



## Full Length Article

# The effects of solvent extraction on nanoporosity of marine-continental coal and mudstone

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## ARTICLE INFO

## Keywords:

Coal  
Mudstone  
Marine-continental facies  
Extraction  
Bitumen  
Nanopore

## ABSTRACT

Coal and organic-rich mudstone develop massive nanopores, which control the storage of adsorbed and free gas, as well as fluid flows. Generation and retention of bitumen and hydrocarbons of oil window reservoirs add more uncertainty to the nanoporosity. Solvent extraction is a traditional way to regain unobstructed pore networks but may cause additional effects due to interactions with rocks, such as solvent adsorbing on clay surfaces or absorbing in kerogens. Selected marine-continental coal and mudstone in Eastern Ordos Basin were studied to investigate how pore structures are affected by these *in-situ*-sorptive compounds (namely residual bitumen and hydrocarbons) and altered by solvent extractions. Solvent extraction was performed to obtain bitumen-free subsamples. Organic petrology, bulk geochemical analyses and gas chromatography were used to characterize the samples and the extracts. Low-pressure argon and carbon dioxide adsorptions were utilized to characterize the nanopore structures of the samples before and after extraction. The samples, both coal and mudstone, are in oil windows, with vitrinite reflectance ranging from 0.807 to 1.135%. The coals are strongly affected by marine organic input, except for the sample C-4; the mudstones are sourced by either marine or terrestrial organic input, or their mixture. As for the coals affected by marine organic input, residual bitumen and hydrocarbons occupying or blocking pores < 10 nm becomes weak with thermal maturation. Bitumen derived from terrestrial organic matter mainly affects small pores, since coal asphaltene molecules are much smaller than petroleum asphaltene molecules. The mudstone M-2 with high extract production showed an increase of nanopores after extraction, due to the exposure of the filled or blocked pores. However, most transitional mudstones saw decreases of the pores because pore shrinkage caused by solvents adsorbing on and swelling clay minerals (mainly kaolinite and illite/smectite mixed layers) counteracts the released pore spaces. Solvent extractions on the coals significantly increased the micropores < 0.6 nm, since the heat of sorption of alkanes reaches the peak in the pores within 0.4–0.5 nm. By contrast, solvent extractions on the mudstones decreased the micropores ~ 0.35 nm, which is perhaps caused by evaporative drying of solvent displacing residual water in clay.

## 1. Introduction

Unconventional reservoirs are enriched with organic matter and share many characteristics of sealing units, including small pore size, low porosity and permeability [1,2]. Pore networks of sediments in petroleum systems control the storage of adsorbed and free gas and fluid flows, which determine whether the sediments can be a reservoir or a cap rock. There have been studies on how pore structures are affected by lithology, mineralogy, total organic carbon (TOC), thermal

maturity, fabric and diagenetic history [3–9], and how pore structures control the gas storage and migration [10–14]. Traditional and state-of-the-art experiments have been used to characterize porosity of fine-grained reservoirs.

Generation and retention of bitumen and hydrocarbon add more uncertainty to porosity of unconventional reservoirs in oil window. These *in-situ*-sorptive compounds (namely residual bitumen and hydrocarbons) condense on or are adsorbed on the pores and thus change gas storage capacity [15]. Additionally, the alternation of porosity

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<https://doi.org/10.1016/j.fuel.2018.07.083>

Received 27 May 2018; Received in revised form 17 July 2018; Accepted 19 July 2018

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**Table 1**  
Mineral composition of the mudstone samples.

Sample	Quartz (wt. %)	Feldspar (wt. %)	Pyrite (wt. %)	Smectite (wt. %)	Illite- Smectite mixed layer (wt. %)	Illite (wt. %)	Kaolinite (wt. %)	Chlorite (wt. %)
M-1	/	/	5.1	/	/	0.9	93.1	0.9
M-2	1.2	/	0.5	2.0	/	3.9	91.4	1.0
M-3	46.1	6.0	/	/	26.3	6.2	11.6	3.8
M-4	34.6	1.0	/	/	14.2	3.2	44.4	2.6

**Table 2**  
Vitrinite reflectance and maceral composition of the coal samples.

Sample	$R_o$ (%)	Maceral composition (v/v %)							
		Vittrinite	Semivitrinite	Fusinite	Semifusinite	Liptinite	Clay	Carbonatite	Pyrite
C-1	0.81	61.63	3.58	21.07	4.38	2.98	2.78	3.58	/
C-2	0.84	29.94	44.31	0.20	10.58	2.40	10.18	2.40	/
C-3	1.01	85.69	0.19	1.74	1.74	3.48	7.16	/	/
C-4	1.14	80.78	7.06	2.55	6.08	1.18	1.77	0.59	/

