



Research paper

Testing reproducibility of vitrinite and solid bitumen reflectance measurements in North American unconventional source-rock reservoir petroleum systems

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ABSTRACT

An interlaboratory study (ILS) was conducted to test reproducibility of vitrinite and solid bitumen reflectance measurements in six mudrock samples from United States unconventional source-rock reservoir petroleum systems. Samples selected from the Marcellus, Haynesville, Eagle Ford, Barnett, Bakken and Woodford are representative of resource plays currently under exploitation in North America. All samples are from marine depositional environments, are thermally mature ($T_{\max} > 445$ °C) and have moderate to high organic matter content (2.9–11.6 wt% TOC). Their organic matter is dominated by solid bitumen, which contains intraparticle nano-porosity. Visual evaluation of organic nano-porosity (pore sizes < 100 nm) via SEM suggests that intraparticle organic nano-pores are most abundant in dry gas maturity samples and less abundant at lower wet gas/condensate and peak oil maturities. Samples were distributed to ILS participants in forty laboratories in the Americas, Europe, Africa and Australia; thirty-seven independent sets of results were received. Mean vitrinite reflectance (VR_o) values from all ILS participants range from 0.90 to 1.83% whereas mean solid bitumen reflectance (BR_o) values range from 0.85 to 2.04% (no outlying values excluded), confirming the thermally mature nature of all six samples. Using multiple statistical approaches to eliminate outlying values, we evaluated reproducibility limit R, the maximum difference between valid mean reflectance results obtained on the same sample by different operators in different laboratories using different instruments. Removal of outlying values where the individual signed multiple of standard deviation was > 1.0 produced lowest R values, generally $\leq 0.5\%$ (absolute reflectance), similar to a prior ILS for similar samples. Other traditional approaches to outlier removal (outside mean ± 1.5 *interquartile range and outside F10 to F90 percentile range) also produced similar R values. Standard deviation values < 0.15*(VR_o or BR_o) reduce R and should be a requirement of dispersed organic matter reflectance analysis. After outlier removal, R values were 0.1%–0.2% for peak oil thermal maturity, about 0.3% for wet gas/condensate maturity and 0.4%–0.5% for dry gas maturity. That is, these R values represent the uncertainty (in absolute reflectance) that users of vitrinite and solid bitumen reflectance data should assign to any one individual reported mean reflectance value from a similar thermal maturity mudrock sample. R values of this magnitude indicate a need for further standardization of reflectance measurement of dispersed organic matter. Furthermore, these R values quantify realistic interlaboratory measurement dispersion for a difficult but critically important analytical technique necessary for thermal maturity determination in the source-rock reservoirs of unconventional petroleum systems.

1. Introduction and background

Determination of the reflectance of vitrinite in sedimentary rocks by optical microscopy has been long regarded as the standard technique for reliable estimation of thermal maturity in petroliferous basins (Curiale and Curtis, 2016; Dow, 1977; Suárez-Ruiz et al., 2012; Taylor et al., 1998). The reflectance of vitrinite (measured under oil immersion, symbolized VR_o , in %), or, in some cases, reflectance of solid bitumen (symbolized BR_o), is used to determine if sedimentary rocks are immature, or have reached the oil, wet gas/condensate, or dry gas stages of petroleum generation. Stages of thermogenic alteration of sedimentary organic matter generally are characterized by diagenesis in the immature realm where VR_o is < 0.5–0.6%, catagenesis in the mature (petroleum generation) stage where VR_o is approximately 0.5–0.6 to 2.0–2.3%, and metagenesis in the overmature stage where VR_o is greater than approximately 2.0–2.3% (Hartkopf-Fröder et al., 2015; Teichmüller, 1987; Tissot and Welte, 1984). We note that not all practitioners agree on usage and application of these VR_o boundaries. In particular, the term ‘overmature’ typically is applied in the fossil fuel industry at the upper limit of liquid hydrocarbon generation at about 1.3–1.5% VR_o (e.g., Peters, 1986; Peters and Cassa, 1994; ASTM, 2015b). Moreover, gas production still is possible from overmature shales where VR_o exceeds approximately 2.0–2.3% (Zagorski et al., 2012). In the past, analysis of VR_o primarily was used in conventional petroleum system evaluation to establish presence of a thermally mature source rock from which petroleum was generating or had been generated in the past (Demaison, 1984; Hunt, 1996; Magoon and Dow, 1994). This still is an important application, but with increasing interest in shale petroleum exploitation since the 1970s (Curtis, 2002) and advent of the ‘shale revolution’ in the United States since about 2005 (Hackley and Cardott, 2016; Wang et al., 2014), VR_o analysis now is commonly used for delineation of ‘sweet spots’

and identification of the prime acreage in unconventional source-rock reservoirs (Curiale and Curtis, 2016; Peters et al., 2016).

Increased need for thermal maturity information in source-rock reservoirs also has sharpened focus on complementary approaches to VR_o analysis. Programmed pyrolysis analysis is a cost- and time-efficient approach to determination of thermal maturity in source rock reservoirs (Espitalie et al., 1985; Peters, 1986), but its interpretation may suffer from contamination by drilling mud or from un-expelled oil (Carvajal-Ortiz and Gentzis, 2015, 2018) as do other bulk geochemical approaches to thermal maturity determination. Other workers have developed bulk and *in situ* spectroscopy-based approaches to assess shale thermal maturity using, e.g., Raman measurements (Hackley and Lünsdorf, 2018; Lupoi et al., 2017, 2019; Romero-Sarmiento et al., 2014; Sauerer et al., 2017, among others). Wilkins et al. (2018) used the same samples of the current study in an *in situ* Raman spectroscopy-based effort to determine thermal maturity, acknowledging that the dry objectives used for micro-Raman spectroscopy limited organic matter identification. Others have used a bulk rock Fourier transform infrared spectroscopy approach (Cheshire et al., 2017; Craddock et al., 2017; Lis et al., 2005), but this method cannot identify or separate compositional variability between individual organic matter types. In addition, careful work has shown that chemical heterogeneity in organic matter, surface quality and matrix effects may limit spectroscopic approaches to thermal maturity determination, even when applied *in situ* (Jubb et al., 2018; Khatibi et al., 2019). While all approaches to source-rock reservoir thermal maturity determination have merit, particularly as complementary tools, there is no widely-accepted substitute for petrographic measurement of reflectance, because this approach is specific to individual organic matter entities, e.g., vitrinite or solid bitumen.

