Research paper

# Chemical and structural characterization of thermally simulated kerogen and its relationship with microporosity

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## ARTICLE INFO

## ABSTRACT

Kerogen was isolated from the Maoming shale at different temperatures to understand changes in chemical, structural and porosity characteristics during artificial maturation. Advanced solid-state $^{13}$C nuclear magnetic resonance (NMR) techniques were employed along with Fourier transform infrared (FT-IR), Raman spectroscopy (RS), stable carbon isotopes, and Rock-Eval pyrolysis to characterize the organic matter (OM), whereas the microporosity and surface properties were elucidated using $N_2$ and $CO_2$ adsorption techniques. As the temperature increased, the aliphatic and carbonyl carbons of the kerogen samples showed remarkable decreases in abundance together with an increase of non-protonated and protonated aromatic carbons. Moreover, the kerogen became more enriched in $^{13}$C and had a higher degree of crystallization with increasing Ro and $T_{max}$. The aromaticity ranged from 46.9% to 94.7% and the minimum aromatic cluster size varied from 10 carbons at 350 °C to 38 carbons at 500 °C, which was significantly related to the microporosity ($V_{0, d-co2}$) of the kerogen samples and their nonlinear sorption of phenanthrene and benzene. The microporosity was extensively affected by the loss of aliphatic carbon and the increase of aromatic fused carbon. When the temperature reached 500 °C, the collapse of aromatic interlayer remarkably reduced the micropore volume in the kerogen, and then resulted in the decreasing adsorption of hydrophobic organic chemicals (HOCs). The above observation confirms the molecular sieve effect in the kerogen samples. In addition, the micro-filling adsorption for HOCs is dominant on the thermally simulated kerogen samples.

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## 1. Introduction

Kerogen is the insoluble macromolecular organic matter (OM) in sedimentary rocks and is by far the most abundant form of OM on Earth (Vandenbroucke and Largeau, 2007). This organic material has undergone geochemical diagenesis and is of prime importance as the source of petroleum and natural gas (Durand, 1980). Due to the heterogeneity, complexity, and insolubility in chemical structure of different kerogen, they have also been identified as ideal sorbate materials for hydrophobic organic contaminants (HOCs) (Huang and Weber, 1997; Johnson et al., 2001; Song et al., 2002; Ran et al., 2003, 2004).

Kerogen is a mixture of various macromolecular moieties encompassing a wide range of compositions and molecular weights. Its changes with increasing maturity couple with

differences in chemical and structural compositions during geochemical processes (Cao et al., 2013b). It has been assumed to consist of two domains: flexible aliphatic moieties and rigid aromatic moieties, which is related to a partitioning phase and a pore-filling phase defined by the dual-sorption model (Xing and Pignatello, 1997; Cornelissen et al., 2005). Therefore, it is necessary to further understand chemical, structural, and nano-porous properties of kerogen and their relationships with the sorption of organic pollutants. To date, many analytical techniques have been developed for the identification and characterization of chemical structure of kerogen, which are commonly classified into two major groups: destructive (indirect) and non-destructive (direct) methods (Tong et al., 2011; Cao et al., 2013a, 2013b). The former techniques such as elemental, isotopic, and pyrolytic analyses destroy the original structure and composition of kerogen and only provide valuable bulk information. In contrast, non-destructive methods are more appropriate in analyzing the specific and detailed structure information of kerogen. Fourier transform infrared (FT-IR), Raman spectroscopy (RS), X-ray photoelectron

spectroscopy (XPS), X-ray diffraction (XRD), and $^{13}$C solid-state nuclear magnetic resonance ($^{13}$C NMR) have been widely employed for the qualitative, semi-quantitative, and quantitative measurements of kerogen during the recent years (Miknis et al., 1979; Dennis et al., 1982; Witte et al., 1988; Kelemen et al., 2007; Petersen et al., 2008; Tong et al., 2011).

Compared with other direct analytical methods, $^{13}$C solid state NMR techniques can offer more accurate structural information on kerogen due to its higher accuracy and quantification capacity. The most extensively used solid-state NMR technique for kerogen is $^{13}$C cross polarization/magic angle spinning (CP/MAS) (Dennis et al., 1982; Witte et al., 1988; Lille et al., 2003; Wei et al., 2005; Werner-Zwanziger et al., 2005). However, it has inherent drawbacks such as low CP efficiency for non-protonated carbons and mobile groups (Cao et al., 2013b). Therefore, many advanced solid-state NMR techniques such as DP/MAS, quantitative DP/MAS plus dipolar dephasing, and $^{13}$C chemical shift anisotropy filter have been developed and applied in the recent years for systematically characterizing kerogen in environments (Mao et al., 2000, 2007, 2010; Mao and Schmidt-Rohr, 2003, 2004; Cao et al., 2013a). Specific functional groups, aromaticity, and aromatic cluster size can be derived from these advanced $^{13}$C NMR techniques for correctly understanding chemical structure of kerogen and its role to the sorption process of HOCs.

