Comparative optical properties of macerals and statistical evaluation of mis-
identification of vitrinite and solid bitumen from early mature Upper
Devonian – Lower Mississippian New Albany Shale: Implications for
thermal maturity assessment

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Abstract

Vitrinite reflectance (VR_o in %) is used routinely to quantify thermal maturity in sedimentary basins. Reflectance and fluorescence of other macerals such as solid bitumen and amorphous organic matter (AOM) can provide an independent means to assess thermal maturity and hydrocarbon generation potential. However, similarity in petrographic characteristics of these macerals, solid bitumen and vitrinite in particular, often causes difficulties with their identification and, consequently, reflectance can be measured on misidentified particles, making reported VR_o values unreliable. The purpose of this study is to compare reflectance values of various macerals in early mature shales and to evaluate the implications of misidentifying solid bitumen and vitrinite for assessing thermal maturity. To address this issue, 15 organic-matter-rich samples from the Upper Devonian/Lower Mississippian New Albany Shale from a corehole in Daviess County, Indiana, were selected. These samples were chosen because they had distinct and easily identified AOM, solid bitumen, vitrinite, and inertinite particles, allowing for statistically relevant comparisons.

VR_o values (0.57 to 0.65%) of the studied sample suite cover the early mature stage, and expressed no trend with depth. In comparison, reflectance values of solid bitumen (BR_o) and AOM ($AOMR_o$) from the same samples are lower, and range from 0.44 to 0.52% and 0.27 to 0.31%, respectively. These differences are accompanied by corresponding differences in chemistry of macerals as demonstrated by the micro-FTIR technique. Specifically, compared to vitrinite and inertinite, solid bitumen shows lower aromaticity, and compared to AOM and alginite, it exhibits shorter aliphatic chains. Reflectance was observed to vary systematically; samples having higher VR_o also feature

elevated solid bitumen and AOM reflectance values. The relationship between vitrinite and solid bitumen can be expressed by the following equation: vitrinite reflectance equivalent (VR_oE in %) = $(0.83 \times BR_o) + 0.22$, whereas for vitrinite and AOM, $VR_oE = (0.84 \times AOMR_o) + 0.38$. Statistical evaluation of the differences in reflectance values caused by maceral misidentification indicates that in extreme cases, when a petrographer cannot distinguish between vitrinite and solid bitumen, the reflectance can be shifted by 0.06–0.09%. For this set of samples, such a difference could shift maturity assessment from early mature to immature. In more common cases, when the analyst can distinguish between the macerals but has difficulties with their overlapping reflectance interval, the reflectance difference that results from misidentification is only within a 0.0–0.02% range. Therefore, if the level of uncertainty in maceral identification can be determined, the calculation of VR_oE values from measured BR_o , can reduce inaccuracy in VR_o values for interpreting the thermal histories of sedimentary basins, which, in turn, is essential for the assessment of oil and gas resources and for building a successful exploration model.

Keywords: reflectance; vitrinite; solid bitumen; New Albany Shale; misidentification; maturity assessment

1. Introduction

Organic petrography has broad application to shale petroleum systems, including determination of thermal maturity, which is critical to hydrocarbon prospecting (e.g., Ma and Holditch 2015; Hackley and Cardott, 2016). Vitrinite reflectance (VR_o in %) is routinely used to quantify thermal maturity in sedimentary basins. However, interpretation of thermal maturity from VR_o measurements is limited by various pitfalls, which include (1) suppression of VR_o (perhydrous vitrinite; Price and Baker, 1985; Wilkins et al., 1992), (2) not recognizing caved vitrinite from shallower zones in a borehole, (3) misidentification of vitrinite, and (4) insufficient measurements resulting in statistically invalid results (Hackley and Cardott, 2016). VR_o is especially prone to errors in organic-rich marine source rocks that lack or contain little land plant material. Therefore, maturity for such source rocks is often interpolated from VR_o values measured in organic-rich units above and below the marine source rock (e.g., Ma and Holditch, 2015).

Reflectance and fluorescence of other macerals such as solid bitumen, amorphous organic matter (AOM), inertinite, and alginite can provide additional or supporting data for evaluating thermal history. However, petrographic distinction of macerals, especially if they occur as very small particles or in low abundances, is difficult, and it becomes a major problem when the macerals occur within reflectance ranges overlapping each other (He et al., 2002; Hackley et al., 2015). For example, reworked vitrinite, vitrinite from cavings, low-reflecting inertinite, and solid bitumen can all be misidentified as indigenous vitrinite (Dow and O'Connor, 1982). In particular, misidentification of vitrinite and solid bitumen is very common because they often appear similar under a

microscope, having similar color and a smooth surface. Because of these similarities, misidentification of vitrinite and solid bitumen has been frequently mentioned as the reason for doubtful maturity assessments (Dow and O'Connor, 1982; He et al., 2002; Hackley et al., 2013; Ryder et al., 2013). Solid bitumen is a secondary maceral genetically defined as solid phase accumulations of hydrocarbons generated in source rocks (Jacob, 1989; Landis and Castaño, 1995). Disseminated solid bitumen can exhibit anisotropic, granular, or relatively uniform (homogenous) forms (Gentzis and Goodarzi, 1990; Landis and Castaño, 1995; Schoenherr et al., 2007). Unlike minerals and kerogen macerals, solid hydrocarbons are not framework matrix constituents of rocks but typically accumulate along bedding planes or occur disseminated in pores (Landis and Castaño, 1995; Mossman and Nagy, 1996). While solid bitumen is easy to recognize when it covers larger areas aligning minerals or filling larger pores and fractures, it often becomes undistinguishable from vitrinite when it occurs as small particles.

Each maceral has a unique path of reflectance evolution as thermal stress increases (Dow and O'Connor, 1982; He et al., 2002). In addition, relationships between reflectance of various macerals change with maturity. For example, Jacob (1989) concluded that solid bitumen reflectance (BR_o in %) was lower than VR_o when VR_o was below 1.0%, approached that of VR_o in the 1.0-1.1% range, and was higher than VR_o when BR_o reached 1.1% or higher. Various relationships were also observed by other researchers (e.g., Robert, 1988; Katz et al., 1988; Bertrand, 1993; Landis and Castaño, 1995; Petersen et al., 2013). Robert (1988) suggested that VR_o and BR_o differed by only about 0.1 to 0.2% in the VR_o range of 0.5 to 1.5%. In turn, Landis and Castaño (1995) found that BR_o was lower than VR_o when VR_o was below 4.0%, but they were apparently

similar when VR_o reached above 4.0%. Considering differences between reflectance of vitrinite and solid bitumen, mistakenly measuring solid bitumen as vitrinite generally results in underestimation of maturity for rocks having VR_o values of up to ~1% (e.g., see Jacob, 1989). Indeed, it has been reported that misidentification between vitrinite and solid bitumen in Devonian shale in the Appalachian Basin (Ryder et al., 2013) led to lower reflectance values and, consequently, to the assessment of lower maturities (i.e. immature stage) compared to the information obtained from biomarker ratios and bulk geochemical data pointing to a position within the oil window (Hackley et al., 2013). Similarly He et al. (2002) suggested that some anomalously low maturity values (0.45 to 0.57%) in their Jurassic source rocks' overpressured zone were due to inaccurate identification of vitrinite, where biomarker maturity and predicted maturity values indicated vitrinite reflectance equivalent between 0.8 and 2.2%. Clearly, a systematic, statistically-sound comparison of reflectances of different macerals could be helpful to create a better understanding of maceral differentiation and maturity determination.

The purpose of this study is to (1) characterize and investigate the reflectance relationships between vitrinite and solid bitumen, AOM, and inertinite in organic matter-rich, early mature Upper Devonian/Lower Mississippian New Albany Shale (NAS), (2) statistically evaluate how misidentification between vitrinite and solid bitumen can influence their final mean reflectance values, and consequently the assessment of thermal maturity, and (3) evaluate the applicability of commonly used equations to calculate VR_o equivalence from BR_o for the shales studied. This is especially important for marine carbonate and pre-Devonian source rocks that commonly do not contain vitrinite, and where BR_o is measured and calculated into VR_o as the thermal maturity indicator. In

addition, micro-FTIR (Fourier Transform Infrared) spectroscopy is used to investigate whether differences in reflectance between macerals are also reflected in their chemical structures.

1.1 Brief geological background

The NAS occurs in the Illinois Basin in Illinois, Indiana, and western Kentucky (Fig. 1), and consists chiefly of organic-rich brownish-black shale, greenish-gray shale, dolomite, and siltstone (Lineback, 1970; Strapoć et al., 2010) with ages ranging from the Upper Devonian to the Early Mississippian (Fig. 2; Cluff et al., 1981). The NAS is a Type II kerogen sequence with six members: Blocher Member, Selmer Member, Morgan Trail Member, Camp Run Member, Clegg Creek Member, and Ellsworth Member (Figs. 2, 3; Lineback, 1970; Strapoć et al., 2010). VR_o values of the NAS range from 0.5-0.7% at the basin's margins in Indiana to 1.5% in southern Illinois (Fig. 1; Strapoć et al., 2010). The southern part of the basin in southern Illinois and adjacent western Kentucky has the highest thermal maturity and the best conditions for oil generation, although southwestern Indiana also has good hydrocarbon generation potential (Barrows and Cluff, 1984). NAS has been widely researched as a gas play (Barrows and Cluff, 1984; Curtis, 2002; Martini et al., 2003) because of its long-standing gas production in Indiana and Kentucky (Barrows and Cluff, 1984; Hamilton-Smith et al., 1994).

