The maturity of Silurian Longmaxi shale in Jiaoshiba, Sichuan Basin: as revealed by laser Raman spectroscopy

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Abstract

Accurate estimates of the thermal maturity of organic matter are important in studies of shale oil and gas, as these data are directly related to the genesis type of shale gas, adsorption capacity of shale and formation of organic pores in organic-rich shale. Longmaxi shale is a major shale gas exploration target in South China and a typical overmature shale gas play. Because Longmaxi shale is Silurian marine strata without vitrinites, it is difficult to determine its maturity accurately. In order to evaluate the maturity of the Longmaxi shale exactly, in this paper, solid bitumen reflectance, basin modeling and laser Raman spectroscopy analyses of solid bitumen were carried out on the shale. The solid bitumen reflectance of Longmaxi shale is range of 2.77–4.14% with a mean of 3.5%, and the corresponding equivalent vitrinite reflectance (EqVRo) is 2.6%; additional information about the maturation is provided by the basin modeling with the constraint of the maximum paleogeothermal about 210–220 °C which was indicated by thermo-acoustic emission measurement, fluid inclusion thermometry and equivalent vitrinite reflectance. In addition, the Raman was applied to Longmaxi shale in Jiaoshiba firstly, and the Raman inter-peak interval between peak G (graphitic band) and peak D (disordered band) is range of 270–279 cm⁻¹, which suggests that equivalent vitrinite reflectance is about 2.67% and is consistent with the results of solid bitumen reflectance, infrared spectrum and basin simulation. Approximate conclusions have been drawn from these different methods, and the thermal evolution of Longmaxi shale in Jiaoshiba area, the largest shale gas field in China, was estimated at approximately 2.5–2.7%, which means that it has reached the overmature dry gas stage. Overall, the findings also imply that Raman spectra of pyrobitumen can be used effectively to evaluate the maturation of the marine shale without vitrinites.

Keywords Laser Raman spectroscopy · Solid bitumen · Thermal maturation · Longmaxi shale · Jiaoshiba in the Sichuan Basin · Vitrinite reflectance

List of symbols

| Symbol | Description |
|--------|-------------|
| SD     | Standard deviation |
| k      | Kurtosis     |
| sk     | Skewness     |
| G      | Graphitic band |
| D      | Disordered band |
| d (G−D) | The Raman inter-peak interval between peak G (graphitic band) and peak D (disordered band) |
| RBS    | Raman band separation |
| FWHM   | Full width at half maximum |
| BRo    | Solid bitumen reflectance |
| EqVRo  | Equivalent vitrinite reflectance |

Introduction

The thermal maturity of shale is of great importance for shale gas exploration (Jarvie et al. 2007; Cardott 2012). The maturity not only has an important impact on the genetic type of natural gas (Rodriguez and Philp 2010; Zumberge et al. 2012; Dai et al. 2014), but also affects the adsorption capacity of shale (Zhang et al. 2012; Hu et al. 2015, 2018) and the formation of organic matter porosity (Bernard...
et al. 2012; Curtis et al. 2012; Bernard and Horsfield 2014; Hu et al. 2017). Hence, accurate estimates of the thermal maturity of shale are critical for shale gas exploration. The petrographic approach that relies on vitrinite reflectance generally is regarded as the most robust analytical approach for maturity determinations. The vitrinite maceral group refers to organic matter derived from the woody tissue of post-Silurian vascular plants. The absence of vitrinite in Longmaxi shale in the Silurian marine stratigraphy in South China makes it difficult to determine the maturity of the shale accurately. Consequently, the lack of maturity information has become a key problem for oil and gas exploration in marine stratigraphy in South China. Longmaxi shale has experienced multi-period tectonic movements, such as the Caledonian, Hercynian, Indosinian, Yanshan, and Himalayan movements, and it also has experienced deep burial and extreme thermal evolution conditions (Guo 1996). There is no vitrinite in Silurian Longmaxi shale, and the solid bitumen reflectance, which is the most widely used estimation method, is usually affected greatly by the genesis and anisotropy of bitumen, which leads to the uncertainty of its reflectance (Landis and Castaño 1995; Petersen et al. 2013). In addition, apatite fission tracks may be not suitable for the analysis of the thermal maturation history of Silurian samples, because the maximum paleo-geothermal level that the Silurian strata experienced is greater than 200 °C (Qin et al. 2008; Zhu et al. 2016), and fission tracks fully anneal at temperatures above 125 °C (Gleadow et al. 1983). Therefore, there is an urgent need to develop an effective method for determining the maturity of Longmaxi shale in southern China.