The presence of organic micropores and their network within OM of shales is likely to be involved in the generation, storage and production of hydrocarbon (Loucks et al., 2009; Ross and Bustin, 2009; Curtis et al., 2012; Romero-Sarmiento et al., 2014). Loucks et al. (2009) found that most of nanopores in the Barnett Shale are associated with grains of OM and their abundance in OM is directly related to thermal maturity. However, Curtis et al. (2012) stated that the thermal maturity alone is insufficient for predicting porosity in the OM and other factors such as OM type and composition could complicate the development and preservation of porosity in shales. Thus, more works are needed to thoroughly understand the relationships among thermal maturity, chemical structure and organic micropore development in OM during kerogen maturation and their roles in hydrocarbon retention processes. It is noted that $N_2$ and $CO_2$ adsorption techniques have been extensively applied for the surface properties and micro-porous evaluation of natural organic matter (NOM) during the last several years (De Jonge and Mittelmeijer-Hazeleger, 1996; Xing and Pignatello, 1997; Kwon and Pignatello, 2005; Ravikovitch et al., 2005; Ran et al., 2013). However, the $N_2$ adsorption technique has been found to underestimate the microporosity of soil/sediment NOM due to the molecular sieving effect, a phenomenon that $N_2$ molecules are unable to diffuse into pores at the lower temperature of 77 K (De Jonge and Mittelmeijer-Hazeleger, 1996; Ran et al., 2013). Some internal micro-pores of organic matrices could not be approached by $N_2$ (Larsen et al., 1995). Therefore, the $CO_2$ adsorption technique, which is not affected by molecular sieving, is more appropriate for probing the micro-porous properties of complex organic materials (De Jonge and Mittelmeijer-Hazeleger, 1996; Ran et al., 2013).

The artificial maturation experiments for kerogen have usually been performed for exploration of potential oil and natural gas in shale and rocks (Behar et al., 1995). Moreover, a series of kerogen obtained from thermally stimulated experiments can also be used as appropriate organic materials for structural investigations (Dennis et al., 1982) and HOCs sorption (Zhang et al., 2014). In the present study, a shale sample collected from Maoming, South China, was thermally treated to generate a series of organic materials with different maturity. A combination of FT-IR, RS, stable carbon isotopes, elemental analyses, Rock-Eval pyrolysis, and several advanced $^{13}$C NMR techniques were applied for qualification and quantification of chemical structure of kerogen, whereas $N_2$ and $CO_2$ adsorption techniques were used to investigate their surface and micro-porous properties. Combined with the previous sorption data of benzene and phenanthrene (Zhang et al., 2014), the effects of chemical structure, surface properties, and microporosity on the sorption of HOCs by kerogen were investigated.

## 2. Materials and methods

### 2.1. Samples

The Maoming shale was collected from the southwest of Guangdong Province, south China and then ground to fine powders (<200 mesh) prior to storage (Ran et al., 2007). Afterwards, the heating temperature from 25 °C to 500 °C was chosen for artificial thermal simulation of shale (Behar et al., 1995; Tissot and Welte, 1978). The pretreatment procedure for the shale is detailed in the previous studies (Yang et al., 2009; Zhang et al., 2014). In brief, six shale samples (5 g for each sample) mixed with deionized water (2 mL for each sample) were separately sealed in six steel ampoules (20 cm$^3$ for each ampoule) and then heated in a muffle furnace with a temperature program from 25 °C to 500 °C (20 °C/min to 200 °C, followed by 2 °C/min from 200 °C to 500 °C). After thermal stimulations, the six treated shale samples (R250, R300, R350, R400, R450, R500) together with the original shale sample (RJ) were firstly treated with 1 N HCl and then demineralized with a mix acid solution of HCl and HF for 5 days. The residual solids were later treated with a mixture solvent of methanol: acetone: benzene (MAB, 1:2.5:2.5, v/v/v) to obtain the corresponding kerogen samples (Zhang et al., 2014).

### 2.2. Bulk analyses

The elemental analysis (C, H, N, and O) was performed using an Elementar Vario EL III instrumental analyzer. The vitrinite reflectance ($Ro$) was measured using a Leitz MPV-3 (Ran et al., 2003). The carbon isotope analyses were carried out using a Finnigan-MAT251 mass spectrometer. The $\delta^{13}C$ values are reported relative to the V-PDB Belemnite standard with an analytical precision of ±0.02‰ (Coplen, 2011).

### 2.3. FT-IR and RS analyses

FT-IR analyses for the kerogen samples were carried out on a Perkin-Elmer 1725 X infrared spectrophotometer. About 1 mg of each kerogen sample was ground to powder (<200 mesh) and mixed with KBr (60 mg) for sample preparation. The mixture sample was then pressed to a disc of roughly 10 mm diameter. FT-IR spectrum for the disc sample was analyzed at 4 cm$^{-1}$ resolution and collected in the range of 4000–400 cm$^{-1}$ wave number.

RS analyses for the kerogen samples were conducted by using the Ranishaw 2000 laser Raman spectrometer. The exciting light is Argon laser and the wavelength of this laser is 514.5 nm. The irradiating power should not exceed 20 mW to avoid the coking phenomenon.

### 2.4. Rock-Eval analyses

All the kerogen samples were analyzed by Rock-Eval 6 (Vinci Technologies, France) (Lafargue et al., 1998). Samples were first heated in an inert, $O_2$-free oven (300 °C–650 °C), followed by combustion in an oxidation oven (400 °C–850 °C). The pyrolysis stage releases two specific populations of hydrocarbons (HC), defined as S1 and S2, which are detected and quantified by flame