Efforts to improve and standardize reflectance measurements of organic matter dispersed in sedimentary rocks have been an objective of an International Committee for Coal and Organic Petrology

(ICCP) working group since 2008 (ICCP, 2009). The working group (currently called 'Identification of Thermal Maturity Relevant Organic Matter') first produced a consensus test method for shale reflectance measurement in 2011 (ASTM D7708: Standard test method for microscopical determination of the reflectance of vitrinite dispersed in sedimentary rocks; ASTM, 2015b). This test method has since been widely adopted by the organic petrography community. For example, it is used in the ICCP Dispersed Organic Matter Vitrinite Reflectance Accreditation program (see <https://www.iccop.org/accreditation/general-information/>), and it has accrued 50 + citations in peer-reviewed literature according to the Scopus citation database (as of June 1, 2019).

An initial interlaboratory study (ILS) to develop precision statistics for ASTM D7708 was conducted in 2012–2013 using a wide array of shale types. Those samples were selected to present the potential range of rock materials which could be tested (Hackley et al., 2015). The samples used in the ILS were immature to overmature for generation of liquid hydrocarbons (0.31–1.53% VR_o), organic-lean to organic-rich (1–22 wt% total organic carbon) and from lacustrine (generally Type I kerogen), marine (generally Type II kerogen) and terrigenous (carbonaceous shale from coal measures with Type III kerogen) environments. Results of the ILS showed that interlaboratory reproducibility of reflectance measurement was improved by use of a common methodology (D7708) compared to earlier interlaboratory exercises (e.g., Borrego, 2009; Dembicki, 1984). However, the ILS also showed poor reproducibility limits (R, defined as maximum difference between valid results obtained on same test material by different operators in different laboratories) for certain sample types. In particular, samples with VR_o > 1.0% had R values of 0.41–0.54, compared to 0.11 to 0.33 for samples with VR_o < 1.0%. It was thought that the poorer reproducibility limits for higher maturity samples might have been, in part, related to low abundance of organic matter. The suggestion was then made that a future ILS should consider high maturity samples with abundant organic matter (Hackley et al., 2015).

The initial ILS looked at a range of shales from immature Eocene Green River Mahogany Zone oil shale to overmature Lower Cretaceous Pearsall Formation. In the present ILS, we elected to look at reproducibility of reflectance measurements in the source-rock reservoir oil and gas resource plays currently under exploitation in the United States, including the Marcellus, Haynesville, Eagle Ford, Barnett, Bakken and Woodford. Six samples were selected on the basis of high thermal maturity and high organic matter content. Samples were distributed in early 2016 to ILS participants in forty laboratories in the Americas, Europe, Africa and Australia. This paper evaluates the results of the ILS in the context of the interlaboratory reproducibility limit

R with the objective to quantify reproducibility limits of organic matter reflectance in thermally mature source-rock reservoirs of unconventional petroleum systems.

2. Methods

2.1. Basic characterization

Samples (Table 1) were analyzed by LECO carbon analyser and by multiple programmed pyrolysis instruments (Rock-Eval 2, Rock-Eval 6, HAWK) per typical methods (Espitalie et al., 1985; Espitalié et al., 1977). Samples were run for programmed pyrolysis as-received and also following Soxhlet extraction using typical methods and solvents (e.g., Dembicki et al., 1976) in multiple laboratories. X-ray diffraction mineralogy analyses were run as per the method described in Hackley et al. (2019) and the X-ray spectra were processed using a custom USGS in-house computer software program (Hosterman and Dulong, 1989). Samples were petrographically evaluated by typical optical and scanning electron microscopy (SEM) methods to ensure suitability for the ILS.

2.2. Instructions for participants

Samples were distributed to ILS participants as non-extracted rock chips which had been processed through a stainless-steel jaw crusher. Samples 1, 4, 5, and 6 were further sieved to pass 8 mesh prior to distribution (these samples had to be reduced from core blocks whereas samples 2 and 3 were already reduced to 8 mesh for prior studies). Instructions sent with the samples were to continue processing the samples as per the typical preparation method of the participant laboratories, e.g., the USGS follows ASTM D2797 (ASTM, 2015a) for sample preparation, which uses 850 µm top size. Participants were asked to measure reflectance as per the ASTM D7708 test method (ASTM, 2015b) which was distributed with samples in hardcopy. The participants were instructed that the ILS would evaluate participant's ability to follow the reporting requirements listed in Section 11 of ASTM D7708, with the intent to document shortcomings and inadequacies present in the test method. Participants were given their choice of reporting format, e.g., via a document, spread sheet, slide show, etc., as long as the information contained in the report adhered to the requirements of D7708. The instructions advised to: '*find and measure sufficient indigenous organic matter representative of in situ thermal maturity in each of the six samples to meet the twenty measurements requirement of ASTM D7708*'. Further, the instructions stated: '*If you cannot find and measure vitrinite, identify what you do find and measure.*'

Table 1
Samples used for this study.