The Raman spectra of organic matter usually consist of two obvious first-order Raman peaks, namely peak D (termed the disordered band, Raman shift at 1250–1450 cm\(^{-1}\)) and peak G (termed the graphitic band, Raman shift at 1500–1610 cm\(^{-1}\)), and the characteristics of these peaks can reflect the chemical structure of the material and also its degree of thermal alteration (Hu and Wilkins 1992; Kelemen and Fang 2001; Beyssac et al. 2002, 2003; Quirico et al. 2005; Guedes et al. 2010; Jehlička et al. 2003; Liu et al. 2013; Zhou et al. 2014). Previous studies that are relevant have mainly focused on coal and carbonized organic matter in sedimentary-metamorphic rocks and kerogen (Hu and Wilkins 1992; Kelemen and Fang 2001; Beyssac et al. 2002, 2003; Quirico et al. 2005; Guedes et al. 2010). Only a few papers have reported on the characteristics of laser Raman spectroscopy data from natural solid bitumen in sedimentary rocks (Hackley and Lünsdorf 2018) and artificial solid bitumen samples (Zhou et al. 2014); importantly, these studies have revealed that the laser Raman parameters of solid bitumen show robust correlations with maturity. However, it is presently uncertain whether these parameters can be applied successfully to the Longmaxi shale. In this study, solid bitumen from Longmaxi shale in the Jiaoshiba area was analyzed by laser Raman spectroscopy to assess the thermal maturity and the results were compared with the maturity information obtained from solid bitumen reflectance, kerogen infrared spectroscopy and basin simulation.

### Samples and methods

#### Samples

The investigated samples were collected from the Silurian Longmaxi shale, with a thickness of 80–102 m, in the eastern part of the Sichuan Basin (Chongqing, China). Samples were mainly collected from two boreholes (well JY1, well JY4) in the Jiaoshiba area (Fig. 1). The Longmaxi shale is a self-sourced and reservoir system, and the strata is also considered as the source rock for the Wolonghe and Shapingba gas fields, in the eastern part of Sichuan Basin. The Jiaoshiba is the first commercial shale gas field in China. The Longmaxi shale that was deposited in a deep shelf environment during the early Silurian has widespread intervals in the Sichuan Basin. The Longmaxi shale has total organic carbon (TOC) contents ranging from 0.55 to 6.28% with a mean of 2.48%, and the organic matter is mainly amorphous (Dai et al. 2014), which indicates that there is enormous potential for hydrocarbon generation (Chen et al. 2014).

![Fig. 1 Structural sketch of the study region and the sampling locations of wells](image-url)
Reflectance of solid bitumen

Eleven core samples were collected from the two boreholes. Each sample was crushed and then prepared as grain mounts for microscopic analyses under reflected light following ASTM Standard D2797. Random reflectance measurements on solid bitumen grains were performed according to the procedure of ASTM D7704-14 and by means of a 3Y-Leica DMR XP microphotometer. Calibration of the microphotometer systems was carried out by using a YAG (yttrium aluminum garnet) ($R_o = 0.903\%$) standard. For each sample, 50 individual solid bitumen particles were measured and their mean value was taken as the solid bitumen reflectance.

Rock thermo-acoustic emission

The apparatus used for measuring rock thermo-acoustic emissions was composed of a heat loading system, PCI-2 acoustic emission test system and data processing system. The working temperature ranged from 20 to 800 °C. The resonant frequency of the sensor was 1–1000 kHz. The temperature and sound frequency were controlled automatically through real-time monitoring with a signal acquisition system using PCI-2 produced by Physical Acoustics Corporation in America. First, the acoustic emission signals generated by the microcracks induced by the increase in temperature during the experiments were detected by the acoustic emission sensor, and then, the signals were amplified and transmitted to the computer acquisition and analysis system. Five shale samples were collected from well YJ1 at the Silurian Longmaxi Formation in the Jiaoshiba area, and these materials were processed into small solid cylinders with a diameter of 2.5 cm and height of 2–4 cm.

Fluid inclusions

For this study, samples were collected from the calcite veins in the fractures of Longmaxi shale at a depth of 2413 m in well JY1 in the Jiaoshiba area. The samples are ground into two-sided polished thin sections for microscopic observation. The experimental instrument used was a NIKON-LV two-channel fluorescence microscope equipped with a Linkam-THMSG600 freezing and heating stage. With this temperature measurement system, the error was ±0.1 °C. The selected salt water inclusions were heated on the THMS600 stage until they reached the homogenization temperature when the bubbles just disappeared.

Raman microspectroscopy

The Raman spectroscopy for Longmaxi shale was completed at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. A HORIBA-JY Xplora delicate-type multifunctional fully automatic microlaser Raman spectroscopy was used for the Raman spectroscopic measurements. The laser wavelength was 532 nm, the exposure time was 10–40 s, and the scanning wave number ranged from 1000 to 3200 cm$^{-1}$. For each sample, five to six individual solid bitumen particles were measured. Curve fitting for the determination of spectral parameters was performed with the Gauss–Lorentz model in the instrument software, and all of the analytical and calculation procedures were conducted following the methods described in an earlier paper (Zhou et al. 2014).

