	gas hydrate stable zone
AOM	甲烷厌氧氧化作用	anaerobic oxidation of methane
MOG	产甲烷作用	methnogenesis
LPTM	晚古新世温度峰值事件	the Latest Paleocene Thermal Maximum
THC	温盐环流	the thermohaline circulation
SMT	甲烷硫酸盐转换界面	sulfate methane transition
CPI	碳优势指数	carbon predominance index
OEP	奇偶优势指数	odd-even predominance
TAR	陆生/水生植物比值	terrestrial aquatic ratio
$\sum nC_{21}^{-}/\sum nC_{22}^{+}$	短链/长链正构烷烃比值	
n-C_{27}/n-C_{31}	木本/草本植物比值	
Pr/Ph	姥鲛烷/植烷比值	
T_{max}	最高热解温度	
S_1+S_2	生烃潜力指数	
S_2/S_3	类型指数	相当于 I_H/I_O
I_H	氢指数	$I_H = wS_2/w\mathrm{TOC}$
I_O	氧指数	$I_O = wS_3/w\mathrm{TOC}$

摘 要

天然气水合物是二十一世纪新能源，我国南海北部陆坡是天然气水合物发育的理想场所，深入研究南海北部陆坡天然气水合物成藏机制和富集规律，为我国海洋天然气水合物资源勘探和开发提供重要的理论依据和指导，具有重要的经济和科学意义。其中气源条件既是天然气水合物形成发育的物质基础，又是天然气水合物成藏的关键。本论文依托国家“973”计划子课题《南海北部天然气水合物成藏的气源条件研究》（项目编号：2009CB21951）、国家自然科学基金项目《南海北部海底沉积层硫酸盐-甲烷体系产消机制及其界面（SMI）特征研究》（项目编号：40976035）和《天然气水合物成藏体系中产甲烷与甲烷厌氧氧化作用生物标志物和分子生物学研究》（项目编号：41276046）等项目，以南海北部珠江口盆地、台西南盆地、琼东南盆地为研究对象，选取天然气水合物潜在区神狐海域 ZS-5，东沙海域 ZD-2、ZD-3，台西南海域 973-4、973-5、ZT-10 浅表层沉积岩芯和六个表层样，以及珠江口盆地和琼东南盆地的深部烃源岩样品，进行沉积和有机地球化学特征研究。结合沉积环境特征及前人在南海北部获得的地质、地球物理和地球化学相关资料，阐明构造对南海北部沉积物发育过程的影响，查明各海域沉积有机质组成、分布特征和物质来源，分析研究区深部烃源岩热解气与浅层微生物成因气源条件，以及不同气源成因条件下沉积物的生物标志物特征，探讨生物标志物对天然气水合物的指示意义。主要得到以下几点认识：

（1）南海北部琼东南盆地、珠江口盆地、台西南盆地先后经历了裂谷期、后裂谷热沉降期和新构造活动期三大阶段，发育有始新统湖相烃源岩、渐新统湖相、湖沼相及海陆过渡相烃源岩和中新统海相烃源岩三套烃源岩。新构造运动使得南海北部陆坡断褶带、滑塌构造、底辟构造等特殊局部构造环境和地质体发育，为深部烃类气体向浅部运移开辟了有利通道。

（2）珠江口盆地珠二坳陷和珠三坳陷的文昌 A 凹陷为主要的产气凹陷，珠二坳陷的气源岩层为文昌组和恩平组 $\mathrm{I}\sim\mathrm{II}_1$ 型过成熟烃源岩和珠海组 III 型低—中等成熟烃源岩；文昌 A 凹陷的气源岩层为文昌组的高成熟—过成熟烃源岩。台西南盆地烃源岩均以产气为主，白垩系—下第三系埋藏深度在 5000m 之下，有过成熟烃趋势，主要烃源岩层为渐新统—下中新统 III 型成熟—高熟海相泥页岩和中生界侏罗系/下白垩统 III 型成熟—高成熟近海陆相泥岩。琼东南盆地中央坳

陷带和北部坳陷带的崖北凹陷为主要的产气凹陷，其渐新统和中新统的腐殖型气源岩已进入高成熟及过成熟阶段，具有较好的生气潜力。此外，珠江口盆地、琼东南盆地和台西南盆地上中新统—上新统、第四系的海相沉积厚度达数千米，大多处于未成熟阶段，是较好的生物成因气源岩。

（3）南海北部东沙海域 ZD-2、ZD-3，神狐海域 ZS-5，台西南海域 973-4、973-5、ZT-10 站位的平均沉积速率介于 0.13~0.73m/ka，满足天然气水合物形成的沉积速率条件（大于 3cm/ka），且东沙海域和台西南海域的沉积速率明显高于神狐海域。浅表层沉积物岩性主要为粉砂和黏土质粉砂，台西南海域的沉积物粒径相对较小。