Code	USGS Field ID	USGS Lab ID	Formation	State	County
1	WV-6 MERC No. 1 7440.7'	E160303-069	Marcellus	WV	Monongalia
2	BP A-8H T.W. George 11366-11366.2'	E160303-070	Haynesville	TX	Harrison
3	Shell 1 Leppard 13671'	E181017-001	Eagle Ford	TX	Bee
4	Blakely No. 1 7223'	E181017-002	Barnett	TX	Wise
5	Whiting BN 1-23H 11352-11358'	E181017-003	Bakken	ND	Billings
6	Pioneer RTC 1 13027'	E181017-004	Woodford	TX	Pecos

Code	Age	API	Latitude	Longitude	Collector
1	Middle Devonian	470612037000	39.669167	-79.974167	John Repetski, USGS
2	Upper Jurassic	422033455700	32.411760	-94.432800	James Donnelly, BEG
3	Upper Cretaceous	420253038901	28.599170	-98.029170	Stephen Ruppel, BEG
4	Mississippian	424973304100	33.00594	-97.402010	James Donnelly, BEG
5	Devonian-Mississippian	330070066000	47.194467	-103.568295	Paul Hackley, USGS
6	Devonian-Mississippian	423713779001	30.785580	-103.461420	Stephen Ruppel, BEG

USGS, U.S. Geological Survey; BEG, Bureau of Economic Geology, The University of Texas at Austin.

The previous ILS exercise (Hackley et al., 2015) asked participants to measure each sample in duplicate to determine repeatability; the current ILS requested only one analysis per sample. Not collecting measurements in duplicate preempts the possibility to evaluate precision per ASTM E691: Standard practice for conducting an interlaboratory study to determine the precision of a test method (ASTM, 2015c). However, it was decided that one analysis per sample would boost participation in the ILS.

2.3. Reflectance determination method

In brief, the D7708 reflectance determination method involves mounting a sedimentary rock sample in epoxy or thermoset type resins, grinding the surface flat and polishing to a final stage of 0.05 μm according to ASTM D2797 (ASTM, 2015a). Using a reflected light microscope with an oil immersion objective, light reflected from sample organic matter is measured at a detector which is calibrated to standards of known reflectance. A wide array of microscope systems and light detection apparatus are available; use of ASTM D7708 is not limited to a certain type of equipment.

3. Samples

Six samples were used for this study. All samples were from collections of the U.S. Geological Survey, previously characterized for another study (Hackley and Cardott, 2016), and representative of the source-rock reservoir petroleum systems currently exploited in North America (Table 1). In all cases, the samples were from conventional oil and gas exploration cores and were selected because they are organic-rich and from thermally mature peak oil to dry gas conditions. Because of advanced thermal maturity, oil-prone macerals alginite and bituminite (which are common in immature marine source rocks) are not recognizable as such due to their conversion to petroleum (e.g., Hackley and Lewan, 2018) or due to the loss of their distinguishing optical properties (Pickel et al., 2017).

3.1. Geochemical screening and mineralogy

Geochemical data compiled from the samples in Table 2 shows total organic carbon (TOC) content ranges from 2.9 to 11.6 wt%, whereas T_{max} values range from 447 to 591 $^{\circ}\text{C}$. These data confirm the organic-rich, thermally mature nature of the sample set (e.g., Baskin, 1997; Peters, 1986; Peters and Cassa, 1994). Production index (PI) values ranging from 0.14 to 0.74 also confirm mature to postmature conditions (Peters and Cassa, 1994). Note that the average programmed pyrolysis parameters in Table 2 exclude results from extracted samples, whereas the average T_{max} values do include results from extracted samples but exclude unreasonable low values (e.g., < 400 $^{\circ}\text{C}$) obtained from analyses of the Marcellus (4 excluded values), Eagle Ford (2 excluded values) and Barnett (1 excluded value) samples. When pro-

grammed pyrolysis data are compiled in the modified van Krevelen Hydrogen Index (HI) vs. Oxygen Index (OI) diagram, samples are shown to have a thermally evolved Type II kerogen (Bakken) or carbon-rich inert organic matter (Type IV) signature (Fig. 1A), near the origin. We note that the Type IV signature is due to high thermal maturity and that a Type II signature would be expected from these marine shale samples at lower maturities. When plotted in the HI vs. T_{max} discriminant diagram (Fig. 1B), the Bakken sample falls in the oil window maturity field, the Woodford sample lies at the threshold between wet and dry gas thermal maturity, whereas the four remaining samples are in the dry gas window. Again, all but the oil window thermal maturity Bakken sample have a carbon-rich inert organic matter (Type IV) signature.

Mineralogical analysis (Table 3) shows that samples dominantly are composed of quartz and illite, except for the Eagle Ford, which contains 54 wt% carbonate. Two samples, the Marcellus and Bakken, also contain a significant proportion of pyrite.

3.2. Marcellus Shale

Sample 1 from the Middle Devonian Marcellus Shale of the Appalachian Basin in West Virginia contains 5.6 wt% TOC content (on average, $n = 6$, Table 2). Difficulties in obtaining reasonable T_{max} values from this sample prompted solvent extraction, which reduced average S1 and S2 by 96 and 79%, respectively. The average T_{max} of 591 $^{\circ}\text{C}$ reported in Table 2 is the mean of 3 analyses, two of which were on extracted sample material. X-ray diffraction (XRD) analysis (Table 3) indicates sample mineralogy is dominated by quartz and clays with a minor amount of pyrite. Organic content is dominated by solid bitumen, which occurs disseminated between mineral grains and occasionally in larger accumulations (Fig. 2A). Petrographic analysis by SEM shows that abundant intraparticle organic nano-porosity (e.g., Loucks et al., 2012) occurs in solid bitumen (Fig. 2B). No organic fluorescence was present in this sample (or in the other samples described herein), consistent with high thermal maturity. Terrigenous macerals vitrinite and inertinite were rare or absent. Previous work on samples from this same core indicated VR_o and BR_o values ranging from 1.6 to 2.3% (Hackley and Cardott, 2016; Streib, 1981).

3.3. Haynesville Formation

Sample 2 from the Upper Jurassic Haynesville Formation in the Gulf Coast Basin of Texas contains 2.9 wt% TOC and has T_{max} of 526 $^{\circ}\text{C}$ (Table 2). Silicate minerals quartz and clays are most abundant (Table 3). The organic matter component is similar to the Marcellus wherein finely disseminated solid bitumen pervades the rock matrix along mineral grain boundaries or occurs in foraminifera chambers (Fig. 2C). This dominant solid bitumen population has high reflectance (generally $> 1.5\%$). A few sparse larger accumulations of solid bitumen also

Table 2
Summary organic carbon and programmed pyrolysis data.