Figure 1. Map of New Albany Shale VR_o in Illinois Basin (compiled by Drobniak and Mastalerz, 2016) based on data from Hasenmueller and Comer (1994), Strapoć et al. (2010) and other unpublished data. The drilling location is marked as a red dot.

Chronostrati-graphic Units					Rock Units						
Global			N. Amer.								
System	Subsystem	Stage	System	Series	GROUP	Formation and Member			Lithology	Thickness Ranges (m)	
Carboniferous	Mississippian	Tournaisian	Mississippian	Osagean	Borden						
				Rockford Limestone							
Devonian	Upper	Famennian	Devonian	Chautauquan	New Albany Shale	Ellsworth Member				0 to 25	
						Clegg Creek Member				22 to 49	
						Camp Run Member
						Morgan Trail Member
	?	Frasnian		Senecan		Selmier Member				6 to 61	
		Blocher Member					2 to 24				
	Middle	Givetian		Erian	Muscatatuck	North Vernon Limestone				0 to 37	
	Eifel-ian										

	Brownish-black shale		Burrows
	Greenish-gray shale		Pyrite
	Gray to dark-gray shale		Spore
	Limestone		

Figure 2. Lithostratigraphy of New Albany Shale in Indiana (after Strapoć et al. (2010) and references therein).

Figure 3. Stratigraphy, depth and gamma ray log of the section studied. The locations of samples (S1-S15) collected for maceral reflectance measurements from drilled core are marked as stars. The Gamma ray log values are not indicated where the signal is off-scale (> 150).

2. Samples and methods

To characterize organic matter populations, 15 samples were selected from a recently drilled core in Daviess County, Indiana (Fig. 1). The samples came from a ~530 to 564 m depth (1739–1850 feet) interval, covering all members of NAS (Table 1; Fig. 3).

Table 1. List of samples and their stratigraphic positions, depths, total organic carbon (TOC) contents, and number of reflectance measurements collected on macerals. The target number of measurements for each maceral was 50. Fewer than 50 measurements on AOM or inertinite are available from those samples where these macerals were sporadic (modified from Mastalerz et al., 2016); n.d. – not determined.

Sample	Depth (m)	Stratigraphic Unit	TOC (wt. %)	Number of Reflectance Measurements			
				Vitrinite	Solid bitumen	AOM	Inertinite
1	533.7-534.0	Ellsworth Member	15.23	50	50	50	50
2	534.9-535.2	Clegg Creek	8.63	50	50	50	50
3	536.1-536.4	Clegg Creek	n.d.	50	50	4	50
4	537.1-537.4	Clegg Creek	9.79	50	50	50	50
5	538.6-538.9	Clegg Creek	11.25	50	50	50	50
6	539.8-540.1	Clegg Creek	10.88	50	50	50	50
7	541.1-541.6	Clegg Creek or Morgan Trail	9.99	50	50	50	50
8	543.2-543.5	Morgan Trail/Camp Run	5.9	50	50	6	50
9	545.0-545.3	Morgan Trail/Camp Run	n.d.	50	50	7	4
10	548.6-548.9	Morgan Trail/Camp Run	n.d.	50	50	0	6
11	550.5-550.8	Morgan Trail/Camp Run	5.01	50	50	2	5
12	553.8-554.1	Morgan Trail/Camp Run or Selmier	7.34	50	50	50	50
13	556.6-556.9	Selmier	n.d.	50	50	0	10
14	559.6-559.9	Blocher	n.d.	50	50	7	8
15	563.3-563.6	Blocher	7.69	50	50	1	50

2.1 Organic petrology

Organic petrographic techniques used in this study include visual maceral examination in reflected white and fluorescent light, and reflectance measurements of vitrinite, solid bitumen, AOM, and inertinite. A Zeiss Photoscope 3 reflected light microscope, a Leica DM 25000 P with a TIDAS PMT IV attachment, and oil immersion objectives were used to measure reflectance of different macerals. Sample preparations and measurements followed standard organic petrography procedures (ICCP, 1975; Strapoć et al., 2010; American Society for Testing and Materials (ASTM, 2016). For each sample, 50 random reflectance measurements were obtained on vitrinite and solid bitumen. Whenever possible, 50 measurements were obtained for AOM and inertinite, but several samples had few AOM and inertinite, and therefore limited the number of available measurements (Table 1).

2.2 A statistical approach to solid bitumen and VR_o measurements

Misidentification between vitrinite and solid bitumen in low maturity Devonian rocks is a common problem with reflectance measurements, and a frequently mentioned cause for questionable maturity determination (e.g., Hackley et al., 2013; Ryder et al., 2013). In the suite of samples selected for this study, both solid bitumen and vitrinite were common, typically easy to identify, and provided an opportunity to statistically evaluate differences in reflectance between various components, to analyze the maturity-related consequence of misidentification of the components, and to introduce a correction based on the level of misidentification.

With regard to the level of misidentification, the upper limit (i.e. worst scenario where the largest correction would be needed) would be the extreme case when a petrographer would misidentify all vitrinite as solid bitumen or all solid bitumen as

vitronite. In turn, the lower limit with no required correction would be the case when a petrographer is confident in all the measurements of both solid bitumen and vitronite.

Assuming that it is equally likely (1) for a petrographer to misidentify macerals (vitronite and solid bitumen in particular), and (2) that misidentification most frequently happens for the overlapping reflectance range, a statistical approach based on the probability density function (PDF) to make weighting adjustment to reflectance measurements that fell into the range where reflectance of solid bitumen and vitronite overlap is proposed, and subsequently a weighted average for each maceral is calculated.

Categorizing measurements into solid bitumen or vitronite populations can be regarded as a binary response model (Agresti and Kateri, 2011). In this model, each given measured value is categorized as being one of the two macerals (i.e. solid bitumen or vitronite). The common approach to fit a PDF to this binary dataset is to use either logistic regression or probit regression depending on how the data are distributed (Aldrich and Nelson, 1984). However, given that the original BR_o and VR_o measurements in samples follow a normal distribution, Gaussian functions based on their mean and standard deviation are a good approximation to their PDFs (Brownlee, 1965). Therefore, instead of using the binary regression model, it is better to derive the weights based on the overlap area between the two PDFs from solid bitumen and vitronite. Then, the measurements within the overlapping reflectance range correspond to two different probabilities: (1) a probability of a specific measurement being BR_o ; and (2) a probability of a specific measurement being VR_o (named P_{sb} and P_v , respectively). Following the same idea of deriving the binary dataset, and assuming that a specific reflectance value in the overlapping reflectance range belongs either to solid bitumen or vitronite, the weight of

the measurement from solid bitumen particles as $P_{sb} / (P_{sb} + P_v)$ and the weight of the measurement from vitrinite particles as $P_v / (P_{sb} + P_v)$ were defined. In this way, both of the weights have the same form as link functions in a logistic regression or probit regression (Aldrich and Nelson, 1984), and thus can be regarded as the probability of the measurements concerning one of the two macerals. With these weights defined, the weighted average and weighted standard deviation of BR_o and VR_o are calculated to obtain the corrected reflectance values.

The statistical approach to correct BR_o and VR_o essentially involves producing weighted averages and weighted standard deviations of BR_o and VR_o from their initial averages and standard deviations. It may be possible, however, that the initial reflectance distributions (i.e. the initial averages and standard deviations) are biased because of the presence of misidentified macerals. Then, although being reduced, some bias will remain in the corrected reflectance. To minimize this effect, the aforementioned statistical approach should be implemented iteratively to further reduce the initial bias. Within each step of the iteration, the weighted averages and weighted standard deviations from the previous step are used to update the two PDFs for solid bitumen and vitrinite, respectively. Then, a new set of weights is calculated to correct for less biased BR_o and VR_o . Consequently, the effect from the bias of the initial distribution decreases gradually with the iteration. This iteration terminates when the updates of weighted averages become very small, which means the initial bias can hardly be further reduced with this statistical approach. In such cases, the final weighted average was used as the definitive corrected values.

2.3 Geometric mean functional regression

Empirical reflectance conversion is widely used to infer the reflectance of vitrinite from the reflectance measurements of solid bitumen among samples lacking vitrinite. Previous studies used a linear regression equation to build a relationship between reflectance values of solid bitumen and vitrinite (Jacob, 1989; Landis and Castaño, 1995; Schoenherr et al., 2007). In this study, reflectance of solid bitumen was measured and recalculated into VR_oE following the equations of Jacob (1989), Landis and Castaño (1995) and Bertrand and Malo (2001) to compare to measured VR_o values and to test the applicability of commonly used equations for the sample suite studied. Having reliable reflectance data both on vitrinite and solid bitumen, a linear regression equation to make a prediction of VR_o from measured BR_o was generated. However, an ordinary linear regression method either makes a predictive regression of Y based on X, or a predictive regression of X based on Y. Those two predictive regressions minimize the sum of the squares of the vertical and horizontal distances, respectively, from the points to the regression line. The assumption behind them is that either the measurements of X or Y are accurate. In this case, the X represents the reflectance of solid bitumen and the Y represents that of vitrinite, and both are considered to have equal uncertainties. To justify the uncertainties in the regression, a functional regression method (also known as standard major axis regression or reduced major axis regression) was used (Teissier, 1948; Ricker, 1973). Teissier (1948) suggested applying the same principle by finding the line which minimized the sum of the products of the vertical and horizontal distance of each point from the line. Following Ricker (1973), a geometric mean functional regression to build a new empirical reflectance conversion was applied. Geometric mean

functional regressions are built between measured reflectances of vitrinite *versus* solid bitumen, and also vitrinite *versus* AOM.

