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# Characterization of methane adsorption on shale and isolated kerogen from the Sichuan Basin under pressure up to 60 MPa: Experimental results and geological implications

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## ABSTRACT

A series of methane adsorption isotherms were measured at pore pressures up to 60 MPa and at 60 °C, 100 °C and 140 °C for dried and overmature Paleozoic shales and isolated kerogen from the Sichuan Basin. At first, the measured excess adsorption increases with increasing pressure, reaches a maximum value at pressures ranging between 8 and 18 MPa and then decreases. The rate of decrease reduces with increasing pressures from 18 to 60 MPa, which is attributed to the nonlinear increase of free methane density with pressure. Additionally, an unusual increase of excess adsorption at pressures from 48 to 60 MPa was observed. Both, the supercritical Dubinin-Radushkevich (SDR)-based and Langmuir-based excess adsorption models, represent the excess adsorption isotherms equally well. The fitted maximum absolute adsorption capacities, when based on raw data from 0 to 30 MPa, are larger by an average of 11.5% when compared to the raw data from 0 to 60 MPa. This deviation indicates that experimentally derived gas adsorption characteristics can be biased with respect to the maximum pore pressure used in the respective experiments. The kerogen contribution to the total methane adsorption capacity of studied Paleozoic shale samples under in-situ hydrostatic pressure and temperature conditions of main shale formations in the Jiaoshiba shale gas play is lower than 50%. However, this contribution should be larger under realistic geological conditions, especially as existent moisture will affect clays stronger than organic matter and therefore reduce the contribution of clay towards the total sorption capacity. The estimated GIP of Paleozoic shales under geological hydrostatic pressure and temperature conditions of main shale formations in the Jiaoshiba shale gas play is 5.36–6.64 $cm^3/g$.

## 1. Introduction

Shale gas resources are globally abundant and shale gas production has continuously increased over the past ten years due to technical advances in horizontal drilling and hydraulic fracturing techniques (Curtis, 2002; Montgomery et al., 2005; E.I.A., 2013; Lv et al., 2017). Many countries have attempted to accurately estimate their shale gas resources in an effort to meet their future energy demands (E.I.A., 2013).

Gas-in-place (GIP) is a key parameter for the estimation of shale gas resources. Gas trapped in shale formations can be divided into three different phases: free gas in pores and fractures, adsorbed gas on various surfaces, and absorbed gas dissolved in any liquids (Curtis, 2002). The most widely used approach for estimating shale GIP is to add those three phases together. According to Curtis (2002) adsorbed gas accounts for 20–85% of GIP within the five major shale formations in the United States. Thus, the estimation of the amount of adsorbed natural gas, which is mainly methane, considerably influences the estimation of GIP.

The amount of adsorbed methane can be determined by laboratory (manometric, gravimetric, volumetric) measurements. The results, usually expressed as excess adsorption isotherms, can be parameterized by various methods, including the Langmuir, the supercritical Dubinin–Radushkevich (SDR) and the simplified local density (SLD) models (Chareonsuppanimit et al., 2012; Gasparik et al., 2012; Clarkson and Haghshenas, 2013; Rexer et al., 2013; Tian et al., 2016). Fitting of parameters, such as density or volume of adsorbed gas phases, can be used to derive "absolute" adsorption isotherms from the experimentally

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obtained excess adsorption isotherms. The absolute adsorption isotherms at various temperatures can be utilized to estimate the thermodynamic parameters of methane adsorption (Ji et al., 2012; Zhang et al., 2012; Rexer et al., 2013; Gasparik et al., 2014a; Tang et al., 2016; Tian et al., 2016).

In recent years, significant research progress has been achieved with respect to Paleozoic shale gas prospects in the Sichuan Basin. Three shale gas fields (Weiyuan, Changning and Jiaoshiba) were discovered and over $30 \times 10^8$ m$^3$ of shale gas were produced by the end of 2014 (E.I.A., 2013; Guo and Zhang, 2014; Zou et al., 2015). The main shale reservoirs in the Sichuan Basin are in the Upper Ordovician to Lower Silurian and may reach depths up to 4000 m where the hydrostatic pressure could well reach 60 MPa (Zou et al., 2014, 2015, 2016). Plenty of research focuses on the methane adsorption characteristics of Paleozoic shales, but mostly is based on methane adsorption measurements with maximum pore pressures smaller than 20 MPa (Yang et al., 2015; Liang et al., 2016; Tian et al., 2016; Li et al., 2017; Xia et al., 2017). Therefore, this experimental study focuses on methane adsorption of shales under hydrostatic pressures up to 60 MPa.

It was established by several studies that organic matter is a main contributor to methane adsorption capacity of shales (Ross and Marc Bustin, 2009; Weniger et al., 2010; Ji et al., 2012; Zhang et al., 2012; Gasparik et al., 2014a; Rexer et al., 2014), but the contribution of organic matter to shale methane adsorption capacity has not been quantitatively studied to our best knowledge.

In this study, methane adsorption measurements, using shales and isolated kerogen from Lower Silurian–Lower Cambrian layers of the Sichuan Basin, at pressures ranging from 0 to 60 MPa and at three different temperatures (60 °C, 100 °C and 140 °C) were performed. The goals were (1) to investigate the methane adsorption capacity and characteristics of Paleozoic shales at hydrostatic pressures and temperatures that cover all geological conditions, (2) to compare methane adsorption characteristics of shales at high and relatively lower pore pressure conditions and (3) to estimate the contribution of kerogen to the shale methane adsorption capacity and GIP of Paleozoic shales.