Code	Formation	TOC	S1	S2	S3	Tmax	HI	OI	PI
1	Marcellus	5.63 (6, 0.35)	5.05 (4, 1.11)	1.78 (4, 0.32)	0.38 (4, 0.17)	591 (3, 25)	31 (4, 7)	7 (4, 4)	0.74 (4, 0.04)
2	Haynesville	2.87 (5, 0.21)	0.41 (4, 0.25)	0.55 (4, 0.41)	0.30 (4, 0.07)	526 (4, 8)	18 (4, 13)	10 (4, 3)	0.44 (4, 0.14)
3	Eagle Ford	5.48 (5, 0.47)	0.28 (4, 0.14)	0.75 (4, 0.33)	0.33 (4, 0.06)	563 (6, 21)	12 (4, 4)	6 (4, 2)	0.29 (4, 0.16)
4	Barnett	3.18 (8, 0.22)	0.38 (6, 0.31)	0.53 (6, 0.18)	0.33 (6, 0.25)	533 (7, 32)	17 (6, 6)	11 (6, 9)	0.38 (6, 0.16)
5	Bakken	10.73 (7, 0.65)	4.12 (6, 0.60)	24.87 (6, 2.83)	0.69 (6, 0.36)	447 (8, 2)	235 (6, 29)	6 (6, 4)	0.14 (6, 0.02)
6	Woodford	11.60 (7, 0.31)	2.93 (6, 0.76)	7.90 (6, 0.82)	0.46 (6, 0.33)	476 (8, 5)	65 (6, 9)	4 (6, 3)	0.27 (6, 0.06)

*TOC, total organic carbon in wt.%, all analyses from LECO carbon analyser; S1, S2 = mg hydrocarbons/g rock; S3 = mg CO_2 /g rock; Tmax in $^{\circ}\text{C}$; HI = hydrogen Index ($\text{S}_2 \cdot 100 / \text{TOC}$); OI = Oxygen Index ($\text{S}_3 \cdot 100 / \text{TOC}$); PI = Production Index ($\text{S}_1 / (\text{S}_1 + \text{S}_2)$). Reported values are average of n analyses from different programmed pyrolysis instruments (Rock-Eval 2, Rock-Eval 6, Hawk), n in parentheses with standard deviation. Average Tmax values include extracted samples and exclude unreasonable low values; all other reported average parameters exclude values from extracted samples.

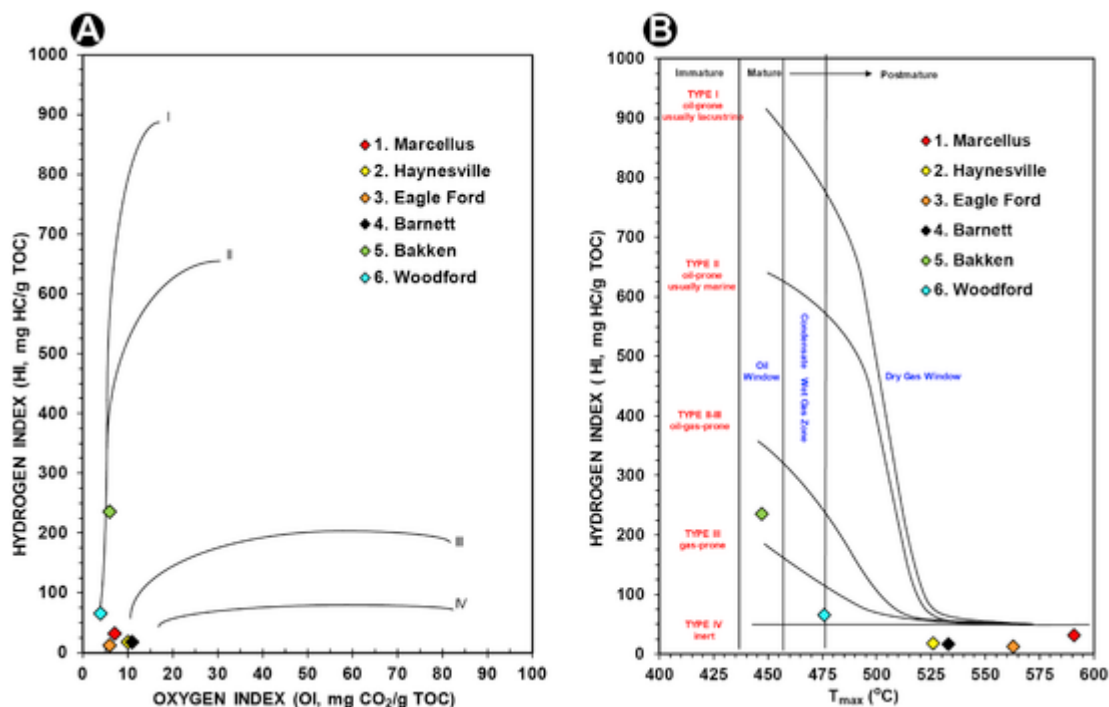


Fig. 1. A. Hydrogen Index (HI, S2*100/TOC in mg hydrocarbons per g total organic carbon) vs Oxygen Index (OI, S3*100/TOC in mg CO₂ per g total organic carbon) modified von Kreylen diagram. The kerogen type evolution lines are based on multiple sources (Espitalie et al., 1985; Hart and Steen, 2015; Peters, 1986). B. Plot of Hydrogen Index (HI, S2*100/TOC in mg hydrocarbons per g total organic carbon) vs T_{max} (°C) showing evolution of kerogen composition with thermal maturity. Maturation boundaries are based on Peters and Cassa (1994) and Baskin (1997). The kerogen type evolution lines are based on Espitalie et al. (1985) and Hart and Steen (2015).