2.4 Micro-FTIR

Micro-FTIR measurements used a Nicolet 6700 spectrometer connected to a Nicolet Continuum microscope operating in reflectance mode, with the ability to characterize areas as small as $30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$. The infrared objective used was $15\times$. Further details about instrumentation were presented by Chen et al. (2012, 2013). Micro-FTIR spectra were obtained in reflectance mode at a resolution of 4 cm^{-1} collecting 1200 scans per sample and using a gold plate standard as background. The spectra cover a wavenumber range of 650 cm^{-1} to 4000 cm^{-1} . The OMNIC program was used for spectral deconvolution, curve-fitting, and determination of peak integration areas. Reflectance micro-FTIR spectra were subjected to Kramers-Kronig transformation (Kronig, 1926; Kramers, 1927; Mastalerz and Bustin, 1997). Peak assignments within spectra were based on Painter et al. (1981, 1985), Wang and Griffiths (1985), and Chen et al. (2014).

3. Results

3.1 General organic matter characteristics

All samples used in this study are organic matter-rich, dark grey shales typical of the Type II kerogen sequence of NAS (Lineback, 1970; Cluff et al., 1981; Strapoć et al., 2010). Organic matter is dominated by AOM (amorphinite, bituminite) and alginite. Terrestrial organic matter in the form of vitrinite and inertinite is less common but distinct. Solid bitumen is present in all samples. VR_o , ranging from 0.57 to 0.65% (Table 2) indicates an early mature stage consistent with previous NAS studies (Barrows et al., 1979; Barrows and Cluff, 1984; Van Berkel et al., 1989; Strapoć et al., 2010).

AOM, solid bitumen, vitrinite and inertinite were selected for detailed comparison of reflectance distribution. Solid bitumen and vitrinite were of particular importance for this comparison, and fifty reflectance measurements were collected on each of them in all samples (typically 20 to 30 measurements are considered statistically adequate for organic matter, Barker and Pawlewicz, 1993; ASTM, 2012). AOM and inertinite had fewer measurements in some samples because either they were rare (inertinite) or did not have large, good-quality areas for measurements (AOM). Only particles identified with high confidence were measured in order to not introduce uncertainty in the basic identification (Fig. 4). AOM typically occurs admixed in the matrix (matrix bituminite) or is concentrated in lenses or layers of diffuse to massive character. Under reflected white light, AOM is dark grey in color and shows weak to no fluorescence. Even though several varieties of AOM can occur in shales (e.g., Thompson and Dembicki, 1986), AOM in the samples studied is relatively homogeneous, majority corresponding to bituminite type I (Teichmüller, 1986). Reflectance was measured on massive lenses or layers appearing free of mineral matter (Fig. 4A, B). Solid bitumen occurred as pore filling, often aligning with mineral grains (Fig. 4C, D), and reflectance was measured only on particles that, because of their shape, left no doubt that it was a secondary maceral that was filling available spaces. With regard to origin, it likely represents pre-oil bitumen (Curiale, 1986). Vitrinite appeared as distinct particles (Fig. 4E, F) of a good, distinguishable size, and often in association with inertinite. Inertinite was common in some samples and occurred as fusinite, semifusinite, and smaller inertodetrinite (Fig. 4G, H).

Mean values, standard deviations, and numbers of reflectance measurements for these four macerals are presented in Tables 1 and 2. Comparison among the mean reflectance of each maceral clearly shows an ascending order in the sequence of AOM, solid bitumen, vitrinite, and inertinite (Table 1, 2). Mean reflectance of AOM presents a narrow range from 0.27 to 0.31% (Table 2; Fig. 5). Reflectance of solid bitumen within each sample follows a normal distribution with mean values ranging from 0.44 to 0.52% and standard deviations below 0.061 (Table 2; Figs. 5, 6). The reflectance of vitrinite also follows a normal distribution and its mean values range from 0.57 to 0.65% (Table 2, Figs. 5, 6). Inertinite is common in most samples. Its mean values range from 1.09% to 1.56%. Because of different macerals present in the inertinite group, standard deviations of reflectance of inertinite are significantly larger than those of other macerals (0.11 to 0.64%).

Comparison of the reflectance distribution of AOM, solid bitumen, vitrinite, and inertinite (Fig. 5) shows that (1) there is minimal overlap between reflectance of AOM and solid bitumen; (2) there is a larger overlapping range between reflectance of solid bitumen and vitrinite; (3) there is minimal overlap between reflectance of vitrinite and inertinite; and (4) there is no overlap between reflectance of AOM and inertinite. Overlap between reflectance values of AOM *versus* solid bitumen, and vitrinite *versus* inertinite is almost negligible, and could be practically eliminated by deleting a few of the smallest and largest values that could result from misidentification, even though great care was taken during analysis. Clearly, the main issue that can influence maturity assessments is an overlap between reflectance of solid bitumen and vitrinite. In the samples, the overlapping reflectance range for these two macerals is generally between ~0.44 to

0.60% (Fig. 5); this range is defined by the lowest value of VR_o and the highest value of BR_o . The percent of reflectance measurements within the overlapping range of vitrinite and solid bitumen varies widely among the samples (Table 3), ranging from 4 to 86% for solid bitumen, and from 4 to 72% for vitrinite. The percentage of overlap in solid bitumen is higher than that of vitrinite.

3.2 Statistically corrected reflectance

To evaluate the influence of maceral misidentification on vitrinite and solid bitumen mean reflectance values in early mature samples, it was first assumed that a petrographer was not able to distinguish between them and that all the particles were identified either as vitrinite or solid bitumen. Following this assumption, Table 4 shows the calculated average reflectance based on 100 measurements (i.e. vitrinite + solid bitumen points) as well as the differences between this average and the original averages of solid bitumen and vitrinite. The overall difference ranges from 0.06 to 0.09% and represents the upper limit of biased reflectance estimation of solid bitumen and vitrinite; for an equal number of measurements, this difference is the same for both macerals. In other words, in early mature samples, if a petrographer could not recognize solid bitumen and measured solid bitumen as vitrinite in these samples, the average VR_o values could be underestimated by 0.06 to 0.09%. In turn, if all particles were treated as solid bitumen, the BR_o would be overestimated by 0.06 to 0.09%.

Such cases of an inability to distinguish vitrinite from solid bitumen are extreme and unlikely to occur for experienced petrographers. Most common cases would misidentify only some particles and, as mentioned earlier, solid bitumen/vitrinite particles within the overlapping reflectance ranges would be most prone to misidentification.

There is some overlap of reflectance values for vitrinite and solid bitumen for all samples (Fig. 5, Table 4). Therefore, for practical purposes, it is more important to know how misidentification of solid bitumen/vitrinite particles in the overlapping range will influence the estimate of maturity.

To address this issue, we used the statistical method based on PDF to correct the mean reflectance of solid bitumen and vitrinite in each sample. All samples had 50 measurements made on both macerals. For each sample, the original and corrected PDFs had been generated. The comparison between mean values and standard deviations before and after correction are shown in Table 3 and Fig. 6. Having the two PDFs generated, the overlap of the 95% confidence interval (i.e. two times the standard deviation) of each PDF can be used to define another statistical estimate of the overlapping range, which is

$$[\mu_{VR} - 2\sigma_{VR}, \mu_{BR} + 2\sigma_{BR}], \quad (1)$$

where μ_{BR} and μ_{VR} are the averages of measured BR_o and measured VR_o , and σ_{BR} and σ_{VR} are the standard deviations of measured BR_o and measured VR_o . This statistical overlapping range is not necessarily the same as the previous overlapping range defined by measured values. The difference between the two values ($\mu_{BR} + 2\sigma_{BR}$ and $\mu_{VR} - 2\sigma_{VR}$) defines the statistical extent of overlap. Fig. 7 reveals that the total correction (i.e. correction of solid bitumen plus vitrinite) has a positive relationship with the statistical extent of overlap (i.e. $[\mu_{BR} + 2\sigma_{BR}] - [\mu_{VR} - 2\sigma_{VR}]$; Table 3), whereas individual corrections for either of the two macerals have no apparent relationship with this statistical extent of overlap. For the samples studied, the correction for the average reflectance of solid bitumen ranges from 0 to 0.02%, and that of vitrinite ranges from 0 to 0.02% (Table 3). Samples 1, 5, 6, 7 and 8 are examples of a relatively large correction

(0.02%) for mean BR_o , and sample 1 is an example of a relatively large correction (0.02%) for mean VR_o . Corrected values are higher than corresponding original values in vitrinite, but they are lower for solid bitumen. The absolute value of correction for solid bitumen is higher than that for vitrinite within the same sample; for example, solid bitumen decreased by 0.02% and vitrinite increased by 0.00% in sample 5 (Table 3).

Inertinite and AOM are much easier to identify than solid bitumen or vitrinite because of their different microscopic appearance and, in most cases, distinctly higher (inertinite) or lower (AOM) reflectance. However, a small overlap could also happen between AOM and solid bitumen, as well as between vitrinite and inertinite. The percentages of those measurements in the overlapping range are ubiquitously lower than 10%, thus are considered to have limited influence on both of the mean values.