Results and discussion

The thermal maturity of Longmaxi shale

Vitrinite reflectance is the most robust of the many techniques available for determining the thermal maturity of organic matter (Hackley and Cardott 2016). Nevertheless, this method is not suitable for the Silurian Longmaxi shale because the vitrinite does not exist in sediments deposited before the Devonian period. Solid bitumen, a product of hydrocarbon generation from kerogen and/or the alteration of once-liquid hydrocarbon, undergoes similar chemical reactions to those that occur in vitrinite, and so the reflectance of solid bitumen under oil immersion also increases with increasing thermal maturity; the reflectance of solid bitumen is sometimes used as a thermal proxy in place of the vitrinite reflectance (Riediger 1993; Petersen et al. 2013; Tian et al. 2013; Sanei et al. 2015; Mählmann and Bayon 2016; Yang 2016; Hackley and Lewan 2018). The Longmaxi shale contains abundant solid bitumen (Dai et al. 2014; Yang 2016; Borjigin et al. 2017), and therefore, the solid bitumen reflectance can be used to study the thermal evolution of organic matter in Longmaxi shale. The origin of solid bitumen in shale formation is complex (Rogers et al. 1974; Jacob 1989). The cracking of liquid hydrocarbons, the shale generated and retained in the shale because of the poor hydrocarbon expulsion effectiveness, represents one of the most important genesis mechanisms (Stasiuk 1997; Hao et al. 2008). In the evolution process of bitumen, through aromatization and condensation reactions, the bitumen reflectance increased gradually, and such a trend was found in both natural and artificial maturation series as the organic matter maturity increased (Xiao et al. 1991; Schoenherr et al. 2007; Hackley and Lewan 2018). Therefore, the solid bitumen reflectance can be used as an important maturation proxy of organic matter and has a clear positive linear correlation with the vitrinite reflectance (Feng and Chen 1988; Jacob 1989). However, the solid bitumen and vitrinite usually show systematically different signatures with increasing...
maturity (Hackley and Lewan, 2018). In both natural and artificial maturation series, the solid bitumen reflectance is lower than the reflectance of co-occurring vitrinite at low thermal maturities ($R_o < 1.0\%$) (Hackley and Lewan 2018) and vitrinite reflectance is lower than the reflectance of co-occurring solid bitumen at higher maturities ($R_o > 1.0\%$) (Feng and Chen 1988; Jacob 1989). Usually, in order to facilitate comparisons of different regions and different samples, the solid bitumen reflectance ($BR_o\%$) can be converted to the equivalent vitrinite reflectance ($R_{eqv}\%$). An empirical formula for converting the solid bitumen reflectance into an equivalent vitrinite reflectance was first proposed by Jacob (1989), and it is expressed as follows:

$$R_{eqv} = 0.618 BR_o + 0.4 \quad (1)$$

This formula has been used widely (Wang and Simoneitb 1995; Obermayer et al. 1997; Xiao et al. 2000; Suchy et al. 2002; Liu et al. 2013; Ji et al. 2015; Tan et al. 2015; Zhang et al. 2015; Kerimov et al. 2017).

An empirical equation for converting solid bitumen reflectance into equivalent vitrinite reflectance was also established by Landis and Castaño (1995), who have measured a large number of samples mainly in coal-bearing strata of the Upper Carboniferous (Pennsylvanian). The correlation equation is:

$$R_{eqv} = 0.917BR_o + 0.376 \quad (2)$$

Although these two empirical equations are both based on geological samples, which contain vitrinite and solid bitumen simultaneously, there are obvious differences between these expressions, which may be related to their derivation in different sedimentary environments. Notably, kerogen compositions in coal-bearing source rock and marine source rock are different, and thus, the liquid hydrocarbon from the kerogen and the solid bitumen from the liquid hydrocarbon cracking also show huge differences in terms of the composition (Yang 2008; Zhang and Philp 2010). This may lead to a difference in the corresponding reflectance. Hence, the equation established by Landis and Castaño (1995) based on the sample from the coal-bearing strata was not quite suitable for the Silurian marine strata in Sichuan.

Feng (1988) also established a regression equation for solid bitumen reflectance and equivalent vitrinite reflectance, based on samples in Permian from the same Sichuan Basin, and this equation is as follows:

$$R_{eqv} = 0.6569BR_o + 0.3364 \quad (3)$$

Notably, the coefficient here is similar to that of the formula established by Jacob (1989). As Jacob’s formula is widely used, in order to facilitate comparisons, formula (1) was used to calculate the equivalent vitrinite reflectance in this study.