Table 3
X-ray diffraction mineralogy data in wt.%.

Code	Formation	LOI	QTZ	FLD	CARB	I/S	ILLITE	KAOL	CHLR	PY	OTHER
1	Marcellus		40	2	4	n.d.	35	n.d.	6	10	3
2	Haynesville		34	4	9	n.d.	38	n.d.	10	5	n.d.
3	Eagle Ford		18	n.d.	54	6	11	2	n.d.	7	1
4	Barnett	2.89	56	3	10	n.d.	21	n.d.	n.d.	6	1
5	Bakken	10.79	43	2	16	n.d.	22	n.d.	4	10	3
6	Woodford	12.92	75	4	1	n.d.	9	n.d.	n.d.	6	n.d.

LOI, loss-on-ignition; QTZ, quartz; FLD, feldspars; CARB, carbonates; I/S, illite-smectite mixed layer clays; KAOL, kaolinite; CHLR, chlorite; PY, pyrite. Values are estimated to be accurate to ± 5 wt%.

are present. A second solid bitumen population (rare in abundance) with lower reflectance (~0.8–1.0%) also occurs in thin veins and vugs. Based on the T_{max} value and production of mostly dry gas in the Haynesville play area (Kaiser, 2012), this second population is not representative of indigenous thermal maturity. The terrigenous maceral inertinite is present whereas vitrinite is rare or absent. Authigenic carbonate occurring as rhombs and spheres frequently is rimmed by solid bitumen (Fig. 2C). Again, solid bitumen contains abundant intraparticle organic nano-pores (Fig. 2D). Previous workers have reported dry gas thermal maturity VR₀ and BR₀ values of about 1.4–1.7% for samples from this same core (Hackley and Cardott, 2016; Hammes and Frébourg, 2012).

3.4. Eagle Ford formation

Sample 3 from the Upper Cretaceous Eagle Ford Formation in the Gulf Coast Basin of Texas contains 5.5 wt% TOC and has T_{max} of 563 °C (Table 2). Unlike the other samples of this study, the Eagle Ford sample contains >50 wt% carbonate (Table 3) and a much smaller quantity of silicate minerals due to distal deposition on a sediment-

starved carbonate platform (Eldrett et al., 2015). Solid bitumen is the dominant organic matter and occurs finely disseminated in the carbonate mineral matrix (Fig. 2E and F). Planktic Globigerina foraminifera are common, and their chambers typically are filled with solid bitumen and contemporaneous re-crystallized carbonate and/or sulfide (Fig. 2E). Structured terrigenous inertinite macerals are common whereas vitrinite is assumed present but qualitatively less abundant (Fig. 2F). Previous work reported BR₀ values of about 1.8% for samples from this same core (Hackley and Cardott, 2016) and calculated (from T_{max}) VR₀ values of about 1.2–1.5% were reported for nearby Eagle Ford samples from similar depths (Zhang et al., 2017). Intraparticle organic nano-porosity is present; preliminary work suggests it is most common in solid bitumen infilling pyrite framboid clusters.

3.5. Barnett Shale

Sample 4 from the Mississippian Barnett Shale in the Fort Worth Basin of Texas contains 3.2% TOC with T_{max} of 533 °C (Table 2). Like the other samples, solid bitumen dominates the organic matter component, occurring dispersed in a matrix of quartz and clays (Fig. 3