3.3 Relationship between reflectance values of vitrinite, solid bitumen, and AOM

The presence of distinct AOM, solid bitumen, and vitrinite in our samples created an opportunity to investigate the relationship between the reflectance values of these three macerals. Fig. 8 shows the relationship between vitrinite and AOM reflectance values, as well as the relationship between vitrinite and solid bitumen reflectance values. The linear regression equation of reflectance of vitrinite is: $VR_oE = (0.83 \times BR_o) + 0.22$, with coefficient of determination $R^2 = 0.68$. Our regression equations from NAS samples were compared with three other published empirical transfer functions that calculate VR_o from solid bitumen from other environments: (1) $VR_oE = (0.618 \times BR_o) + 0.4$ (Jacob, 1989); (2) $VR_oE = (BR_o + 0.41)/1.09$ (Landis and Castaño, 1995); and (3) $VR_o = (BR_o - 0.059)/0.936$ (Bertrand and Malo, 2001). The calculated VR_oE values from the first two equations are higher than the measured reflectances in our samples (Table 5), with those

based on Jacob's (1989) equation being closer to the measured VR_o values. In turn, Bertrand and Malo's (2001) equation yielded lower reflectances compared to the measured VR_o values (Fig. 8).

To compare reflectance of AOM to that of vitrinite, only samples with 50

Figure 4. Photomicrographs of typical New Albany Shale macerals. A and B - examples of AOM; C and D - examples of solid bitumen; E and F - examples of vitrinite, and G and H - examples of inertinite. Reflected white light, oil immersion.

Figure 5. Histograms of maceral reflectances from selected samples. All panels share the same legend as shown in panel A. Panels A, D, G, J, and M show histograms of measured reflectances of AOM, solid bitumen, vitrinite, and inertinite. For better comparison, panels B, E, H, K, and N show histograms of measured reflectances of solid bitumen and vitrinite alone, and panels C, F, I, L, and O show histograms of measured reflectances of AOM and inertinite alone.

Figure 6. Histogram of vitrinite and solid bitumen random reflectance values in selected samples. The X-axis shows the measured maceral reflectance (%), the left Y-axis shows the number of measurements in their corresponding reflectance (%), and the right Y-axis shows the probability density for each measurement interval. Dashed and solid lines represent original and corrected PDFs in each sample.

Table 2. Measured maceral (i.e. solid bitumen, vitrinite, AOM, and inertinite) mean random reflectance values and their standard deviations, along with corrected solid bitumen and vitrinite mean reflectance values and their standard deviations, and corresponding differences in comparison to original measured values. BR_o = solid bitumen reflectance (%); BR_ostd = solid bitumen reflectance standard deviation; VR_o = vitrinite reflectance (%); VR_ostd = vitrinite reflectance standard deviation; IR_o = inertinite reflectance (%); IR_ostd = inertinite reflectance standard deviation; AOMR_o = amorphous organic matter reflectance (%); AOMstd = amorphous organic matter reflectance standard deviation; n.d. = not determined.

Sample	Measured BR _o (%)	BR _o std	Measured VR _o (%)	VR _o std	Measured IR _o (%)	IR _o std	Measured AOMR _o (%)	AOMstd
1	0.49	0.045	0.63	0.073	1.24	0.384	0.31	0.031
2	0.45	0.050	0.61	0.067	1.56	0.521	0.27	0.035
3	0.46	0.047	0.61	0.046	1.27	0.469	0.28	0.017
4	0.46	0.037	0.61	0.045	1.43	0.495	0.27	0.029
5	0.48	0.053	0.61	0.049	1.36	0.640	0.29	0.032
6	0.52	0.061	0.65	0.054	1.34	0.509	0.31	0.036
7	0.49	0.052	0.63	0.054	1.31	0.437	0.28	0.041
8	0.46	0.060	0.63	0.063	1.21	0.345	0.28	0.039
9	0.45	0.039	0.58	0.057	1.09	0.111	0.28	0.024
10	0.45	0.030	0.61	0.047	1.06	0.468	n.d.	n.d.
11	0.45	0.039	0.59	0.047	1.10	0.271	0.31	0.014
12	0.46	0.044	0.59	0.038	1.20	0.436	0.27	0.036
13	0.44	0.037	0.57	0.035	1.60	0.504	n.d.	n.d.
14	0.44	0.035	0.58	0.040	1.39	0.361	0.30	0.028
15	0.45	0.045	0.59	0.063	1.19	0.290	0.29	n.d.

Table 3. Measured and corrected solid bitumen and vitrinite mean random reflectance values, along with differences between measured and corrected reflectances. BR_o = solid bitumen reflectance (%); VR_o = vitrinite reflectance (%). The total correction refers to correction of solid bitumen plus vitrinite. The statistical extent of overlap is calculated as $[\mu_{BR} + 2\sigma_{BR}] - [\mu_{VR} - 2\sigma_{VR}]$ (see Equation 1).

Sample	Measured BR_o (%)	Corrected BR_o (%)	BR_o difference between measured and corrected (%)	Measured VR_o (%)	Corrected VR_o (%)	VR_o difference between measured and corrected (%)	Statistical extent of overlap (%)	Total correction (%)	Percentage of reflectance measurements in the overlapping range (%)	
									Solid bitumen	Vitrinite
1	0.49	0.47	0.02	0.63	0.65	0.02	0.096	0.04	86	44
2	0.45	0.45	0.00	0.61	0.62	0.01	0.074	0.01	26	22
3	0.46	0.45	0.01	0.61	0.62	0.01	0.036	0.02	4	26
4	0.46	0.46	0.00	0.61	0.61	0.00	0.014	0.00	4	6
5	0.48	0.46	0.02	0.61	0.61	0.00	0.074	0.02	56	72
6	0.52	0.50	0.02	0.65	0.66	0.01	0.100	0.03	40	64
7	0.49	0.47	0.02	0.63	0.64	0.01	0.072	0.03	20	32
8	0.46	0.44	0.02	0.63	0.64	0.01	0.076	0.03	20	20
9	0.45	0.44	0.01	0.58	0.59	0.01	0.062	0.02	28	8
10	0.45	0.45	0.00	0.61	0.61	0.00	0.000	0.00	8	2
11	0.45	0.45	0.00	0.59	0.59	0.00	0.032	0.00	4	2
12	0.46	0.45	0.01	0.59	0.60	0.01	0.034	0.02	14	10
13	0.44	0.44	0.00	0.57	0.58	0.01	0.014	0.01	10	12
14	0.44	0.44	0.00	0.58	0.58	0.00	0.010	0.00	8	4
15	0.45	0.44	0.01	0.59	0.60	0.01	0.076	0.02	20	12

Table 4. Measured solid bitumen and vitrinite mean random reflectance values based on 50 measurements, and mean reflectance values of solid bitumen plus vitrinite based on 100 measurements. BR_o = solid bitumen reflectance (%); VR_o = vitrinite reflectance (%). Difference* refers to calculated average reflectance based on 100 measurements (vitrinite + solid bitumen points) and the original averages of solid bitumen and vitrinite. The difference is the same for equal point measurements of solid bitumen and vitrinite in a sample.

Sample	BR _o (%)	VR _o (%)	Mean value of all BR _o plus VR _o points (%)	Difference (%)*
1	0.49	0.63	0.56	0.07
2	0.45	0.61	0.53	0.08
3	0.46	0.61	0.54	0.08
4	0.46	0.61	0.54	0.08
5	0.48	0.61	0.55	0.07
6	0.52	0.65	0.59	0.06
7	0.49	0.63	0.56	0.07
8	0.46	0.63	0.55	0.09
9	0.45	0.58	0.52	0.07
10	0.45	0.61	0.53	0.08
11	0.45	0.59	0.52	0.07
12	0.46	0.59	0.53	0.07
13	0.44	0.57	0.50	0.07
14	0.44	0.58	0.51	0.07
15	0.45	0.59	0.52	0.07

Table 5. Measured solid bitumen and vitrinite mean random reflectance values and calculated VR_oE from empirical equations of Jacob (1989); Bertrand and Malo (2001); Landis and Castaño (1995). BR_o = solid bitumen reflectance (%); VR_o = vitrinite reflectance (%).

Sample	BR _o (%), this study	VR _o (%), this study	Calculated VR _o E (%) based on BR _o from empirical equations		
			Jacob, 1989	Landis and Castaño, 1995	Bertrand and Malo, 2001
1	0.49	0.63	0.70	0.83	0.46
2	0.45	0.61	0.68	0.79	0.42
3	0.46	0.61	0.68	0.80	0.43
4	0.46	0.61	0.68	0.80	0.43
5	0.48	0.61	0.70	0.82	0.45
6	0.52	0.65	0.72	0.85	0.49
7	0.49	0.63	0.70	0.83	0.46
8	0.46	0.63	0.68	0.80	0.43
9	0.45	0.58	0.68	0.79	0.42
10	0.45	0.61	0.68	0.79	0.42
11	0.45	0.59	0.68	0.79	0.42
12	0.46	0.59	0.68	0.80	0.43
13	0.44	0.57	0.67	0.78	0.41
14	0.44	0.58	0.67	0.78	0.41
15	0.45	0.59	0.68	0.79	0.42

Figure 7. Scatter plot and linear regression between statistical extent of overlap and total correction. Y-axis refers to the correction of solid bitumen plus vitrinite. X-axis refers to the statistical extent of overlap (i.e. $[\mu_{BR} + 2\sigma_{BR}] - [\mu_{VR} - 2\sigma_{VR}]$).

