



Full Length Article

Pore size constrains on hydrocarbon biodegradation in shales from the Second White Speckled Shale Formation of the Western Canada Sedimentary Basin

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HIGHLIGHTS

- Second White Speckled Shale Formation (2WS) is organic rich and immature.
- No obvious hydrocarbon biodegradation can be illustrated by molecular compositions.
- The commonly used biodegradation indicators are illusive in shale system.
- Pore size distribution is the key control for microbial activity and methanogenesis.

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ABSTRACT

A suite of eight source rock samples from the Second White Speckled Shale Formation in southeast Alberta biogenic gas field of the Western Canada Sedimentary Basin have been characterized geochemically and physically to investigate biodegradation influence on molecular compositions of extractable organic matter and its constrains. Bulk geochemical analysis indicates the studied sediments are organic rich with total organic carbon content greater than 3.0%, dominated by Type II kerogen and at immature stage of thermal evolution. Molecular compounds in the saturated hydrocarbon fraction are dominated by *n*-alkanes, isoprenoid alkanes, steranes and hopanoids. Pore size distribution based on N₂ gas adsorption isotherms indicates that pores are dominantly in mesopore-size range with diameter between 2 and 50 nm, which are far smaller than the average size of bacteria. The commonly used biodegradation parameters such as ratios of short-chain to long-chain *n*-alkanes, isoprenoid alkanes to *n*-alkanes and hopanes to both *n*-alkanes and isoprenoid alkanes illustrate no obvious biodegradation influence; implying microbial activities have been ceased in the studied shale sequence due to physical impediment for microorganisms.

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1. Introduction

Microbial degradation of organic matter (OM) in the subsurface is well documented in oil reservoirs but much less understood for shales although biogenic gas is supposed to be derived from such process. In oil reservoir, biodegradation takes place at the oil water contact (OWC). The ubiquitous vertical compositional gradients in biodegraded columns imply mass transport control on degradation rates with nutrients from basal water and hydrocarbon diffusion toward the OWC [1–5]. Geochemists have made substantial

advances in their ability to describe empirically the geochemical sequences of subsurface oil biodegradation with preferential loss of *n*-alkanes, followed by the removal of isoprenoid alkanes, light molecular weight aromatic hydrocarbons and highly branched and cyclic saturated hydrocarbons [6–10].

In shale system, in situ sedimentary OM is most likely the primary source of electron donors for microbial activity in the deep subsurface and the driving force behind the biogeochemical reaction network is the degradation of OM. The conversion of the complex OM to methane relies on the cooperation of numerous microorganisms along a metabolic cascade [11–15]. While the occurrence of microbial methane is widely recognized in numerous basins [16–18], little is known about the fractions of OM consumed or the signatures of hydrocarbon biodegradation associated with

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biogenic gas generation. A few studies have shown that microbial communities associated with immature source rocks are able to utilize the dissolved OM present in organic-rich shales as source of organic carbon and electron donors [19–21]. However, most studies suggested that deeply buried OM-rich black shales can directly provide a suitable substrate for ongoing microbial activity in deep subsurface [11,12,22,23]. Ironically, biodegradation of OM in shale seems minimal as indicated by the New Albany Shale from the Illinois Basin and elsewhere except the Antrim Shale [24]. Only short-chain (C_{15} – C_{19}) *n*-alkanes appear to be microbially altered in shale extracts with minimal evidence for losses of acyclic isoprenoid alkanes and aromatic hydrocarbons [21,25]. In order to fully understand the mechanisms responsible for the biodegradation of OM in shales and the biomarker signatures that are indicative of these processes, more research is required.

In the present study, we investigated the molecular compositions and pore size distributions of organic-rich shale from the Second White Speckled Shale (2WS) Formation in prolific biogenic gas production region of the Western Canada Sedimentary Basin (WCSB), and aimed at connecting the spatial distribution of biodegradation influence on OM to the petrophysical property of the host rocks. These results help constrain the processes involved in biodegradation of OM from shale and assist in recognizing sites favorable for methanogenesis.

2. Geological background

The 2WS Formation within the Colorado Group in the WCSB records a period of maximum sea level in the Cretaceous Western Interior Seaway (WIS) during late Cenomanian to Early Turonian (93–91 Ma). This formation has been described as laminated, non-bioturbated limestones to marlstones in Saskatchewan, calcareous claystone to siltstone in eastern and southern Alberta, and calcareous siltstone in northwestern Alberta [26]. The speckled nature of this unit is due to the abundance of millimeter- (or smaller) sized fecal pellets composed of calcareous coccolithic debris [27]. This unit thickens from about 25 m at the Saskatchewan-Manitoba boundary to over 90 m in the Peace River Arch area of northwestern Alberta [26]. The abundance of pelagic organisms, coupled with widespread bottom water anoxia, resulted in high TOC values (up to 12 wt%) and dominantly Type II kerogen [26,28,29].