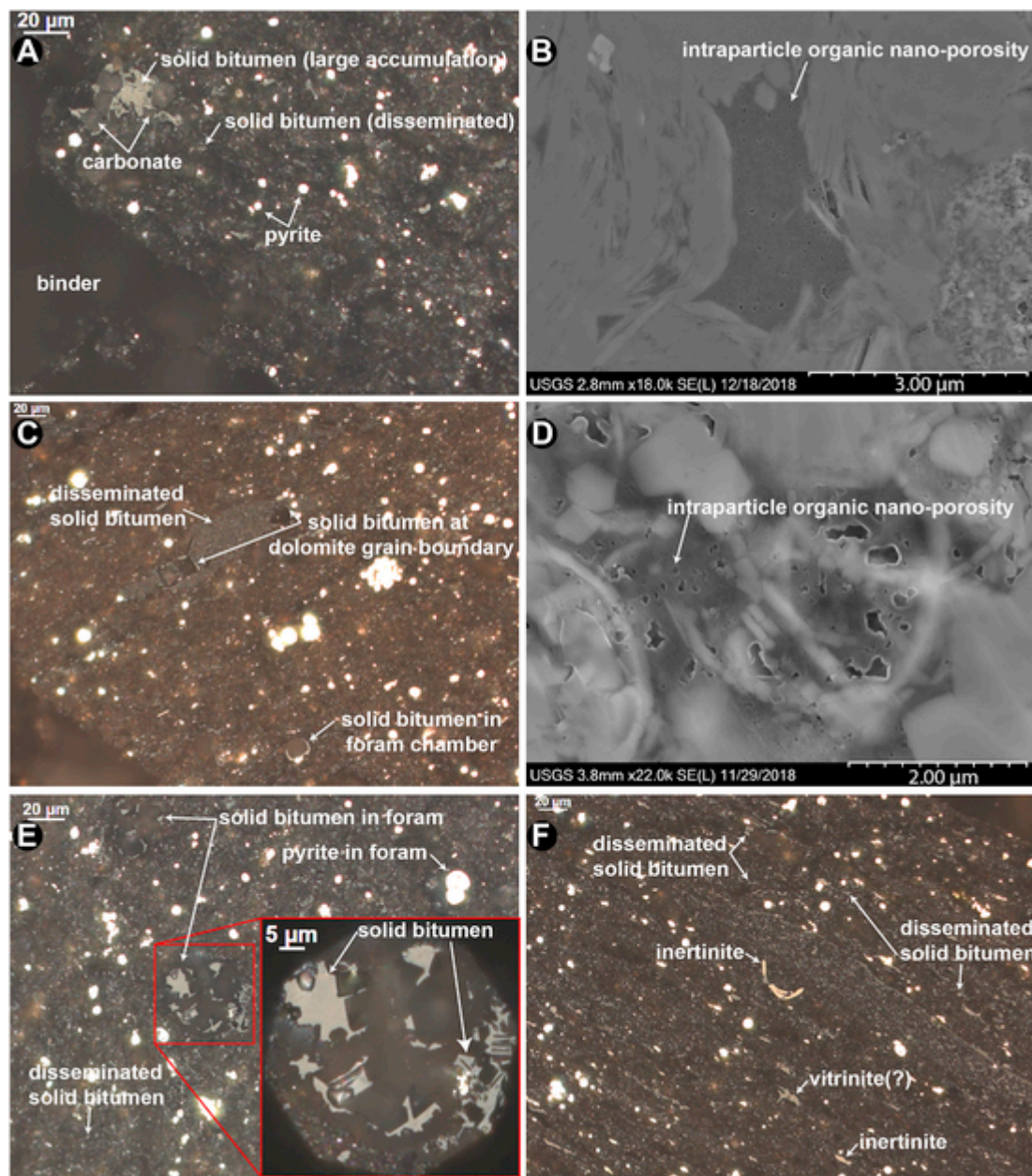


Fig. 2. A. Photomicrograph of large (~30 μm) solid bitumen accumulation and disseminated solid bitumen in Marcellus Shale sample 1 under oil immersion in white incident light. B. Scanning electron microscopy (SEM) micrograph of Marcellus Shale sample 1 showing intraparticle organic nano-porosity in solid bitumen. C. Photomicrograph of solid bitumen in Haynesville Formation sample 2 under oil immersion in white incident light, showing disseminated solid bitumen and solid bitumen in foraminifera chambers and along dolomite mineral grain boundaries. D. SEM micrograph of Haynesville Formation sample 2 showing intraparticle organic nano-porosity in solid bitumen with inorganic inclusions. E. Photomicrograph of solid bitumen in foraminifera chamber in Eagle Ford Formation sample 3 under oil immersion in white incident light. F. Photomicrograph of inertinite and vitrinite (?) with disseminated solid bitumen in Eagle Ford Formation sample 3 under oil immersion in white incident light.

A). Embayment textures (euhedral mineral terminations intruding organic matter, e.g., Hackley and Cardott, 2016; Hackley and Lewan, 2018; Hackley et al., 2018; Hackley et al., 2017a, 2017b; Peters et al., 2018) are common and intraparticle organic nano-porosity is abundant (Fig. 3B; this sample is from the same core as pioneering studies of organic nano-porosity in ion-milled shale samples by Loucks et al., 2009). The terrigenous maceral inertinite is rarely observed, occurring as fine-grained dispersed fragments (Fig. 3A), rounded char particles or in elongate lath and spindle textures. Previous work on this same core has reported a wide range of VR_o and BR_o values from about 1.3 to 2.0% (Hackley and Cardott, 2016; Lewan and Pawlewicz, 2017; Loucks et al., 2009; Romero-Sarmiento et al., 2014).

3.6. Bakken Shale

Sample 5 from the Devonian-Mississippian upper Bakken Shale in the Williston Basin of North Dakota contains 10.7 wt% TOC and is at peak oil thermal maturity with T_{max} of 447 $^{\circ}\text{C}$ (Table 2), similar to previous T_{max} data reported by Fishman et al. (2015). This is the lowest maturity sample studied herein with a BR_o value of about 0.9% (Hackley and Cardott, 2016). Disseminated solid bitumen dominates the organic component, locally occurring in accumulations > 20 μm in diameter or containing inclusions of granular high reflectance micrinite (?) (Fig. 3C). Fine-grained inertinite char also is present. Unlike the other samples of this study, intraparticle organic nano-porosity is