Figure 8. Linear regression between measured reflectance values of AOM and vitrinite (A) and solid bitumen and vitrinite (B), respectively. For comparison, panel B shows relationships between calculated VR_0E based on other empirical equations from Jacob (1989), Landis and Castaño (1995), and Bertrand and Malo (2001).

measurements were used for building a linear regression relationship to be comparable to vitrinite and solid bitumen; the equation relating VR_0 to the reflectance of AOM is as follows: $VR_0E = (0.84 \times AOMR_0) + 0.38$, with a coefficient of determination $R^2 = 0.61$.

Fig. 9 shows the fitted linear equations using the geometric mean functional regression method of VR_0 versus $AOMR_0$ and VR_0 versus BR_0 . The new calibrated

functional regression equation between AOM (with 50 measurements) and vitrinite reflectance values is $VR_oE = (AOMR_o \times 1.08) + 0.31$ and the equation between solid bitumen and vitrinite reflectance values is $VR_oE = (BR_o \times 1.01) + 0.14$ (Fig. 9).

Figure 9. Geometric mean functional regression (solid black line) between measured reflectance values of AOM and vitrinite, and reflectance values of solid bitumen and vitrinite (Ricker, 1973). Dashed grey lines are ordinary linear predictive regressions of Y (VR_o) based on X ($AOMR_o$), and of X ($AOMR_o$) based on Y (VR_o), respectively.

3.4 Variations in functional group abundances among maceral groups

The purpose of using micro-FTIR analysis was to investigate whether differences in reflectances between macerals are also reflected in their chemical structures, and in particular, if chemical functional groups can differentiate between vitrinite and solid bitumen. Micro-FTIR is capable of characterizing chemical properties of *in situ* particles of macerals as small as 20-30 μm . The main difficulty with this technique is to recognize and identify macerals under a dry objective. Therefore, sample 1 ($VR_o = 0.63\%$) was selected because of its high abundance of different macerals with relatively large sizes and relatively easy maceral identification. To facilitate maceral identification, photomicrographs under a reflected light microscope were taken prior to FTIR analysis. After micro-FTIR analysis, the sample was analyzed under oil immersion to confirm or modify maceral identification. IR signals deriving from the following functional groups

were of particular interest to this study: (i) aromatic CH_x stretching between wavenumbers $3000\text{--}3100\text{ cm}^{-1}$, (ii) aliphatic CH_x stretching at $2800\text{--}3000\text{ cm}^{-1}$, (iii) oxygenated groups at $1650\text{--}1800\text{ cm}^{-1}$, and (iv) aromatic $\text{C}=\text{C}$ ring stretching at $1550\text{--}1650\text{ cm}^{-1}$ (Chen et al., 2012).

The micro-FTIR spectra of alginite, AOM, solid bitumen, vitrinite, and inertinite typical for these early mature samples are compared in Fig. 10. Each spectrum represents the average of two or three spectra of the maceral. Most macerals were very small, often not larger than $30\text{ }\mu\text{m}$, close to the detection limits of the technique. Although the spectra are noisy, most functional groups were easily detectable. Among these macerals, alginite and AOM exhibit the strongest absorbance of aliphatic CH_x stretching at $2800\text{--}3000\text{ cm}^{-1}$, and the lowest intensities in aromatic $\text{C}=\text{C}$ ring vibration at 1600 cm^{-1} . Vitrinite and inertinite display relatively strong peaks at $2800\text{--}3000\text{ cm}^{-1}$ and 1600 cm^{-1} , and solid bitumen seems to be placed in between alginite and vitrinite. Solid bitumen, vitrinite, and inertinite feature more distinct absorbance of oxygenated groups at $\sim 1710\text{ cm}^{-1}$ compared to AOM and alginite. The $\text{C}=\text{O}$ peak intensity in vitrinite and inertinite was roughly inversely proportional to the intensity of aliphatic CH_x stretching at $2800\text{--}3000\text{ cm}^{-1}$, which is consistent with the fact that carboxyl/carbonyl groups derive from the oxidation of aliphatic moieties (Chen et al., 2012). Vitrinite and inertinite represent terrestrial input, and the consumption of aliphatic groups could have taken place during transport to the place of deposition. Compared to the spectra of solid bitumen, vitrinite is characterized by similar intensities of aliphatic CH_x bands, but stronger intensities of the aromatic stretching region at $3000\text{--}3100\text{ cm}^{-1}$ and oxygenated groups at $1650\text{--}1800\text{ cm}^{-1}$.

Figure 10. Micro-FTIR spectra of alginite, AOM, solid bitumen, vitrinite, and inertinite from sample 1 ($VR_0 = 0.63\%$).

3.5 FTIR-derived ratios

The chemical heterogeneity of alginite, AOM, solid bitumen, vitrinite, and inertinite maceral groups was examined using ratios of selected peaks. Following Chen et al. (2013), the peak area ratios in the FTIR spectra (Table 6) were used to evaluate chemical characteristics of different macerals: (1) aromaticity, (2) aliphatic chain length, and (3) hydrocarbon potential expressed by an ‘A’ factor. The selection of these indices was dictated by the quality of the bands. Some bands were not defined well enough to determine their areas.

Table 6. Ratios derived from FTIR spectra (modified from Chen et al., 2013, and references therein).

Ratio indices	Index calculation	Band region (cm ⁻¹)
Aromaticity (AR)	CH _{ar} stretching / CH _{al} stretching	(3000–3100) / (2800–3000)
‘A’ factor	CH _{al} stretching / (CH _{al} stretching + C=C)	(2800–3000) / [(2800–3000)+1600]
Aliphatic chain length	CH ₂ /CH ₃	(2900–2940) / (2940–3000)

Direct comparison of FTIR ratios of alginite, AOM, solid bitumen, vitrinite, and inertinite from several representative particles in shale samples demonstrates that these macerals were distinctly different from each other in terms of aromaticity, CH₂/CH₃ ratios, and the ‘A’ factor (Fig. 11). The aromaticity of alginite, AOM, and solid bitumen is lower than that of vitrinite and inertinite. Conversely, the CH₂/CH₃ ratios of alginite and AOM are about five times as high as those for solid bitumen, and nearly a hundred times higher than vitrinite and inertinite from the same shale samples. The higher CH₂/CH₃ ratio for alginite and AOM reflects longer alkyl chain lengths and less alkyl branching (Lin and Ritz, 1993; Chen et al., 2013). Compared to vitrinite and inertinite, solid bitumen shows higher CH₂/CH₃ ratios and lower aromaticity. Inertinite has higher aromaticity compared to vitrinite.

Figure 11. Histograms showing variations in maceral chemistries. Alginite and AOM exhibit the lowest aromaticity and the highest CH₂/CH₃ ratios. Vitrinite and inertinite display the highest aromaticity and low CH₂/CH₃ ratios.

4. Discussion

In pre-Devonian shales and many organic-rich marine shales in general, BR_o is used as a thermal maturity indicator because of the absence or scarcity of vitrinite (Bertrand, 1993; Gentzis and Goodarzi, 1990; Landis and Castaño, 1995; Hwang et al., 1998; Petersen et al., 2013). Even in Devonian rocks, because of the scarcity of vitrinite, petrographers introduce bias and misidentify vitrinite populations because solid bitumen is the primary organic matter used for reflectance measurements (Bertrand, 1993; Hackley et al., 2013; Ryder et al., 2013). At low maturity levels, misidentifying solid

bitumen for vitrinite has been suggested as a reason for lower reflectance values and an overall underestimation of maturity levels (Dow and O'Connor, 1982; He et al., 2002; Hackley et al., 2013; Ryder et al., 2013). This, in turn, influences the assessment of hydrocarbon generation potential, and oil generation in particular. It has been demonstrated from numerous basins worldwide (no low organic sulfur systems involved) that oil and non-microbially generated organic gases are found in rocks with VR_o below 0.6% (Peterson and Hickey, 1987; Galimov, 1988; Bazhenova and Arefiev, 1990; Muscio et al., 1994; Hwang et al., 1998; Ramaswamy, 2002; Lewan et al., 2006; Xu et al., 2008; Cardott, 2012; Redden, 2012), which is the value traditionally considered to represent the onset of oil generation (Radke et al., 1986; Hunt, 1990; Peters and Cassa, 1994; Pepper and Corvi, 1995; Pollastro et al., 2003). Misidentification of solid bitumen for vitrinite is mentioned among several other possible reasons for inaccurate reflectance values (Carr, 2000; He et al., 2002; Borrego et al., 2006; Hackley et al., 2013; Hackley and Cardott, 2016). Therefore, it is important to understand the relationship between reflectance values of solid bitumen and vitrinite to evaluate the implications of reflectance differences between these two macerals, and also the implications of their misidentification.

The suite of NAS samples selected for this study provides an excellent opportunity to analyze the relationship between vitrinite and solid bitumen reflectance. All samples had sufficient number of distinct particles of solid bitumen and vitrinite for a statistically relevant comparison. Reflectance of vitrinite, ranging from 0.57 to 0.65% (Table 2), covers most of the early mature stage of oil generation. However, measuring

solid bitumen with a reflectance range from 0.44 to 0.52% (Table 2) as vitrinite would place these rocks in an immature zone, without any expectation of oil generation.

For the shale samples studied, based on morphology, color, and differences in the form of occurrence, solid bitumen and vitrinite could be identified with high confidence in most cases, but misidentification of solid bitumen and vitrinite still turned out to be somewhat problematic in their overlapping reflectance ranges. Previous studies suggested that this problem could not be easily corrected *via* kerogen concentration or solvent extraction, and was primarily related to operator training and background (e.g., Hackley et al., 2015). Hackley et al. (2013) also suggested that reflectance of vitrinite was a poor predictor of thermal maturity in the early mature stage, partly because reported measurements in Devonian shale often included some reflectance of solid bitumen. The present study employs a statistical method assuming that vitrinite and solid bitumen reflectance follows a normal distribution, and their values in the overlapping range could be simulated with PDFs. Therefore, the misidentified portion of reflectance measurements is properly minimized by weighting adjustment.