The Silurian Longmaxi shale in the Sichuan Basin has undergone long-term geological evolution and multi-period tectonic movements, and its maturity has reached the overmature stage (Hu and Xie 1997; Liu 2005; Pu 2008). In recent years, the reflectance of solid bitumen has been used as an indicator to study the thermal maturity of the Silurian Longmaxi shale in the Upper Yangtze region extensively. For example, Liu (2005) measured the solid bitumen reflectance of the Silurian Longmaxi shale in the north margin of the Middle and Upper Yangtze region, and the equivalent vitrinite reflectance was found to be 2.8–3.2\%, which indicates that it has reached the overmature stage. Furthermore, Borjigin (2006) reported that the solid bitumen reflectance of the southeast margin of the Upper Yangtze area is 2.28–3.36\%, and its equivalent vitrinite reflectance is 1.83–2.54\% with a mean of 2.19\%, which are values that are indicative of the overmature stage.

The solid bitumen reflectance of Longmaxi shale in the Jiaoshiba area ranges from 2.77 to 4.14\%, and the mean value was 3.5\% (Fig. 2a), which suggests that the thermal evolution of organic matter has reached the overmature stage. The solid bitumen reflectance was converted into the equivalent vitrinite reflectance by the empirical formula of Jacob (1989), and the $R_{eqv}$ ranged from 2.11 to 2.96\%; while the average value was 2.60\% (Fig. 2b), these values also indicated that the shale has reached the dry gas window.

Kerogen is a type of high molecular weight organic matter (OM) that can crack to form oil and gas. The structure of kerogen, or its functional groups, changes regularly during the process of thermal evolution (Tissot et al. 1984). The chemical structure of kerogen and corresponding changes during thermal maturation can be investigated by nuclear magnetic resonance (NMR) spectroscopy (Mao et al. 2010; Agrawal and Sharma 2018). The spectral distribution of vibrational frequencies of kerogen, as detected by infrared spectroscopy, can be used to estimate the relative abundance of different functional groups in kerogen (Li et al. 2007; Han et al. 2013; Wang et al. 2015a). With increasing maturation, the intensity of the aliphatic bands is gradually reduced; meanwhile, the polycyclic aromatic hydrocarbons are further polycondensed, and the intensity of the bands associated with the condensed aromatic hydrocarbons is gradually increased. These changes, i.e., the decrease in the aliphatic bands and the increase in the polycyclic aromatic hydrocarbon bands, can be detected by infrared spectroscopy (Tissot 1984; Ganz and Kalkreuth 1991; Xiao et al. 1998; Pomerantz et al. 2016). Ganz and Kalkreuth (1991) indicated that the absorption peaks of the aromatic C=C bonds will be shifted toward a minimum wavenumber ($W_{min}$) with increasing maturity. Based on more than 100 samples of different kerogens, Ganz and Kalkreuth (1991) established a correlation of vitrinite reflectance with the $W_{min}$ systematically. Infrared spectroscopy analyses of kerogen in the
Longmaxi shales from the Jiaoshiba area showed that the aliphatic bands were exhausted, the aromatic C=C bands appeared medium sized, and the $W_{\text{min}}$ of the aromatic C=C bands ranged from 1580 to 1582 cm$^{-1}$ (Gao et al. 2019). Combined with the established empirical diagram (Ganz and Kalkreuth 1991), the equivalent vitrinite reflectance values were obtained in the range of 2.5–2.7% (Fig. 3). This result is basically consistent with the maturity reflected by the solid bitumen reflectance.

The Raman spectra of solid OM can reflect the chemical structure characteristics and the chemical structure changes with the increasing maturation. Therefore, the laser Raman spectra of OM can be used to evaluate the thermal history of OM in sedimentary rock (Hu and Wilkins 1992; Kelemen and Fang 2001; Beysaes et al. 2002, 2003; Jehlička et al. 2003; Quirico et al. 2005; Guedes et al. 2010; Zhou et al. 2014). Many studies have reported on correlations between Raman spectral parameters and OM thermal maturity; this OM included vitrinite macerals (Liu et al. 2013; Bonoldi et al. 2016; Sauerer et al. 2017) and solid bitumen (Liu et al. 2013; Zhou et al. 2014; Hackley and Lünsdorf 2018). These studies revealed that some laser Raman parameters have definite maturity significance. However, the Raman parameters are influenced by many factors including the peak-fitting method used (Lupoi et al. 2017), the laser wavelength (Lünsdorf and Lünsdorf 2016; Lünsdorf 2016) and the type of OM in both natural and artificial series (Wang et al. 2015b; Hackley and Lünsdorf 2018). The effect of natural and artificial samples on the variability of the Raman response is complicated. There are systematic differences in Raman parameters between natural and artificial series with solid bitumen reflectance values (Hackley and Lünsdorf 2018), as well as similar trends in Raman parameters between natural and artificial series with solid bitumen reflectance values (Wang et al. 2015b; Hackley and Lünsdorf 2018). The source of the difference in the Raman response from these solid bitumen and vitrinite values could have possibly been due to their undetermined differences in carbon chemistry. At the higher reflectances of vitrinite (about 3.5–3.8%), the RBS showed...
a reversal trend; this phenomenon was also reported by Liu et al. (2013). This reflects the complexity of the evolution of OM, and it means that caution is necessary when evaluating the thermal maturity by using Raman spectra.