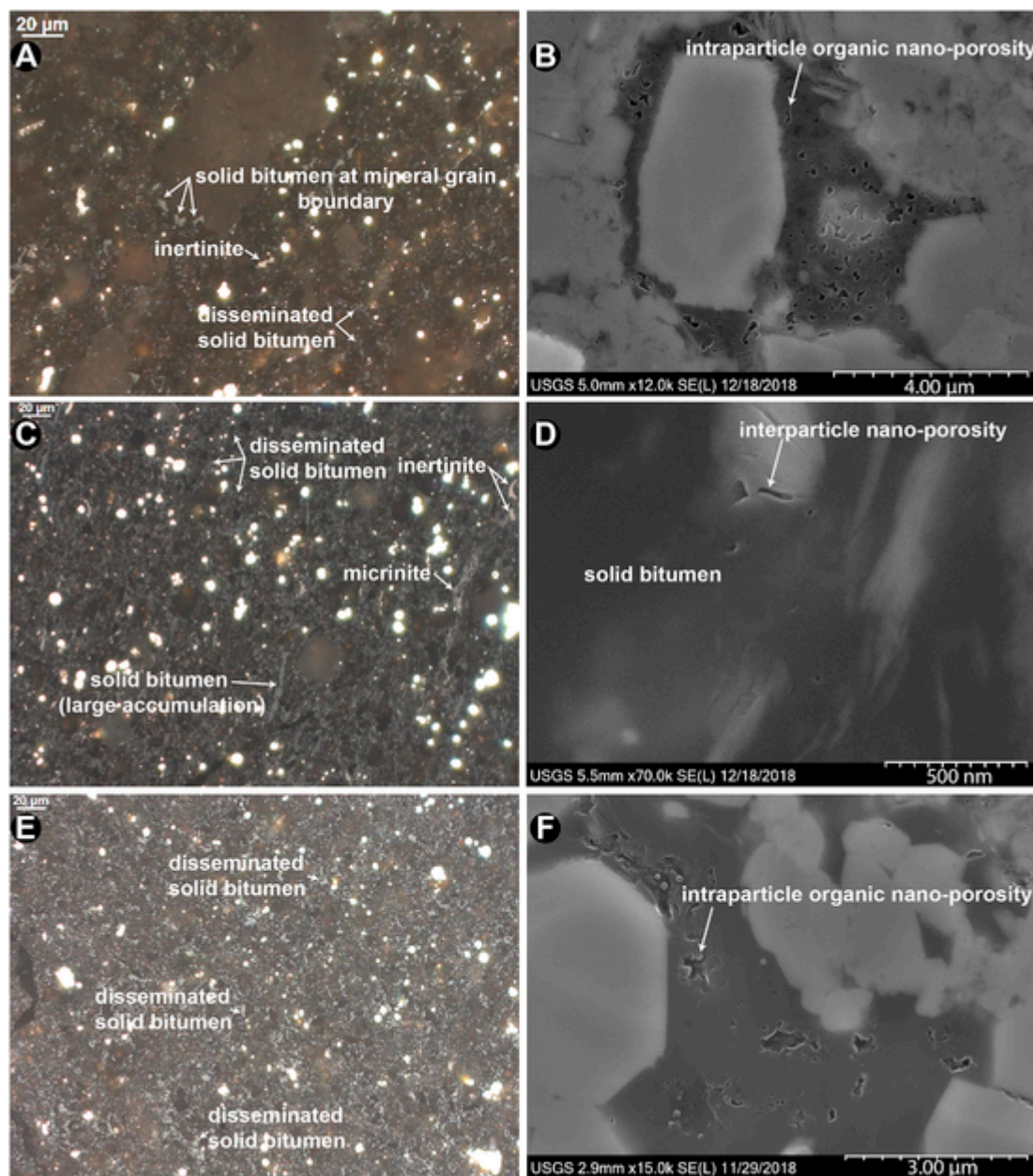


Fig. 3. A. Photomicrograph of disseminated and solid bitumen occurring at mineral grain boundaries in Barnett Shale sample 4 under oil immersion in white incident light. B. Scanning electron microscopy (SEM) micrograph of Barnett Shale sample 4 showing intraparticle organic nano-porosity in solid bitumen. C. Photomicrograph of disseminated and larger accumulations of solid bitumen in Bakken Shale sample 5 under oil immersion in white incident light. D. SEM micrograph of Bakken Shale sample 5 showing interparticle nano-porosity at the contact between solid bitumen and the inorganic matrix. E. Photomicrograph of disseminated solid bitumen in Woodford Shale sample 6 under oil immersion in white incident light. F. SEM micrograph of Woodford Shale sample 6 showing intraparticle organic nano-porosity in solid bitumen.

rare to absent (Fig. 3D), presumably due to lower thermal maturity, and imaged porosity primarily occurs as interparticle features at the margins of mineral grains.

3.7. Woodford Shale

Sample 6 is from the Devonian-Mississippian Woodford Shale from the Delaware Basin of west Texas. The ILS sample contains 11.6 wt% TOC with T_{max} of 476 °C (Table 2) and is dominated by quartz followed by a small component from illite (Table 3). Previous workers reported VR_0 and BR_0 values of about 1.1–1.5% from the same Woodford core (Hackley and Cardott, 2016; Harris et al., 2013; Kibria et al., 2018) indicative of wet gas and condensate window thermal maturity. Similar to the previous samples, solid bitumen is the dominant or-

ganic matter (Cardott et al., 2015), occurring as a network ground-mass finely disseminated along mineral interstices (Fig. 3E). Embayment textures adjacent to authigenic minerals are common. Intraparticle organic porosity is present (Fig. 3F) but qualitatively not as common as in samples 1–4. Fine-grained inertinite is rare.

3.8. Sample summary

Summarizing, samples used for this ILS are representative of the source-rock reservoirs in unconventional resource plays currently under exploitation in the United States. All samples represent marine depositional environments, are thermally mature, and contain moderate to high organic matter content. Organic matter dominantly is solid bitumen, which contains intraparticle nano-porosity. Visual appreciation

of organic nano-porosity via SEM suggests intraparticle organic pores are most abundant in dry gas maturity samples and less abundant at lower maturities, consistent with previous studies (e.g., Chen and Xiao, 2014; Curtis et al., 2012; Klaver et al., 2015, 2016; Ko et al., 2018; Löhr et al., 2015; Modica and Lapierre, 2012; Pommer and Milliken, 2015, among others).

4. Results

Thirty-seven independent sets of reflectance measurements were received, including four instances where one set of results was the combined work of more than one analyst. All analysts (except see Acknowledgments section) share co-authorship on this paper and each analyst had opportunity to provide input to the paper at multiple stages of writing and review. As results were submitted via email to the ILS convener (P. Hackley), each participant received immediate feedback via a chart showing comparison of their result with the current group mean result for each sample. This approach allowed near real-time feedback to participants and provided an immediate independent check on their ability to obtain reflectance results in comparison to the group mean. Such feedback is desirable to petrographic laboratories as an efficient and economical quality assurance program and is thought to improve participation in ILS programs. Similar to the prior ILS (Hackley et al., 2015), several analysts chose to submit updated results after initial feedback, exclusively for cases where an insufficient number of measurements (e.g., <5 per sample) had been collected during the first analysis. Four analysts with an initial insufficient number of measurements (e.g., 0 to 2 measurements per sample) elected not to update their results for unknown reasons; these participants also are included in authorship but their results are excluded. During initial feedback, several petrographers asked for and were given information on sample provenance, including age, formation name, basin and location, and total organic carbon content. Again, similar to the previous ILS, in no case where updated results were provided are the data considered to be 'excessively sanitized', e.g., changes to reported VR_o or BR_o values were 0.1% or less in the few cases where an analyst elected to provide updated results based on initial submission of an insufficient number of measurements.

Results are compiled in Table 4 and illustrated graphically in Fig. 4. The results in Table 4 are not listed in the same order as the co-authorship order of this paper, which is alphabetical by last name.