Because correcting solid bitumen and vitrinite reflectance is essentially applying lower weights to the values in the overlapping range, the correction depends on both the weights and the values that have been assigned lower weights. In principle, the lower the weights and the more lowered-weight values are in the maceral, the larger the corrections will be. The weight for any given measurement is defined by the corresponding value of the PDFs of solid bitumen and vitrinite. The PDFs are calculated from the mean and standard deviation of the measurements from the two groups. Therefore, no simple

relationships exist between the correction and each of the four variables (i.e. two means and two standard deviations from each group).

The lower weighting of values relate not only to the number of measurements within the overlapping reflectance range, but also to the distribution of those values. For instance, if one group has anomalously large numbers of measurements at the tails of the distribution in the overlapping range, its weighted average will have a larger shift due to assigned lower weights of more measurements. This is not presented as a simple relationship among the samples, since the distributions and overlapping ranges all vary between different samples.

Although individual corrections of either solid bitumen or vitrinite are affected by several different variables, a linear relationship is revealed between the total correction and the statistical extent of overlap (i.e. $[\mu_{BR} + 2\sigma_{BR}] - [\mu_{VR} - 2\sigma_{VR}]$; Fig. 7). Due to the fact that the actual distribution of measurements never perfectly follows the normal distribution, the corrections of solid bitumen and vitrinite for some samples deviate from this linear relationship.

The statistical simulation used in this study indicates that to account for the possibility of misidentification between vitrinite and solid bitumen in the overlapping reflectance range, the reflectance values would need to be corrected only by 0.02% or less. This is a very small difference that would not significantly influence maturity assessment. This further demonstrates that at this maturity level, VR_o values collected by an experienced petrographer are rather accurate, even if there is an occasional misidentification of solid bitumen as vitrinite. Because the difference between vitrinite and solid bitumen diminishes with maturity until they converge at $VR_o \sim 1\%$ (Jacob,

1989; Robert, 1988; Katz et al., 1988; Bertrand, 1993; Petersen et al., 2013), occasional misidentification of solid bitumen for vitrinite should not influence maturity assessment in any significant way in the whole oil window (early mature and mid mature stages). At late and post-mature stages (condensate – wet gas and dry gas windows), solid bitumen is the dominant organic matter type in most shales (Hackley and Cardott, 2016), and its reflectance becomes the most reliable petrographic maturity indicator.

The simultaneous occurrence of abundant vitrinite, solid bitumen, and AOM in organic matter-rich shales presents an opportunity to compare the reflectances of these three macerals throughout the early mature stage (i.e. studied samples with VR_o ranges from 0.57 to 0.65%). The usefulness of the reflectance of organic matter other than vitrinite as thermal maturity indicators has been demonstrated in sedimentary basins of various ages (Jacob, 1989; Bertrand, 1993; Landis and Castaño, 1995; Bertrand and Malo, 2001; Schoenherr et al., 2007). For the samples studied, both solid bitumen and AOM reflectance show a strong linear correlation with VR_o , reinforcing the utility of these macerals in the assessment of thermal maturity. With the different chemistries of these three macerals (i.e. from AOM with least aromatic and longest aliphatic chains to vitrinite and inertinite with most aromatic and much shorter aliphatic chains; Fig. 9) and corresponding differences in reflectances (i.e. lowest in AOM, intermediate in solid bitumen, and highest in vitrinite), each type of maceral followed its own maturation path during diagenesis. The systematic pattern of slightly increasing maturity (VR_o from 0.57 to 0.65%) makes the combination of macerals especially useful in shales with very sparse or absent vitrinite, at least for the samples of similar maturation level. .

The equation developed in this study for calculating VR_oE from solid bitumen ($VR_oE = (0.83 \times BR_o) + 0.02$) shows differences in results compared to other empirical equations developed earlier for other basins. Out of two equations in common use, the equation of Jacob (1989) is closer to measured vitrinite/solid bitumen relationships than the equation of Landis and Castaño (1995); both equations result in higher VR_oE values compared to measured values in this study (Fig. 8). The equation of Bertrand and Malo (2001) yields lower VR_oE values compared to the measured values. The differences between collected data from this study and VR_oE calculated from other equations can be related to (1) a lack of indigenous VR_o data (Bertrand, 1993), (2) mixing of locally derived and significantly migrated solid hydrocarbons (Jacob, 1989; Bertrand, 1993), or (3) mixing of morphological types (Jacob, 1989). Other problems may be related to the variability of maturity levels (Bertrand and Malo, 2001). Specifically, the equation of Bertrand and Malo (2001) is based on rocks with a higher maturity range (VR_o between 1 to 2%) in the Siluro-Devonian of the Gaspé Belt Basin in Canada. Our calibration is based on early mature Devonian-Mississippian NAS covering a relatively narrow thermal maturity range from 0.57 to 0.65% VR_o . This comparison demonstrates that applications of conversion factors between vitrinite and solid bitumen from previous empirical equations (Jacob, 1989; Bertrand, 1993; Landis and Castaño, 1995; Bertrand and Malo, 2001) should be used with caution, carefully considering rock maturity and the type of organic matter.

5. Conclusions

1. AOM, solid bitumen and vitrinite are valuable macerals in the assessment of thermal maturity of organic matter-rich shales within the oil window. For the Devonian New Albany Shale sequence studied here, strongly correlated reflectances of AOM, solid bitumen, and vitrinite range from 0.27 to 0.31%, 0.44 to 0.52% and 0.57 to 0.65%, respectively. Reflectance differences between these macerals are paralleled by chemical differences reflected by functional group distribution, specifically aromaticity and the length of aliphatic chains. Compared to vitrinite and inertinite, solid bitumen shows lower aromaticity, and AOM and alginite exhibit longer aliphatic chain lengths. This suggests that even optically similar solid bitumen and vitrinite can be distinguished by chemical structure differences at the maturity level studied.

2. A statistical method was introduced to evaluate how misidentification between solid bitumen and vitrinite could potentially influence the final mean reflectance values, and thus the assessment of the maturity level. The results suggest that there is a small possibility that experienced petrographers can make significant mistakes with maturity measurements in early mature shales that contain both solid bitumen and vitrinite. Mistakes that could typically be made by misidentifying solid bitumen as vitrinite are small and will not significantly influence the maturity assessment. We caution, however, that our data represent only a relatively narrow maturity range, and the relationships between macerals and difficulty of their identification will change at higher maturity.

3. Transfer functions of reflectance values between vitrinite and solid bitumen from empirical equations developed for different basins and rocks with different maturity levels should be used with caution. The relationships between reflectance of solid

bitumen and vitrinite developed in this study for New Albany Shale differ from those developed for other formations and maturity levels.

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References

- Agresti, A., Kateri, M., 2011. Categorical data analysis, In: Lovric, M. (Eds.), International Encyclopedia of Statistical Science. Springer Berlin Heidelberg, pp. 206–208.
- Aldrich, J.H., Nelson, F.D., 1984. Linear Probability, Logit, and Probit Models. SAGE.
- American Society for Testing and Materials, 2016. Annual book of ASTM standards: 2016. Section 5, Petroleum Products, Lubricants, and Fossil Fuels. Vol. 05.06, Volume 05.06 Gaseous Fuels; Coal and Coke; Catalysts; Bioenergy and Industrial Chemicals from Biomass. D7708 method.
- Barker, C.E., Pawlewicz, M.J., 1993. An empirical determination of the minimum number of measurements needed to estimate the mean random vitrinite

- reflectance of disseminated organic matter. *Org. Geochem.* 20, 643–651.
[http://dx.doi.org/10.1016/0146-6380\(93\)90050-L](http://dx.doi.org/10.1016/0146-6380(93)90050-L).
- Barrows, M.H., Cluff, R.M., Harvey, R.D., 1979. Petrology and maturation of dispersed organic matter in New Albany Shale Group of Illinois Basin (abs.). *AAPG Bull.* 63, 1575–1575.
- Barrows, M.H., Cluff, R.M., 1984. New Albany Shale Group (Devonian-Mississippian) source rocks and hydrocarbon generation in the Illinois Basins, In: Demaison, G., Murris, R.J. (Eds.), *Petroleum Geochemistry and Basin Evaluation*. AAPG Memoir 35, Tulsa, pp. 111-138.
- Bazhenova, O.K., Arefiev, O.A., 1990. Immature oils as the products of early catagenetic transformation of bacterial-algal organic matter. *Org. Geochem.* 16, 307–311.
[http://dx.doi.org/10.1016/0146-6380\(90\)90050-A](http://dx.doi.org/10.1016/0146-6380(90)90050-A).
- Bernard, S., Horsfield, B., Schulz, H-M., Wirth, R., Schreiber, A., Sherwood, N., 2012, Geochemical evolution of organic-rich shales with increasing maturity: A STXM and TEM study of the Posidonia Shale (Lower Toarcian, northern Germany). *Mar. Petrol. Geol.* 31, 70–89. <http://dx.doi.org/10.1016/j.marpetgeo.2011.05.010>.
- Bertrand, R., 1993. Standardization of solid bitumen reflectance to vitrinite in some Paleozoic Sequences of Canada. *Energy Sources* 15, 269–287.
<http://dx.doi.org/10.1080/00908319308909027>.
- Bertrand, R., Malo, M., 2001. Source rock analysis, thermal maturation and hydrocarbon generation in Siluro-Devonian rocks of the Gaspé Belt basin, Canada. *Bull. Can. Pet. Geol.* 49, 238–261. <http://dx.doi.org/10.2113/49.2.238>.