Jubb et al. (2018) reported that the Raman thermal maturity parameters can vary widely across distances of ≤ 5 μm within the same organic grains because of the chemical heterogeneity, and so additional care must be adopted when estimating the maturation by using Raman spectra. The variability of the Raman response is high in the low maturity samples, while the chemical heterogeneity is lost for samples with higher thermal maturity, which means that the uncertainty will be lower in samples with a higher degree of maturation. As reflected by the solid bitumen reflectance, the Longmaxi shale has reached the dry gas stage, so the Raman thermal maturity should have a less variability.

Previous studies have established empirical formulas for the determination of the equivalent vitrinite reflectance by using Raman parameters (Liu et al. 2013; Wilkins et al. 2014, 2015). For example, based on the linear correlations between the vitrinite reflectance of coals and the RBS and peak height ratios (Dh/Gh), Liu et al. (2013) established two empirical formulas to calculate the equivalent vitrinite reflectance (R_{eqv}%) with the two Raman parameters. From early maturation to high maturation (VR_o < 3.8%), the empirical formula can be regressed between the Raman band separation (d (G–D)) and the equivalent vitrinite reflectance. The correlation equation is:

\[ R_{eqv} = 0.0537d(G–D) − 11.21 \]  

(4) when VR_o > 3.8%, the empirical formula can be regressed between the Raman peak height ratio (Dh/Gh) and the vitrinite reflectance as:

\[ R_{eqv} = 1.1659h(Dh/Gh) + 2.7588 \]  

(5) which can be applied to studies of overmature source rock. Wilkins et al. (2014) also established the RaMM (Raman maturity method) based on a multi-linear regression equation to determine the equivalent vitrinite reflectance from Raman spectra of inertinite, which covers the range of 0.4–1.2% equivalent vitrinite reflectance, and the range can be extended with a second equation to 1.0–2.5% (Wilkins et al. 2015). All of the established equations were based on the Raman spectra of vitrinite or inertinite, and the Raman responses varied between the different OM types present in shale due to the compositional differences among them and their own innate heterogeneity (Beyssac et al. 2003; Henry et al. 2018) (Fig. 4); thus, all of the established equations based on vitrinite might be not suitable for thermal maturity evaluations of source rocks without vitrinite containing solid bitumen.

Raman spectra also showed a robust correlation to the measured solid bitumen reflectance values and were therefore used to construct a regression equation for calculations of BR_o equivalent values, data which were then used to obtain the equivalent vitrinite reflectance. Zhou (2014) and Wang (2015b) reported that when the solid bitumen reflectance was less than 3.8%, in addition to the Raman band separation (d (G–D)), the peak D position (WD) and full width at half maximum of peak D (FWHM-D) also showed a good linear correlation with the solid bitumen reflectance. When the solid bitumen reflectance was more than 3.8%, the Raman peak height ratio (Dh/Gh) also had a good linear correlation with the solid bitumen reflectance. Solid bitumen in different basins may have a different chemical composition or microstructure (Yu et al., 2018), and there may be a different correlations for the Raman parameters and reflectance of solid bitumen. Hence, it is recommended that calibrations be conducted locally for each shale type when using Raman spectroscopy as a thermal proxy because of the differences in solid bitumen carbon chemistry (Hackley and Lünsdorf, 2018).

According to the data for solid bitumen reflectance and Raman parameters in the Sichuan Basin and adjacent areas (Table 1), a linear regression equation for the equivalent

![Fig. 4 The correlation between the Raman band separation and reflectance of vitrinite and solid bitumen](image-url)
reflectance of the solid bitumen (EqBRo, %) was established. The equivalent reflectance of the solid bitumen had a clear linear relationship with the Raman band separation (d (G−D)) (R2 = 0.95), the peak D position (W_D) (R2 = 0.87) and the full width at half maximum of peak D (FWHM-D) (R2 = 0.86) (Fig. 5a, b, c). There was no obvious correlation detected between the equivalent reflectance of the solid bitumen and the Raman peak height ratio (Dh/Gh) (R2 = 0.0018) (Fig. 5d). Therefore, an equation was established between the Raman band separation (d (G−D)) and the equivalent reflectance of the solid bitumen (EqBRo), and the reflectance calculated from Raman parameters can be derived as follows:

\[
\text{EqBRo} = 0.0626d(G−D) − 13.48 \quad (R^2 = 0.95) \quad (6)
\]

