



Kerogen based characterization of major gas shales: Effects of kerogen fractionation



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ABSTRACT

Research into the origin and the mode of entrapment and expulsion of natural gas from unconventional plays requires the isolation and separation of kerogen in its purest and most intact form from the rock matrix. This study expands on the comparative analysis of the effects that isolation methods, conservative closed system versus conventional open system, have on kerogen's elemental, isotopic and physical properties. Four major gas shales, including the Barnett, the Marcellus, the Haynesville and a Polish gas shale, were chosen. In addition, the Monterey shale, though not strictly a gas shale, was included to address the effects on sulfur rich, Type II-S kerogen.

Results indicate that the kerogen residues from the conventional open system method showed lower recovery and higher mineral content than those from the conservative closed system method. Differences were manifested in the elemental analysis data, where kerogens isolated using the open system method showed a significant deficit in the organic C, H, O, S and N material balance. Furthermore, the recovered residues show different sulfur content and $\delta^{34}\text{S}$ composition, most likely attributable to differences in pyrite content. Nevertheless, the relative abundances of the various macerals in the kerogen residues from the same parent shale are not very different; neither was the bulk $\delta^{13}\text{C}$ composition of the recovered residues. This is not particularly surprising, considering that in all the five cases examined in this study, the organic matter was fairly homogeneous.

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1. Introduction

Kerogen is the predominant form of organic matter in sedimentary rocks and the precursor to hydrocarbon generation. Its concentration in the rocks and its characterization are crucial for resource assessment, understanding the origin of the oil and gas, basin thermal history, and source rock depositional environments. Examining the kerogen properties and characteristics is also critical to a better understanding of the way gas shales store, retain and release natural gas (Lu et al., 1995; Ritter, 2003; Loucks et al., 2009; Ambrose et al., 2010). Effective porosity in gas shales is now thought by some to lie mostly within the organic microstructure of the kerogen (Ambrose et al., 2010). The study of the effective porosity in gas shales cannot be accomplished without the isolation of the kerogen from the rock matrix. Kerogen isolation can be done via an open, conventional method as is typically done in palynological preparations, or via a conservative, closed method (Vandenbroucke and Largeau, 2007; Ibrahimov and Bissada, 2010). In the study of open versus closed system kerogen isolation

methods by Ibrahimov and Bissada (2010), it was found that conventional open system methods for kerogen isolation yielded kerogens that were not representative of the organic matter as it exists in the rock. Recovery of research quality kerogen requires special conservative separation procedures that preclude fractionation and ensure effective mineral removal, quantitative recovery and chemical preservation of the organic matter (Ibrahimov and Bissada, 2010).

The purpose of this study is to expand on the comparative analysis of the effects that the two different kerogen isolation methods, closed versus open, have on kerogen's elemental, isotopic and physical properties. Any observed differences are examined to determine how they may affect subsequent interpretation of the kerogen's source, thermal maturity and physical properties.

Standard screening procedures, including total organic carbon (TOC) analysis, Rock-Eval pyrolysis and X-ray diffraction (XRD) for mineralogy, as well as sulfur forms analysis, were carried out on the native rocks. In addition, the isolated kerogens were examined for their carbon and sulfur isotopic compositions, their residual mineral content, their organic elemental composition and vitrinite reflectivity.

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2. Samples and methods

2.1. Samples

The suite of samples used in this study include specimens of four gas shales, three from the United States (the Marcellus, the Barnett and the Haynesville) and one from an undisclosed location in Poland (Fig. 1). The Monterey shale, while not strictly a shale resource system, is included in the suite to test the effects of the isolation methods on sulfur rich, Type II-S kerogen. The specimens include both conventional core and cuttings mostly from wells drilled with water-based drilling fluids. A brief description of the specimens and whole-rock properties (Table 1) is given below.

2.1.1. Barnett shale

The Barnett shale is located in the Fort Worth Basin near Fort Worth, Texas. This Mississippian siliceous shale has generated both low sulfur oil and natural gas. The hydrocarbons from the Barnett shale were generated from a marine Type II kerogen composed mainly of amorphous organic matter and has yielded large amounts of natural gas (Hill et al., 2007). The Barnett was

deposited in a marginal deep water basin in the southern margin of the Laurussian platform (Ruppel and Kane, 2006). The Barnett has a total porosity of 4–5%.

The main Barnett shale sample used in this study is a thermally immature sample from an outcrop in a quarry in San Saba County. It has a TOC content of 10.7%, hydrogen index (HI) of 371 mg HC/g TOC and a total hydrocarbon generation potential (THGP) of 40.5 mg HC/g rock (Table 1).