- Borrego, A.G., Araujo, C.V., Balke, A., Cardott, B., Cook, A.C., David, P., Flores, D., Hámor-Vidó, M., Hiltmann, W., Kalkreuth, W., Koch, J., Kommeren, C.J., Kus, J., Ligouis, B., Marques, M., Mendonça Filho, J.G., Misz, M., Oliveira, L., Pickel, W., Reimer, K., Ranasinghe, P., Suárez-Ruiz, I., Vieth, A., 2006. Influence of particle and surface quality on the vitrinite reflectance of dispersed organic matter: Comparative exercise using data from the qualifying system for reflectance analysis working group of ICCP. *Int. J. Coal Geol.* 68, 151–170.
<http://dx.doi.org/10.1016/j.coal.2006.02.002>.
- Brownlee, K.A., 1965. *Statistical Theory and Methodology in Science and Engineering*. Wiley, New York.
- Cardott, B.J., 2012. Thermal maturity of Woodford Shale gas and oil plays, Oklahoma, USA. *Int. J. Coal Geol.* 103, 109–119.
<http://dx.doi.org/10.1016/j.coal.2012.06.004>.
- Carr, A.D., 2000. Suppression and retardation of vitrinite reflectance, Part 1. Formation and significance for hydrocarbon generation. *J. Pet. Geol.* 23, 313–343.
<http://dx.doi.org/10.1111/j.1747-5457.2000.tb01022.x>.
- Chen, Y., Mastalerz, M., Schimmelmann, A., 2012. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. *Int. J. Coal Geol.* 104, 22–33.
<http://dx.doi.org/10.1016/j.coal.2012.09.001>.
- Chen, Y., Caro, L.D., Mastalerz, M., Schimmelmann, A., Blandón, A., 2013. Mapping the chemistry of resinite, funginite and associated vitrinite in coal with micro-

- FTIR. *J. Microsc.* 249, 69–81. <http://dx.doi.org/10.1111/j.1365-2818.2012.03685.x>.
- Chen, Y., Furmann, A., Mastalerz, M., Schimmelmann, A., 2014. Quantitative analysis of shales by KBr-FTIR and micro-FTIR. *Fuel* 116, 538–549. <http://dx.doi.org/10.1016/j.fuel.2013.08.052>.
- Cluff, R.M., Reinbold, M.L., Lineback, J.A., 1981. New Albany Shale Group of Illinois. *Ill. State Geol. Surv. Circ.* 518.
- Curiale, J.A., 1986. Origin of solid bitumens, with emphasis on biological marker results. *Org. Geo.* 10(1-3), 559–580. [http://dx.doi.org/10.1016/0146-6380\(86\)90054-9](http://dx.doi.org/10.1016/0146-6380(86)90054-9).
- Curtis, J.B., 2002. Fractured shale-gas systems. *AAPG Bull.* 86, 1921–1938.
- Dow, W.G., O'Connor, D.I., 1982. Kerogen maturity and type by reflected light microscopy applied to petroleum exploration, In: Staplin, F.L., Dow, W.G., Milner, C.W.D., O'Connor, D.I., Pocock, S.A.J., van Gijzel, P., Welte, D.H., Yüklér, M.A. (Eds.), *How to Assess Maturation and Paleotemperatures*. SEPM Short Course 7, Tulsa, pp. 133–157.
- Drobniak A., Mastalerz M., 2016. IGS Story Map. <https://dev.igs.indiana.edu/igsmap/index.cfm?custom=https://iu.maps.arcgis.com/apps/MapJournal/index.html?appid=41ccf17b2b254f06ae1908d44df84aa1>.
- Galimov, E.M., 1988. Sources and mechanisms of formation of gaseous hydrocarbons in sedimentary rocks. *Chem. Geol.* 71, 77–95. [http://dx.doi.org/10.1016/0009-2541\(88\)90107-6](http://dx.doi.org/10.1016/0009-2541(88)90107-6).
- Gentzis, T., Goodarzi, F., 1990. A review of the use of bitumen reflectance in hydrocarbon exploration with examples from Melville Island, Arctic Canada, In:

- Vito F.N. and Charles E.B. (Eds.), Application of Thermal Maturity Studies to Energy Exploration. Rocky Mountain Section (SEPM), pp. 23–36.
- Hackley, P.C., Ryder, R.T., Trippi, M.H., Alimi, H., 2013. Thermal maturity of northern Appalachian Basin Devonian shales: Insights from sterane and terpane biomarkers. *Fuel* 106, 455–462. <http://dx.doi.org/10.1016/j.fuel.2012.12.032>.
- Hackley, P.C., Araujo, C.V., Borrego, A.G., Bouzinos, A., Cardott, B.J., Cook, A.C., Eble, C., Flores, D., Gentzis, T., Gonçalves, P.A., Mendonça Filho, J.G., Hámor-Vidó, M., Jelonek, I., Kommeren, K., Knowles, W., Kus, J., Mastalerz, M., Menezes, T.R., Newman, J., Oikonomopoulos, I.K., Pawlewicz, M., Pickel, W., Potter, J., Ranasinghe, P., Read, H., Reyes, J., Rosa Rodriguez, G.D.L., Alves Fernandes de Souza, I.V., Suárez-Ruiz, I., Sýkorová, I., Valentine, B.J., 2015. Standardization of reflectance measurements in dispersed organic matter: Results of an exercise to improve interlaboratory agreement. *Mar. Pet. Geol.* 59, 22–34. <http://dx.doi.org/10.1016/j.marpetgeo.2014.07.015>.
- Hackley, P.C., Cardott, B.J., 2016. Application of organic petrography in North American shale petroleum systems: A review. *Int. J. Coal Geol.* 163, 8–51.
- Hamilton-Smith, T., Hasenmueller, N.R., Boberg, W.S., Smidchens, Z., Frankie, W.T., 1994. Gas production, In: Hasenmueller, N. R., and Comer, J. B. (Eds.), Gas potential of the New Albany Shale (Devonian and Mississippian) in the Illinois Basin: GRI92-0391/Illinois Basin Studies 2, pp. 23-39.
- Hasenmueller, N.R. and Comer, J.B., 1994. Gas potential of the New Albany Shale (Devonian and Mississippian) in the Illinois Basin, Illinois Basin Studies 2: Final Report. Gas Research Institute, KY, IL, IN, 83p.

- He, S., Middleton, M., Kaiko, A., Jiang, C., Li, M., 2002. Two case studies of thermal maturity and thermal modelling within the overpressured Jurassic rocks of the Barrow Sub-basin, North West Shelf of Australia. *Mar. Pet. Geol.* 19, 143–159.
[http://dx.doi.org/10.1016/S0264-8172\(02\)00006-5](http://dx.doi.org/10.1016/S0264-8172(02)00006-5).
- Hunt, J.M., 1990. Generation and migration of petroleum from abnormally pressured fluid compartments (1). *AAPG Bull.* 74, 1–12.
<http://dx.doi.org/10.1306/0c9b21eb-1710-11d7-8645000102c1865d>.
- Hwang, R.J., Teerman, S.C., Carlson, R.M., 1998. Geochemical comparison of reservoir solid bitumens with diverse origins. *Org. Geochem.* 29, 505–517.
[http://dx.doi.org/10.1016/S0146-6380\(98\)00078-3](http://dx.doi.org/10.1016/S0146-6380(98)00078-3).
- ICCP (International Commission for Coal Petrology), 1975. *International Handbook of Coal Petrography*, 2nd Supplement to 2nd Edition. Centre National de la Recherche Scientifique, Paris.
- Jacob, H., 1989. Classification, structure, genesis and practical importance of natural solid oil bitumen (“migrabitumen”). *Int. J. Coal Geol.* 11, 65–79.
[http://dx.doi.org/10.1016/0166-5162\(89\)90113-4](http://dx.doi.org/10.1016/0166-5162(89)90113-4).
- Katz, B.J., Pheifer, R.N., Schunk, D.J., 1988. Interpretation of discontinuous vitrinite reflectance profiles. *AAPG Bull.* 72, 926–931.
<http://dx.doi.org/10.1306/703c9113-1707-11d7-8645000102c1865d>.
- Kramers, H.A., 1927. La diffusion de la lumiere par les atomes, In: *Atti Del Congresso Internazionale Dei Fisici*. pp. 545–557.
- Kronig, R. de L., 1926. On the theory of dispersion of X-Rays. *J. Opt. Soc. Am.* 12, 547.
<http://dx.doi.org/10.1364/JOSA.12.000547>.