Then, combined with the equation of Jacob (1989), the correlation between the laser Raman parameter and the equivalent maturity can be established as follows:

\[
R_{eq} = 0.0386d(G−D) − 7.9306 \quad (7)
\]

According to the occurrence of solid bitumen, there are two types of bitumen in the Silurian Longmaxi shale in the Jiaoshiba area: One is in the form of amorphous filling material in the pores of the shale, generally with a granular structure, and the other is in the form of striped filling material in bedding-parallel microcracks in the shale (Fig. 6). The laser Raman spectra of the solid bitumen displayed two obvious first-order characteristic peaks, which included the D peak distribution at 1328–1339 cm\(^{-1}\) and the G peak distribution at 1605–1612 cm\(^{-1}\), respectively. According to the Raman spectral parameters of the Longmaxi shale and empirical formula (7), the maturity of Longmaxi shale ranges from 2.53 to 2.81% with a mean of 2.67% (Table 2, Fig. 7). This result is consistent with the solid bitumen reflectance data. It indicates that the Longmaxi shale in the Jiaoshiba area has reached the overmature stages.

### The maximum paleo-geothermal level and basin simulation

When rock experiences internal or external stress or deformation, and the energy accumulation reaches a certain level, then part of the strain energy will be released from the energy accumulation zone in the form of stress waves (acoustic). Kaiser (1950) first found the irreversible phenomenon of acoustic emissions in metallic materials and called this the Kaiser effect. Goodman (1963) found that the Kaiser effect also exists in compression tests of rock, and the principle has been widely used in the study of the stress–strain characteristics of rock. When rock is heated, this also can produce a thermal Kaiser effect. In such cases, the rock records the maximum temperature that it had experienced.
throughout its long geological history. If a rock is heated and records the acoustic emission signals, when the temperature exceeds the maximum temperature the rock once experienced, the acoustic emission signals will suddenly increase at that temperature, and then, that temperature can be used to represent the highest temperature once experienced by the rock (Xi et al. 1996; Li et al. 2011). Xi (1996) measured the highest temperature experienced by Panshan inclusions by using the thermo-acoustic emission approach and found that the inclusions had experienced a temperature of 830 °C; this result is very consistent with the 800–860 °C estimate based on single-pyroxene geothermometers and two-pyroxene geothermometers. Zhang et al. (2014) studied the highest paleo-temperatures of the lower Paleozoic marine shale in the western Middle Yangtze area by using thermo-acoustic emission approach and achieved good application effects.

When rocks undergo high-temperature metamorphism or experience a strong extrusion force in the fault zone, the internal structure will be destroyed and the Kaiser effect will disappear. In this study, samples selected for the thermo-acoustic emission analyses were taken from the drill core, where the original structure was not destroyed and the thermal Kaiser effect was not affected. Through the analysis of the relationship between the thermo-acoustic emission characteristics and temperature of the shale samples in the study area, the results showed that the acoustic emission signals of the samples changed significantly with the increase in temperature. The samples from JY1-2 and JY1-4 showed strong signals at the low-temperature stage, which may have been the result of the heterogeneity in the two samples (Li et al. 2011), but the thermal acoustic emission signals still were relatively concentrated. Over, the sudden increase in the accumulative signal was a good indicator of the threshold temperature (Fig. 8). The maximum temperature that the shale experienced was found to range from 203 to 221 °C with mean of 213.3 °C (Table 3).

Fluid inclusions are portion of mineralizing fluid that become trapped in defects or cave-like mineral structures during the growth of the lattice, in which the material is sealed in the minerals. Fluid inclusions have been used widely in studies of petroleum geology. The homogenization temperature of brine inclusions usually is equivalent to or near the capture temperature, which represents the paleo-geothermal
Fig. 6 Photomicrographs of solid bitumen in Longmaxi shale, Jiaoshiba area (a, c, e, g) and Raman spectra of solid bitumen (b, d, f, g) are measured at the black cross “+” in figures (a, c, e, g)
conditions at that time (Emery and Robinson 1993; Lu et al. 2004).

The fluid inclusion microthermometric data indicated that there were two main types of fluid inclusions in the study area, namely methane inclusions and brine inclusions (Fig. 9). The content of brine inclusions was found to be less than that of methane inclusions with a proportion of approximately 30–40%, while the methane inclusions accounted for approximately 60–70%. The shapes of the brine inclusions included square, rhombic, round, oval and irregular shapes, with diameters of 3–7 μm. The inclusions were brown, black-brown or black under the transmission light, and most of the inclusions did not display fluorescence activity, though a few inclusions showed weak blue-white fluorescence, and which is often associated with hydrocarbon-bearing brine inclusions. In regard to the methane inclusions, the shapes included elliptical, square, diamond, polygonal, and irregular shapes with diameters of 1–10 μm, but most of the inclusions had diameters of less than 5 μm. The inclusions had a linear or beaded distribution mostly. The colors usually appeared as brown-light brown, and the liquid hydrocarbon phase showed blue or blue-white fluorescence.