## 2. Samples and methods

### 2.1. Samples

Three outcrop shale samples from the Lower Silurian (SCNS005), the Upper Ordovician (SCN013) and the Lower Cambrian (SCN009) in northeast Sichuan Basin, China and their isolated kerogen were utilized in this study. All three shale samples are overmature with $R_o$ values ranging from 2.0 to 3.5% and the kerogen type was type I (Zou et al., 2014, 2015, 2016; Tuo et al., 2016). The kerogen in the shale samples was obtained by following the Chinese National Standard GB/T 19144-2010. In brief, shale samples were crushed to powder and treated with hydrochloric acid to remove carbonates and hydrofluoric acid to remove silicates. Hereafter, the kerogen was isolated using heavy liquid suspension.

### 2.2. TOC and X-ray diffraction analysis

For both analyses the shale samples were crushed to a grain size of < 0.15 mm. About 0.1 g of the powder was placed in a porous crucible and treated with hydrochloric acid (4 mol/L) to remove carbonates. After drainage of the acid from the crucible was completed, the crucible and the sample were dried at 80 °C. Hereafter, the total organic carbon content (TOC) of shale and kerogen samples was measured using a Leco CS344 Carbon/Sulfur Analyzer. The X-ray diffraction analyses on shale and kerogen samples were performed using a Rigaku Ultima IV diffractometer with Cu-Kα radiation at 40 kV and 40 mA. Each scan was taken from 2° to 60° with a step interval of 0.02° and a rate of 4.0°/min.

### 2.3. Methane adsorption measurements

Methane adsorption isotherms of shale and kerogen samples were measured at temperatures of 60 °C, 100 °C, 140 °C and pore pressures ranging from 0 to 60 MPa in the Key Laboratory of Petroleum Resources, Gansu Province at Lanzhou, China. The measurements were performed on a gravimetric high pressure sorption analyzer (Rubotherm, ISOSORP-HP III Static) with a magnetic suspension balance. The measurement procedure to obtain the adsorption isotherms can be summarized in three steps: (1) sample pretreatment, where about 5 g of powdered sample material with a grain size of < 0.2 mm was placed in a measuring cell and degassed at 150 °C at vacuum conditions for 20 h to remove adsorbed moisture and volatile matter; (2) buoyancy measurement, which is based on the Archimedes principle to obtain the mass and volume of the sample using helium (99.999%, pressures up to 5 MPa) and (3) adsorption measurement, which is based on the gravimetric method and has been documented frequently in the literature (Dreisbach et al., 2002; Keller and Staudt, 2005; Gasparik et al., 2014b; Tang et al., 2016). After the buoyancy measurement, the system was evacuated again for 2 h to remove residual helium. Hereafter, the measuring cell was heated to the experimental temperature and sequentially charged with methane (99.99%) to 15 designated pressure points to obtain adsorption isotherms. For each pressure point the equilibration time, which was experimentally obtained beforehand, was set to 2 h. The excess adsorption of methane can then be obtained through the mass change of the sample and the buoyancy of the sample under experimental conditions. During the buoyancy and adsorption measurements, free methane and helium densities were obtained via the NIST package using the Setzmann & Wagner equation (Setzmann and Wagner, 1991). The experimental uncertainties were calculated following the method reported by Keller and Staudt (2005).

### 2.4. Calculation of absolute methane adsorption

Excess adsorption of methane ($n_{excess}$) can be directly obtained from experimentally measured quantities and its relation to the absolute adsorption of methane ($n_{abs}$) is given by Eqs. (1) and (2).

$$n_{excess} = n_{abs} - V_{ads} \bullet \rho_g \tag{1}$$

$$n_{excess} = n_{abs}\left(1 - \frac{\rho_g}{\rho_{ads}}\right) \tag{2}$$

Here, $V_{ads}$ is the volume of adsorbed methane, $\rho_{ads}$ is the density of adsorbed methane and $\rho_g$ is the density of free methane at experimental temperature and pressure conditions. The latter can be obtained via the NIST package using the Setzmann & Wagner equation (Setzmann and Wagner, 1991). To calculate the absolute adsorption from excess adsorption, the volume or the density of adsorbed methane is required.

Absolute adsorption isotherms are usually described by the Langmuir model, which assumes monomolecular layer adsorption on a given surface (Langmuir, 1918; Gasparik et al., 2012; Zhang et al., 2012; Tian et al., 2016). Eq. (3) is one expression of the Langmuir model.

$$n_{abs} = n_0 \bullet \frac{P}{P_L + P} \tag{3}$$

Here, $n_0$ is the maximum absolute adsorption capacity at a given temperature, $P$ is the equilibrium pressure and $P_L$ is the Langmuir pressure, which represents the pressure at which the amount of adsorbed methane equals half of the maximum adsorption capacity of methane.

Absolute adsorption isotherms can also be described by the supercritical Dubinin–Radushkevich (SDR) equation, which is based on a pore-filling mechanism (Kaneko and Murata, 1997; Sakurovs et al., 2007; Clarkson and Haghshenas, 2013; Rexer et al., 2013; Tian et al., 2016).