A variety of play types sourced from the 2WS exist across this vast system including, biogenic gas, light oil, and minor amounts of thermogenic gas. Significant biogenic gas resources are found in shallow Cretaceous reservoirs in southeast Alberta and southwest Saskatchewan. The biogenic gas is considered to be internally sourced, having been generated during the bacterial breakdown of detrital organic material. The methane is isotopically light with $\delta^{13}C$ ranging from -66 to -75‰ and the gas is dry with $C_1/\Sigma C_{1-5} > 0.98$ [16,18]. It is perhaps one of the largest biogenic gas field known in the world, with a total gas production of 0.43 trillion cubic meters and a total recoverable biogenic gas amount over 1.42 trillion cubic meters [30].

3. Sample and methods

Samples of the present study are from well 100/3-33-49-10W4 with continuous core of the 2WS Formation at depth of 500–540 m in biogenic gas producing region of southeast Alberta. Eight samples (numbered 1–8) were collected and characterized by geochemical and petrophysical methods.

Rock-Eval pyrolysis was performed using a Rock-Eval II analyzer. About 70 mg pulverized rock sample is heated at $25\text{ °C}/\text{min}$ to 600 °C in an inert atmosphere to obtain routine parameters.

Maceral composition and vitrinite reflectance were measured on whole rock under microscopy.

The pore size distribution and specific surface area of studied samples were measured by nitrogen gas adsorption isotherms using QuadraSorb Station 3 automatic analyzer. The standard material used for the N_2 adsorption is GBW13912 mesoporous aluminum oxide (Al_2O_3). The sample was degassed for 12 h under a temperature of 110 °C until the interior pressure reached a quasi-vacuum of 1.33×10^{-8} Pa. The physical processes of isothermal adsorption and desorption were performed under 77.3 K (-195.85 °C) in a liquid nitrogen environment. The adsorption to desorption pressure ratio varies from 0.001 to 0.994. Four data points were selected on the Brunauer-Emmett-Teller (BET) curve to derive specific surface area by means of linear regression. The pore size distribution was obtained by using Barrett-Joyner-Halenda (BJH) theory and density functional theory (DFT).

Extractable organic matter (EOM) was isolated by Soxhlet extraction of about 60 g of crushed shale using dichloromethane (DCM) and methanol (93:7 v/v) for 72 h. Take about 50 mg extract, add a suite of internal standards (Squalane and d4 Cholestane for saturated hydrocarbon fraction) and put on a polar Florisil solid phase extraction (SPE) cartridge to remove asphaltene. The soluble material was then separated into hydrocarbon and polar fractions using hexane and DCM as elute in a C18 SPE cartridge [31]. The hydrocarbon fraction was further divided into the aromatic and saturated hydrocarbon fractions using a method described by Bastow et al. [32].

The saturated hydrocarbon fractions were analyzed by using an Agilent 5973 MSD system interfaced to a Varian 6890N gas chromatography. An HP-5MS fused silica capillary column ($30\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$ film thickness) was used. The oven temperature was initially set at 40 °C for 5 min, programmed to reach 220 °C at $4\text{ °C}/\text{min}$ and then to 325 °C at $2\text{ °C}/\text{min}$ increments. The final hold time of 15 min. Helium was used as a carrier gas with constant flow rate of $1\text{ cm}^3/\text{min}$. The interface temperature was 300 °C . The selected ion monitoring (SIM) scan mode was performed and peak area was used for concentration calculation without response factor calibration.

4. Results

4.1. Bulk geochemical compositions

Rock-Eval pyrolysis is a routine organic geochemical technique that provides reliable information on the amount and maturity of the organic material. The studied samples are rich in organic matter with total organic carbon (TOC) contents ranging from 3.2 to 9.4%, which can be ranked as excellent source rocks. TOC contents show an increase trend from bottom to the top (Fig. 1A), which is consistent with an overall transgression sequence during the deposition of the 2WS Formation. The Hydrogen Index ($HI = S_2 \times 100/\text{TOC}$) corresponds to the quantity of cracking organic compounds from kerogen, or hydrocarbons from S_2 , relative to the TOC in the sample, measured in mg hydrocarbon/g TOC. HI in the studied samples vary from 350 to 540 mg HC/g TOC, suggesting typical Type II kerogen. HI increases from the deepest sample to maximum value at 525 m then decreases upwards (Fig. 1B). Rock-Eval T_{max} values can be used to estimate the level of thermal maturity for OM within the sediments, their values increase progressively along with the level of thermal maturity. The onset of oil generation is generally considered to begin when T_{max} values reach 435 °C [33]. The T_{max} values of the studied samples range from 400 to 423 °C , reflecting immature stage in terms of oil generation, which can be further confirmed by measured vitrinite reflectance of 0.47% (average of 3 measured samples). The deepest sample has much higher T_{max} value than others, which

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