During the tests, it was found that the homogenization temperatures of some brine inclusions reached or even exceeded 280 °C, and these materials did not freeze even if the temperature was reduced to −80 °C. These inclusions were categorized as inhomogeneous fluid inclusions and were excluded when analyzing the homogenization temperatures. In addition, as the temperature increased, a few of the brine inclusions broke; it is thought that leakage occurs after the formation of the inclusion, and thus, these too were excluded when analyzing the homogenization temperature. In this study, 22 effective homogenization temperatures for the brine inclusions were obtained. The inclusion thermometry results were in the temperature range of 190–250 °C.

| Sample ID | Peak D | Peak G | d (G–D) | h (D/G) | R_eqv (%) |
|-----------|--------|--------|----------|---------|-----------|
| J-1       | 1335.52 | 4170.80 | 1610.11 | 6000.78 | 274.60 | 0.70 | 2.67 |
| J-2       | 1333.21 | 3020.37 | 1608.67 | 4168.53 | 275.46 | 0.73 | 2.70 |
| J-3       | 1333.26 | 2830.05 | 1608.81 | 3813.76 | 275.56 | 0.75 | 2.71 |
| J-4       | 1334.07 | 4995.18 | 1608.96 | 7175.87 | 274.88 | 0.70 | 2.68 |
| J-5       | 1334.51 | 4979.31 | 1608.81 | 6993.44 | 274.30 | 0.72 | 2.66 |
| J-6       | 1334.80 | 4509.37 | 1609.53 | 6602.97 | 274.74 | 0.69 | 2.67 |
| J-7       | 1334.65 | 3932.94 | 1608.09 | 5553.97 | 273.43 | 0.71 | 2.62 |
| J-8       | 1335.09 | 5302.59 | 1609.68 | 7779.56 | 274.59 | 0.68 | 2.67 |
| J-9       | 1334.80 | 4240.51 | 1609.10 | 6324.51 | 274.30 | 0.70 | 2.66 |
| J-10      | 1336.24 | 4072.69 | 1609.97 | 5602.62 | 273.73 | 0.73 | 2.64 |
| J-11      | 1335.29 | 4423.72 | 1609.71 | 6291.28 | 274.42 | 0.71 | 2.66 |
| J-12      | 1334.94 | 4508.89 | 1609.97 | 6460.64 | 275.03 | 0.70 | 2.69 |
| J-13      | 1335.95 | 4423.20 | 1609.82 | 6395.14 | 273.87 | 0.69 | 2.64 |
| J-14      | 1334.51 | 4391.30 | 1610.11 | 6338.09 | 275.61 | 0.70 | 2.71 |
| J-15      | 1336.19 | 3903.54 | 1609.41 | 5456.26 | 273.22 | 0.72 | 2.62 |
| J-16      | 1333.74 | 3458.17 | 1609.78 | 4900.69 | 276.04 | 0.74 | 2.72 |
| J-17      | 1335.42 | 3881.80 | 1610.02 | 5640.75 | 274.59 | 0.70 | 2.67 |
| J-18      | 1333.26 | 4840.83 | 1608.45 | 6927.03 | 275.20 | 0.70 | 2.69 |
| J-19      | 1334.51 | 5342.11 | 1609.24 | 7648.02 | 274.74 | 0.70 | 2.67 |

\[ d (G–D) = W_G – W_D, \text{ band separation; } h (D/G), \text{ band intensity ratio; } R_{\text{eqv}} \text{ (\%). calculated reflectance according to the formula } R_{\text{eqv}} = 0.0386(d(G–D)−7.9306) \]
(Fig. 10), and the main peak was located between 210 and 220 °C. The results of inclusion thermometry were basically consistent with the thermal acoustic emission results.