- Landis, C.R., Castaño, J.R., 1995. Maturation and bulk chemical properties of a suite of solid hydrocarbons. *Org. Geochem.* 22, 137–149. [http://dx.doi.org/10.1016/0146-6380\(95\)90013-6](http://dx.doi.org/10.1016/0146-6380(95)90013-6).
- Lewan, M.D., Kotarba, M.J., Curtis, J.B., Więclaw, D., Kosakowski, P., 2006. Oil-generation kinetics for organic facies with Type-II and -IIS kerogen in the Menilite Shales of the Polish Carpathians. *Geochim. Cosmochim. Acta* 70, 3351–3368. <http://dx.doi.org/10.1016/j.gca.2006.04.024>.
- Lin, R., Ritz, G.P., 1993. Reflectance FT-IR microspectroscopy of fossil algae contained in organic-rich shales. *Appl. Spectrosc.* 47, 265–271. <http://dx.doi.org/10.1366/0003702934066794>.
- Lineback, J., 1970. Stratigraphy of the New Albany Shale in Indiana. *Indiana Geol. Surv. Bull.* 44, 72p.
- Ma, Y. Z., and Holditch, S., 2015. *Unconventional Oil and Gas Resources Handbook: Evaluation and Development*. Gulf Professional Publishing.
- Martini, A.M., Walter, L.M., Ku, T.C.W., Budai, J.M., McIntosh, J.C., Schoell, M., 2003. Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian shale gas play, Michigan basin. *AAPG Bull.* 87, 1355–1375. <http://dx.doi.org/10.1306/9f82f69e-4bda-4f66-95b70e2bd2cc912f>.
- Mastalerz, M., Bustin, R.M., 1997. Variation in the chemistry of macerals in coals of the Mist Mountain Formation, Elk Valley coalfield, British Columbia, Canada. *Int. J. Coal Geol.* 33, 43–59. [http://dx.doi.org/10.1016/S0166-5162\(96\)00003-1](http://dx.doi.org/10.1016/S0166-5162(96)00003-1).

- Mastalerz, M., Karayigit, A., Hampton, L., Drobniak, A., 2016. Variations in gas content in organic matter-rich low maturity shale; Example from the New Albany Shale in the Illinois Basin. *J. Pet. Nat. Gas* 1, 5.
- Mossman, D.J., Nagy, B., 1996. Solid bitumens: an assessment of their characteristics, genesis, and role in geological processes. *Terra Nova* 8, 114–128.
<http://dx.doi.org/10.1111/j.1365-3121.1996.tb00736.x>.
- Muscio, G.P.A., Horsfield, B., Welte, D.H., 1994. Occurrence of thermogenic gas in the immature zone—implications from the Bakken in-source reservoir system. *Org. Geochem.* 22, 461–476. [http://dx.doi.org/10.1016/0146-6380\(94\)90119-8](http://dx.doi.org/10.1016/0146-6380(94)90119-8).
- Painter, P.C., Snyder, R.W., Starsinic, M., Coleman, M.M., Kuehn, D.W., Davis, A., 1981. Concerning the application of FTIR to the study of coal: A critical assessment of band assignments and the application of spectral analysis programs. *Appl. Spectrosc.* 35, 475–485. <http://dx.doi.org/10.1366/0003702814732256>.
- Painter, P., Starsinic, M., Coleman, M., 1985. Determination of functional groups in coal by fourier transform interferometry, In: *Fourier Transform Infrared Spectra: Applications to Chemical Systems*. Academic Press, pp. 169–240.
- Pepper, A.S., Corvi, P.J., 1995. Simple kinetic models of petroleum formation. Part I: oil and gas generation from kerogen. *Mar. Pet. Geol.* 12, 291–319.
[http://dx.doi.org/10.1016/0264-8172\(95\)98381-E](http://dx.doi.org/10.1016/0264-8172(95)98381-E).
- Peters, K.E., Cassa, M.R., 1994. Applied source rock geochemistry, In: Magoon, L.B., Dow, W.G. (Eds.), *The Petroleum System—From Source to Trap*. AAPG Memoir 60, Tulsa, pp. 93–117.

- Petersen, H.I., Schovsbo, N.H., Nielsen, A.T., 2013. Reflectance measurements of zooclasts and solid bitumen in Lower Paleozoic shales, southern Scandinavia: Correlation to vitrinite reflectance. *Int. J. Coal Geol.* 114, 1–18.
<http://dx.doi.org/10.1016/j.coal.2013.03.013>.
- Peterson, N.F., Hickey, P.J., 1987. California Plio-Miocene oils: Evidence of early generation, In: Richard F.M. (Eds.), *Exploration for Heavy Crude Oil and Natural Bitumen*. Am. Assoc. Pet. Geol. Stud. Geol. 25, pp. 351–359.
<http://repository.icse.utah.edu/dspace/handle/123456789/8382>.
- Pollastro, R.M., Hill, R.J., Jarvie, D.M., Henry, M.E., 2003. Assessing undiscovered resources of the Barnett-Paleozoic total petroleum system, Bend Arch–Fort Worth Basin Province, Texas. AAPG Southwest Section Convention, Fort Worth Texas, 18p.
<http://www.searchanddiscovery.com/pdfz/documents/pollastro/images/article.pdf.html>
- Price, L.C., Baker, C.E., 1985. Suppression of vitrinite reflectance in amorphous rich kerogen—A major unrecognized problem. *J. Pet. Geol.* 8, 59–84.
<http://dx.doi.org/10.1111/j.1747-5457.1985.tb00191.x>.
- Radke, M., Welte, D.H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. *Org. Geochem.* 10, 51–63.
[http://dx.doi.org/10.1016/0146-6380\(86\)90008-2](http://dx.doi.org/10.1016/0146-6380(86)90008-2).
- Ramaswamy, G., 2002. A field evidence for mineral-catalyzed formation of gas during coal maturation. *Oil Gas J.* 100, 32–36. <http://www.ogj.com/articles/print/volume->

100/issue-38/exploration-development/a-field-evidence-for-mineral-catalyzed-formation-of-gas-during-coal-maturation.html

- Redden, J., 2012. SHALETECH—Unlocking the secrets of the U.S.’ largest onshore oil reserves: Monterey/Santos. *World Oil* 88–96.
http://www.slb.com/~media/Files/industry_challenges/unconventional_gas/industry_articles/20133001_world_oil_monterey.pdf
- Ricker, W.E., 1973. Linear regressions in fishery research. *J. Fish. Res. Board Can.* 30, 409–434. <http://dx.doi.org/10.1139/f73-072>.
- Robert, P., 1988. *Organic Metamorphism and Geothermal History: Microscopic Study of Organic Matter and Thermal Evolution of Sedimentary Basins*, Springer Netherlands, D. Reidel Publishing Company, Dordrecht.
- Ryder, R.T., Hackley, P.C., Alimi, H., Trippi, M.H., 2013. Evaluation of thermal maturity in the low maturity Devonian shales of the northern Appalachian Basin. *Am. Assoc. Pet. Geol. Search Discov. Artic.* 10477.
http://www.searchanddiscovery.com/pdfz/documents/2013/10477ryder/ndx_ryder.pdf.html
- Schoenherr, J., Littke, R., Urai, J.L., Kukla, P.A., Rawahi, Z., 2007. Polyphase thermal evolution in the Infra-Cambrian Ara Group (South Oman Salt Basin) as deduced by maturity of solid reservoir bitumen. *Org. Geochem.* 38, 1293–1318.
<http://dx.doi.org/10.1016/j.orggeochem.2007.03.010>.
- Strapoć, D., Mastalerz, M., Schimmelmann, A., Drobniak, A., Hasenmueller, N.R., 2010. Geochemical constraints on the origin and volume of gas in the New Albany

- Shale (Devonian–Mississippian), eastern Illinois Basin. AAPG Bull. 94, 1713–1740. <http://dx.doi.org/10.1306/06301009197>.
- Teissier, G., 1948. La relation d'allometrie sa signification statistique et biologique. Biometrics 4, 14–53. <http://dx.doi.org/10.2307/3001695>.
- Teichmüller, M., 1986. Organic petrology of source rocks, history and state of art. Org. Geochem 10, 581–599. [http://dx.doi.org/10.1016/0146-6380\(86\)90055-0](http://dx.doi.org/10.1016/0146-6380(86)90055-0).
- Thompson, C.L., Dembicki, H., 1986. Optical characteristics of amorphous kerogens and the hydrocarbon-generating potential of source rocks. Int. J. Coal. Geol. 6(3), 229–249. [http://dx.doi.org/10.1016/0166-5162\(86\)90003-0](http://dx.doi.org/10.1016/0166-5162(86)90003-0).
- Van Berkel, G.J., Quirke, J.M.E., Filby, R.H., 1989. The Henryville Bed of the New Albany shale—I. Preliminary characterization of the nickel and vanadyl porphyrins in the bitumen. Org. Geochem. 14, 119–128. [http://dx.doi.org/10.1016/0146-6380\(89\)90066-1](http://dx.doi.org/10.1016/0146-6380(89)90066-1).
- Wang, S.-H., Griffiths, P.R., 1985. Resolution enhancement of diffuse reflectance i.r. spectra of coals by Fourier self-deconvolution: 1. C-H stretching and bending modes. Fuel 64, 229–236. [http://dx.doi.org/10.1016/0016-2361\(85\)90223-6](http://dx.doi.org/10.1016/0016-2361(85)90223-6).
- Wilkins, R.W.T., Wilmshurst, J.R., Russell, N.J., Hladky, G., Ellacott, M.V., Buckingham, C., 1992. Fluorescence alteration and the suppression of vitrinite reflectance. Org. Geochem. 18, 629–640. [http://dx.doi.org/10.1016/0146-6380\(92\)90088-F](http://dx.doi.org/10.1016/0146-6380(92)90088-F).
- Xu, Y., Wang, Z., Wang, X., Zheng, J., Du, H., 2008. Low-mature gases and typical low-mature gas fields in China. Sci. China Ser. D: Earth Sci. 51, 312–320. <http://dx.doi.org/10.1007/s11430-008-0011-x>.