（4）南海北部陆坡柱状沉积物有机碳含量为 0.39~1.26%，一般均大于 0.5%，与 Blake Ridge 地区沉积物相当，可为 CO_2 还原产生甲烷提供较充足的有机质；ZD-3 和 973-4 的有机碳含量比 ZS-5 相对较高，这与沉积速率和粒度大小的差异一致。有机碳同位素组成 δ^{13}C（PDB）为-26.94~-21.10‰，呈阶段式变化，氧同位素 II 和 IV 期相对于氧同位素 I 和 III 期 δ^{13}C 偏重，是冷期陆源高等植物输入的比例有所降低所致。

（5）神狐海域 ZS-5 和东沙海域 ZD-2、ZD-3 柱状样沉积物中有机质为 II_2~III 型，腐殖型（偏气型）。三个柱状样都具有较高的氧碳原子比，说明其具有丰富的陆源高等植物有机质来源，其富里酸和胡敏酸向干酪根的转化过程能为产甲烷菌提供大量 CO_2 作为生物成因甲烷碳源。

（6）南海北部浅表层沉积物中正构烷烃一般呈双峰—后峰高型分布，以 n-C_{16}~n-C_{20} 和 n-C_{27}~n-C_{31} 为中心，主峰碳分别为 C_{18}（或 C_{19}）和 C_{29}（或 C_{31}）。短链烷烃在较慢的沉降过程中有明显损失，它们呈弱偶碳优势被认为主要源于海底微生物直接输入。指示陆源有机质来源的奇碳优势的长链烷烃在岩芯中的分布特征与气候变化一致。表层样中 S-83 接收了来自珠江口的大量陆源有机质，而其它站位的陆源有机质主要通过大气输送从而表现出受与陆地距离控制。沉积物中未成熟的藿烷生物标志物大量检出表明强烈的微生物活动以及细菌来源的有机质输入，其成熟度随埋藏深度有所升高。

（7）南海北部浅表层沉积物中检出一系列脂肪酸甲酯化合物，其与研究区沉积物中脂肪酸的分布特征一致。本研究提出脂肪酸甲酯源于脂肪酸的甲酯化过

程的假设，由甲烷氧化菌和产甲烷古菌等产生的甲醇为该过程提供甲氧基。研究区在氧同位素 II 期发生的天然气水合物分解过程甲烷释放可能通过增强甲烷厌氧氧化等细菌作用而加速脂肪酸甲酯化过程，从而使脂肪酸甲酯含量在氧同位素 II 期对应的层位 ZD3-2（400~420 cm）和 ZS5-2（241~291 cm）达到最大值。

（8）珠三坳陷文昌组以 II_1 型干酪根为主，TOC 一般在 1% ~ 5%，主要为藻类及细菌来源，C_{29}20S/（20S+20R）与 C_{29}ββ/（ββ+αα）关系图表明为成熟或成熟—高成熟烃源岩，已部分进入裂解产气阶段；恩平组母质类型为 II-III 型，TOC 平均 1.12%，主要为高等生物来源，以生气为主，生烃能力相对低于文昌组；珠海组为 II-III 型干酪根，TOC 含量均小于 1%，具有一定的生烃能力。恩平组指示陆源高等植物来源的 C_{29} 规则甾烷含量相对于珠海组要高，这与由陆向海转变的沉积层序相一致。

（9）末次冰期南海北部发生了天然气水合物失稳分解和甲烷释放，主要证据如下：①氧同位素 II 期底栖有孔虫碳同位素组成 $\delta^{13}C$ 负偏（约-2‰）；②脂肪酸甲酯相对含量在 $\delta^{13}C$ 负偏的层位较高，这受甲烷释放通过加速生成作为酯化所需甲氧基的甲醇的影响；③规则八面体结构的草莓状黄铁矿集合体，以及管状和有孔虫外壳黄铁矿的出现；④东沙海域 08CF7 钻孔记录的沉积物磁化率异常；⑤贫 ^{13}C 同位素的冷泉碳酸盐岩的发现。此外，底栖有孔虫 $\delta^{13}C$ 最小值对应于 Bølling/Allerød 暖期，这可能表明在间冰阶温度升高和因海平面下降引起的压力降低都对南海北部水合物分解产生影响。

关键词：南海北部陆坡；天然气水合物；气源岩；沉积有机地球化学

Abstract

Gas hydrate, as resource of the twenty-first century, is widely developed in the northern slope of the South China Sea. Further study on gas hydrate accumulation mechanism and enrichment patterns is required, to provide an important theoretical basis and guidance for marine gas hydrate resource exploration and development. Among them, gas source condition is not only the material basis of gas hydrate formation, but also the key factor for gas hydrate accumulation. This research is based on the National Major Fundamental Research and Development Project “Basic study on gas hydrate accumulation laws and exploitation in the South China Sea” (No. 2009CB219501), the National Natural Science Foundation projects “Research on the sulphate-methane system prosumer mechanism and its interface (SMI) characteristics of the sediments in the northern South China Sea” (project number: 40976035), and “Research on biomarkers and molecular biology of methnogenesis and anaerobic oxidation of methane in gas hydrate system” (project number: 41276046). We chose the Qiongdongnan Basin, the Pearl River Basin and the Taixinan Basin as the research areas, selected sediment core ZS-5 from Shenhu area, cores ZD-2 and ZD-3 from Dongsha area, cores 973-4, 973-5 and ZT-10 from Taixinan area, and six surface sediments, and source rock samples from the Pearl River Mouth Basin and Qiongdongnan Baisn, to study their deposition and organic geochemical characteristics. Combining sedimentary environment and the geological, geophysical and geochemical data of the South China Sea by predecessors, we clarified the impact of structure during the development of sediment; identified the organic matter composition, distribution and material source of various areas; analyzed pyrolysis gas condition of deep source rocks and microbial gas condition of shallow sediment, and biomarkers in sediments from different gas source condition; discussed the significance of biomarkers for gas hydrate. It was enumerated as below:

(1) The Qiongdongnan Basin, the Pearl River Mouth Basin and the Taixinan Basin had experienced three phrases: rift, rift thermal subsidence and neotectonic movement. It developed Eocene lacustrine source rock, Oligocene lacustrine, paludal

facies and transitional facies source rock, and Miocene marine source rock. The neotectonic movement made the local tectonic setting and geological body, such as fault-fold belt, slump structures and diapirs, developed in the northern South China Sea, beneficial to the deep gas migration to the shallow.

(2) Zhu II depression and Zhu III depression Wenchang A sag were the major gas production depression in the Pearl River Mouth Basin. The gas source rocks in Zhu II depression were type I~II_1 over-mature rocks in Wenchang and Enping formations, and type III low-medium mature rocks in Zhuhai formation. The gas source rocks in Wenchang A sag were mature—over-mature rocks in Wenchang formation. The source rocks in the Taixinan Basin mainly produced gas. Cretaceous—Lower Tertiary burial depth was below 5000m, over-matured. The main source rocks were type III mature—over-mature marine shale of Oligocene—Lower Miocene, and type III mature—over-mature offshore continental mudstones of Mesozoic Jurassic/Lower Cretaceous. The central depression zone and the Yabei sag of the northern depression were the major gas production depression in the Qiongdongnan Basin. Their humic gas source rocks of Oligocene and Miocene had entered mature and over-mature stage and had good potential for gas production. In addition, the depth of marine deposit of Upper Miocene—Pliocene and Quaternary was up to several kilometers in the Qiongdongnan Basin, the Pearl River Mouth Basin and the Taixinan Basin, mostly in the immature stage, which were good biogenic gas source rocks.

(3) The average sedimentation rates of cores ZD-2, ZD-3, ZS-5, 973-4, 973-5 and ZT-10 in the northern South China Sea were between 0.13 and 0.73 m/ka, meet the gas formation condition (>3cm/ka). The deposition rate at the Dongsha area and the Taixinan area were significantly higher than the Shenhu area. The lithology of shallow sediments was mainly silt and clayey silt. The grain size of sediments in the Taixinan Basin was relatively small.

(4) The TOC of the core sediments from the northern South China Sea were between 0.39% and 1.26%, generally greater than 0.5%, which were consistent with the sediments from Blake Ridge and could provide plenty of organic matter for the

methane production from CO_2 reduction. The TOC contents of ZD-3 and 973-4 were relatively higher than ZS-5, which was consistent with the deposition rate and particle size differences. The $\delta^{13}C$ (PDB) of organic matter were between -26.94‰ and -21.10‰ and changed by stage. Less terrigenous higher-plants input in the Cold period caused the $\delta^{13}C$ a little heavier in MIS II and IV than in MIS I and III.

(5) The organic matter in cores ZS-5, ZD-2 and ZD-3 were type II_2~III, gas generating humic kerogen. They had high levers of O/C atomic ratio, indicating abundance of higher-plant origin. When fulvic acid and humic acid transformed to kerogen, it could provide large amount of CO_2 as biogenic methane carbon source.

(6) The distribution of lipids in surface and subsurface sediments from the northern South China Sea was determined. The *n*-alkanes showed a bimodal—higher at post peak distribution that is characterized by a centre at n-C_{16}–n-C_{20} with maximum calues at C_{18} (or C_{19}) and n-C_{27}–n-C_{31} as well as at C_{29} (or C_{31}). The short chain alkanes suffered significant losses caused by slow deposition in the water column, their occurrence with a slight even carbon predominance in shallow seafloor sediments was ascribed mainly to a direct input from the benthos. The long chain alkanes with odd C–number predominance indicate terrigenous organic matter transportion. S-83 received much organic matter from the estuary, while the other surface samples were mainly from atmospheric transport and so affected by the distance from the mainland. Immature hopanoid biomarkers reflected intense microbial activity for bacteria–derived organic matter input and gradually increasing of maturity by burial depth.

(7) Abundant *n*-fatty acid methyl esters whose distributions were coincidence with fatty acid distribution were detected in all samples. We proposed that the FAMEs observed were from methyl esterification of fatty acids; methanol production by methanotrophs and methanogenic archaea related to anaerobic methane oxidation and sulfate reduction provides O–methyl donor for fatty acid methylation. The CH_4 released from hydrate dissociation in oxygen isotope stage II of Cores ZD3 and ZS5, which has been confirmed by the negative $\delta^{13}C$ excursion and spherical pyrite aggregates occurrence, may have accelerated the above process and thus made the