The vitrinite reflectance is one of the most important indicators of thermal maturity, and such data have been used widely in explorations for petroleum resources. Except for time, the evolution of vitrinite is mainly related to the paleo-geothermal conditions. Thus, the vitrinite reflectance can be used to estimate the maximum temperatures that the shale experienced. The use of vitrinite reflectance to estimate the paleo-geothermal conditions had been described in detail by Karweil (1955), Cannan (1974), Hood et al. (1975) and Barker and Goldstein (1990). The time required for the stabilization of OM thermal maturation is about $10^6$–$10^7$ years (Barker and Pawlewicz 1986), and this is a relatively short period of time relative to the geological age on the scale of
millions of years. So time has little influence on the thermal maturation of sedimentary OM, and the maximum burial temperature \( T_{\text{max}} \) is the most influential control during thermal maturation (Barker and Pawlewicz 1986). Barker (1983) has shown that there exists a strong correlation of \( T_{\text{max}} \) and \( R_o \), which can be expressed as follows:

\[
T_{\text{max}} = \frac{\ln(R_o \%) + 0.8324}{0.00683}
\]  
(8)

With an updated compilation of \( T_{\text{max}} \) and \( R_o \) data, Barker and Pawlewicz (1994) improved the correlation equation:

\[
T_{\text{max}} = \frac{\ln(R_o \%) + 1.68}{0.0124}
\]  
(9)

According to the equivalent vitrinite reflectance of 2.5–2.7% discussed above and formula (9), it can be suggested that the maximum paleo-geothermal value was 209–216 °C generally. This result is also consistent with the results of thermo-acoustic emission and fluid inclusion thermometry analyses.

Vitrinite reflectance is a comprehensive reflection of the temperatures and duration of time acting on the strata. Based on the known thermal history, the vitrinite reflectance can be calculated. The most applied model is the EasyR\(_{o}\)% model established by Sweeney and Burnham (1990). Based on the maximum paleo-geothermal value indicated by the thermal-acoustic emission, fluid inclusion thermometry and vitrinite reflectance analyses, the EasyR\(_{o}\)% model was used to simulate the thermal maturity history of Silurian strata in the study area. For the simulation parameters, the ancient surface temperature was set to 18 °C. According to previous studies, the distribution of ancient heat flow was in the range of 45–70 mW/m\(^2\) in this area (Lu et al. 2007). The study area belonged to the intracratonic basin during

### Table 3 Measured results for Longmaxi shale obtained by thermo-acoustic emissions

| Well | Sample ID | Depth (m) | Lithology | Measured highest paleo-temperature (°C) |
|------|-----------|-----------|-----------|----------------------------------------|
| JY1  | JY1-1     | 2365.16   | Shale     | 218.0                                  |
| JY1  | JY1-2     | 2368.30   | Shale     | 217.0                                  |
| JY1  | JY1-3     | 2372.47   | Shale     | 221.0                                  |
| JY1  | JY1-4     | 2391.81   | Shale     | 207.7                                  |
| JY1  | JY1-5     | 2396.91   | Shale     | 203.0                                  |
| Average |         |           |           | 213.3                                  |

### Fig. 9 Photomicrographs under transmitted light of representative inclusions in calcite veins from well JY1. (a) and (b) Representative brine inclusions and methane inclusions were trapped in calcite veins from the sample (Longmaxi shale, measured at a depth of 2413 m) under transmitted light.

### Fig. 10 Frequency histogram of homogenization temperatures determined by inclusions in calcite veins in Longmaxi shale from wells JY1, at a depth of 2413 m
Table 4  The maturity of Longmaxi shale indicated by different methods

| Methods                        | Maturity (%) |
|--------------------------------|--------------|
| Reflectance of solid bitumen   | 2.60         |
| Infrared spectroscopy          | 2.50–2.70    |
| Basin simulation                | 2.60–2.90    |
| Raman microspectroscopy        | 2.67         |

the Cambrian-Silurian, with a paleo-heat flow of 54 mW/m² generally. During the early part of late Permian ages to the Middle Triassic, the study area was influenced by the regional extension and the eruption of the Emeishan basalt, and the paleo-heat flow value increased quickly up to the present day value. Through one-dimensional basin simulations, the maturity of Longmaxi shale was estimated to be range of about 2.6–2.9% which is basically consistent with the above results indicated by the solid bitumen reflectance, infrared spectrum analysis of kerogen and laser Raman spectroscopy data (Table 4).

Conclusions

1. The characteristics of Raman spectroscopic parameters for solid bitumen can be used to study the thermal maturation of organic matter, and in this study, the results for Longmaxi shale were found to be in good agreement with the results from solid bitumen reflectance, infrared spectroscopy and basin modeling.

2. There was a good linear relationship between the equivalent vitrinite reflectance and the Raman band separation \([d (G–D)]\) of solid bitumen, and this relationship can be expressed as follows: \(R_{eqv} = 0.0386 d (G–D) – 7.9306\). The correlation coefficient was as high as 0.98. Therefore, the thermal maturation of solid bitumen in Longmaxi shale can be revealed by Raman spectroscopy. The Raman band separation \([d (G–D)]\) of solid bitumen in Longmaxi shale ranged from 272 to 276 cm\(^{-1}\), and the calculated vitrinite reflectance was about 2.67% according to the above empirical formula.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest. This article does not contain any studies with human participants or animals performed by any of the authors. Informed consent was obtained from all individual participants included in the study.

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