**Table 3**  
Maceral compositions of the mudstone samples.

Sample	Maceral composition (v/v %)					TI <sup>a</sup>	Kerogen Types <sup>b</sup>
	Sapropelinite	Resinite	Liptinite without Resinite	Vitrinite	Inertinite		
M-1	/	/	4	70	26	−76.5	III
M-2	89	/	11	/	/	94.5	I
M-3	2	/	10	74	14	−62.5	III
M-4	44	/	48	6	2	61.5	II <sub>1</sub>

<sup>a</sup> Kerogen type index (TI) is calculated by the following equation,  $TI = 100a + 80b_1 + 50b_2 + (-75)c + (-100)d$ , where  $a$ ,  $b_1$ ,  $b_2$ ,  $c$  and  $d$  are the percentage of sapropelinite, resinite, liptinite free of resinite, vitrinite and inertinite, respectively.

<sup>b</sup> Kerogen types is determined by TI. The ranges of TI values of type I and II<sub>1</sub>, type II<sub>1</sub> and II<sub>2</sub>, and type II<sub>2</sub> and III, are > 80, 80–40, 40–0 and < 0, respectively.

further changes the thermal and electrical conductivity, which have numerous applications in reservoir engineering and petrophysics [16–22]. Due to the abundance of bitumen, there is no correlation between microporosity and TOC in thermally immature shale [23,24]. Solid-state nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the bulk chemical and structural information of bitumen and kerogen [25–27]. Synchrotron-based scanning transmission X-ray microscopy (STXM) combined with X-ray absorption near edge structure (XANES) spectra provides spatially-resolved geochemical information of bitumen and nanoporous pyrobitumen as a response to the thermal evolution of kerogen [28]. Residual bitumen infilling causes the absence of original organic pores, which has been verified by imaging unextracted and extracted mudstones [29,30].

As for early mature or mature lacustrine shale, the residual bitumen in pores dramatically affects the pore structures and methane sorption [31]. Specific surface areas and pore volumes of marine and lacustrine shale generally increase after solvent extraction, apart from a few exceptions in marine shale [27,31–34]. Bitumen-free porosity of shales after solvent extraction are higher than those measured in as-received samples, and bitumen-filled porosity decreases with thermal maturity [5]. All previous studies focused on oil prone mudstones (including lacustrine and marine mudstones), while transitional coal and mudstone were rarely reported. Compositions and textures of both organic matter and minerals of transitional sediments are much different from those of marine or lacustrine mudstones. For examples, transitional coal and mudstone may be sourced by a mixture of terrestrial and marine organic input. Additionally, high kaolinite content is a major feature of marine-continental or coal-bearing mudstone [35,36].

Solvent extraction is suggested to be conducted to ensure that pore throats are unobstructed [32,37]. However, chemical and physical interactions between solvent and kerogen or between solvent and

minerals may alter the pore structure and cause inaccurate “real porosity” (porosity free of hydrocarbons and soluble bitumen). For examples, 1) Solvent extraction causes swelling of clay and kerogen; 2) solvent absorbs in organic matter and/or adsorbs on clay surfaces; 3) solvent extraction may completely or partially dissolve porous resins or asphaltene [27,32,38].

This study aims to investigate how pore structures of marine-continental coal and mudstone are affected by *in-situ*-sorptive bitumen and hydrocarbons and altered by solvent extractions through comparing pore parameters of the samples before and after solvent extraction. Sample features, including thermal maturity, maceral compositions, hydrocarbons potential and TOC, were characterized by organic petrology, Rock-Eval pyrolysis and other bulk analysis methods. Gas chromatography was used to analyze the properties of the extracts. Nanopore structures were characterized by low-pressure Argon (Ar) and carbon dioxide (CO<sub>2</sub>) adsorption. This study clarifies what the extractable compounds of transitional coal and mudstone are like, and how they affect pore structures, and gains insights into the mechanisms of solvent extraction altering pore structures.

## 2. Samples and methods

### 2.1. Samples

Taiyuan and Shanxi Formations (belonging to Carboniferous and Permian Systems) in Ordos Basin, China were deposited in a marine-continental transitional facies. The transitional facies refers to the deposits between continental and marine settings, ranging from lagoonal flat and fluvial-delta environments [39]. These strata are composed of a sequence of interbedded coal, mudstone and sandstone, forming a combination of different types of unconventional natural gas reservoirs. Joint development of coalbed methane, shale gas and tight

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