2.1.2. Monterey shale

The Monterey shale in this study is from the southern coast of California (Santa Maria Basin). It is a Miocene siliceous shale of Type II marine kerogen, high in sulfur. Orr (1986) addressed the presence of the Type II-S kerogen especially in the Santa Maria Basin. The Monterey in this study has a TOC content of 6.1%, a HI of 654 mg HC/g TOC and a THGP of 42.0 mg HC/g rock (Table 1). On average the Monterey shale has a total porosity of about 11% (U.S. EIA, 2011). This shale is predominantly an oil prone source rock, but also yields natural gas. The Monterey shale was deposited in a sediment starved, dysaerobic to anoxic marine basin (Curiale and Odermatt, 1988).

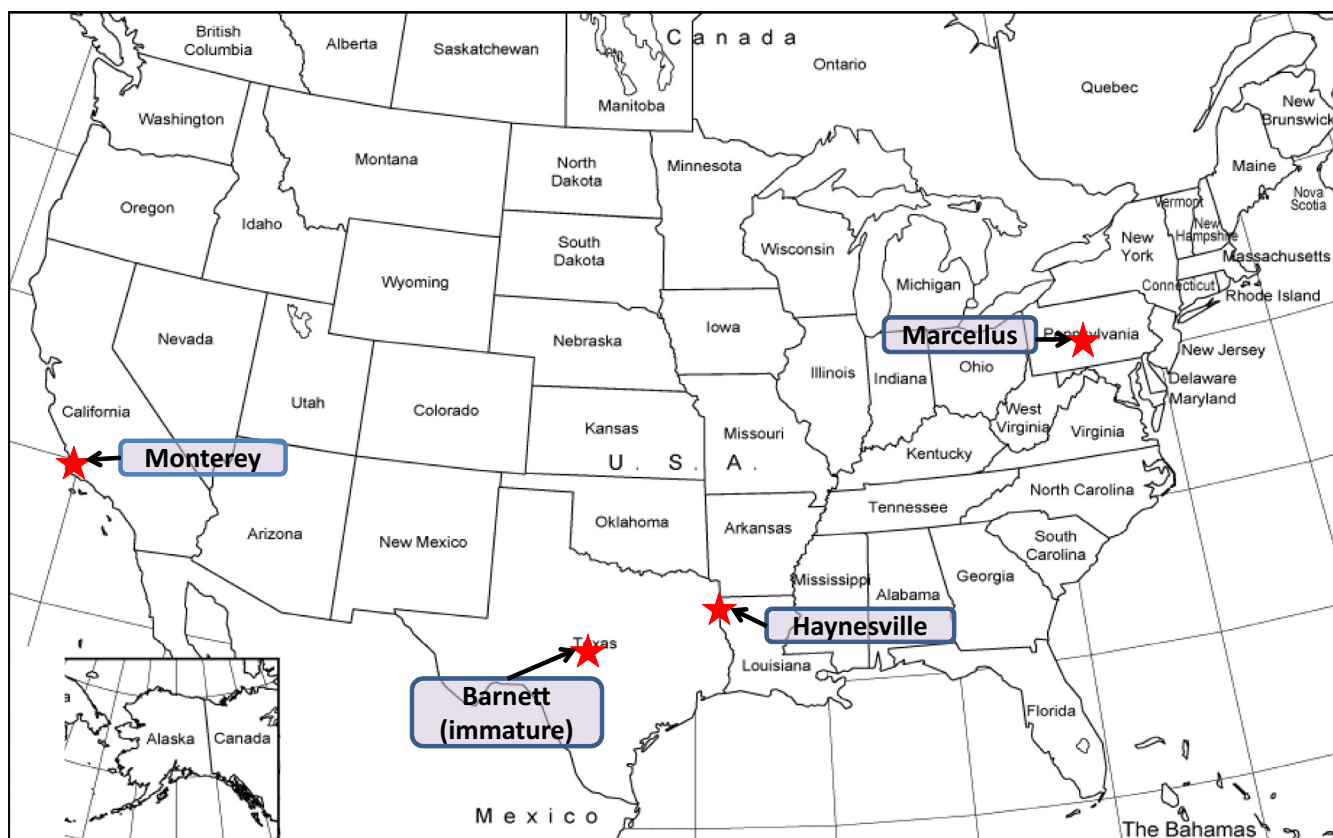


Fig. 1. Map of sample locations. The Polish shale is not shown. Source: United-States-Map.com.

Table 1
Rock-Eval pyrolysis results for the whole-rock.

Sample	TOC (wt%)	S1 (mg HC/g rock)	S2 (mg HC/g rock)	THGP (mg HC/g rock)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC CO ₂ /g TOC)	T _{max} (°C)
Monterey	6.1	2.17	39.87	42.04	654	18.6	408
Barnett (immature)	10.7	0.78	39.70	40.48	371	10.0	418
Haynesville	2.0	0.47	0.35	0.82	18	3.5	463
Marcellus ^a	9.0	0.32	0.87	1.19	10	4.0	478
Polish shale	4.5	0.09	0.21	0.30	5	2.6	455

^a Bitumen free results due to extraction of oil-based drilling mud.

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