More than one-half of analysts reported solid bitumen reflectance measurements; ten analysts reported only solid bitumen reflectance, i.e., these ten analysts did not identify and measure any vitrinite in any sample. Thirteen analysts reported only vitrinite reflectance, i.e., these analysts did not identify and measure solid bitumen in any sample. We speculate these differences are due to wide variability in the specific training and experience of the diverse set of analysts engaged in this ILS. Fourteen analysts reported both solid bitumen and vitrinite reflectance measurements. Group mean (including data from all analysts) solid bitumen and vitrinite reflectance measurements are consistent with previously reported values for these samples or for other samples from the same core (as presented in sections 3.2 to 3.7), ranging from 0.85% (Bakken, sample #5) to 2.04% (Eagle Ford, sample #3) for solid bitumen, and 0.90% (Bakken) to 1.83% (Marcellus, sample #1) for vitrinite (Fig. 4). However, we note that the group mean values reported in Fig. 4 include measurements which are clearly outliers according to multiple means of statistical evaluation, as will be shown below. Group standard deviation (GSD) values ranged from 0.09 to 0.43 for solid bitumen and from 0.19 to 0.47 for vitrinite. GSD was lowest for both vitrinite and solid bitumen in the Bakken which has the lowest mean reflectance value; however, GSD did not increase systematically with increasing mean R_o value as would be expected due to increasing optical anisotropy of organic matter (Hackley et al., 2015). GSD was highest for vitrinite in the Marcellus where the greatest dispersion in re-

ported mean vitrinite reflectance value occurred (from 0.92 to 2.73%). GSD was highest for solid bitumen in the Haynesville where six analysts selected the low reflecting (rare) solid bitumen as representative of thermal maturity. It is unclear why these analysts selected this population as representative of thermal maturity as it is clearly post-diagenetic and much less abundant than the pervasive pre-diagenetic solid bitumen (terms in the sense of Robert, 1988). It is speculated that this population was selected based on the following instruction from Jacob (1989): '[I]f several migrabitumen generations occur, the generation with the lowest reflectance is representative for the degree of maturity ...'. However, its presence in trace amounts as fracture fill and at rock fragment margins and the abundance of the higher reflecting solid bitumen population are key indicators that the low reflecting population is not indicative of indigenous thermal maturity, and instead represents a later stage migration, in the opinion of the majority of analysts who measured solid bitumen reflectance in this study.

Group mean reflectance values for solid bitumen and vitrinite reflectance did not show a consistent and systematic less than or greater than relationship to each other. Instead, group mean values fall close to a one-to-one line, and are related by a linear regression coefficient (r^2) of 0.85 (Fig. 5). This result is not unexpected, as previous empirical and experimental studies have shown reflectance of co-occurring solid bitumen and vitrinite to be similar at VR_o and BR_o values > 1.0% (Ferreiro Mählmann and Le Bayon, 2016; Hackley and Lewan, 2018; Jacob, 1989; Landis and Castaño, 1995; Robert, 1988; Schoenherr et al., 2007).

Participant experience in organic petrography analysis ranged from <5 years to >40 years, and about 30% of participants had >30 years experience (Fig. 6). No correlation was observed between participant years of experience and precision of performance [considering average unsigned multiple of standard deviation (AUSMD) as a performance measure, i.e., distance of the participant's result to the mean value (Borrego, 2009; Borrego et al., 2006; Hackley et al., 2015; Mendonca et al., 2010)]. Nevertheless, participants with the most years of experience generally had lower AUSMD values (Fig. 7), indicating the importance of training and expertise to the interpretive measurement of dispersed organic matter reflectance. However, we note that the presence of outlying measurements in the data pool may unduly influence evaluation with respect to AUSMD. Moreover, perhaps a better measure is the number of years of experience that participants have in evaluation of marine source rocks and the total number of samples evaluated, which could be recorded in a future ILS.

Laboratories with multiple analysts tended to return results very similar to each other, indicating some level of discussion between participants or similar conceptual training. For example, in the case of sample #2 from the Haynesville Formation containing a secondary low reflectance solid bitumen population (Fig. 4), three analysts at one laboratory incorrectly selected this same non-representative population as the organic matter for measurement of indigenous thermal maturity.

This ILS did not control for sample preparation differences. It is presumed that analysts followed standard test method D7708 which specifies samples are to be prepared via ASTM D2797 ending with a 0.05 μm polishing abrasive (ASTM, 2015a). If analysts used a coarser polishing compound at the final stage of preparation, it is possible that lower reflectance values would be obtained (e.g., Borrego, 2017).

5. Discussion

5.1. Vitrinite versus solid bitumen reflectance

The 'shale revolution' in North America has increased focus on petrographic analysis of source-rock reservoirs and this in turn has led to the understanding that solid bitumen commonly is the dominant organic matter in thermally mature mudrocks (Cardott et al., 2015; Hackley, 2017; Hackley and Cardott, 2016; Mastalerz et

Table 4
Reflectance data from ILS participants.

Petrographer ID	Marcellus		Haynesville		Eagle Ford		Barnett		Bakken		Woodford		
	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6		
	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	
1	Ro	1.68		1.73		1.80		1.54		0.90		1.37	
	s.d.	0.24		0.14		0.17		0.18		0.06		0.09	
	no.	80		60		70		50		50		50	
2	Ro	1.74	2.28	1.55	1.78	2.04	2.22	1.60	1.84	0.78	0.87	1.45	
	s.d.	0.13	0.30	0.09	0.18	0.15	0.18	0.08	0.22	0.06	0.05	0.13	
	no.	20	38	13	31	19	50	11	25	11	50	39	
3	Ro	1.35	1.61	1.47	1.44	1.61	1.76	1.47	1.42	0.84	0.65	0.91	0.82
	s.d.	0.11	0.10	0.21	0.11	0.30	0.13	0.14	0.12	0.08	0.10	0.11	0.13
	no.	22	21	22	10	16	38	21	19	30	20	23	26
4	Ro	2.25		1.88		1.91		1.77		0.81		1.26	
	s.d.	0.20		0.13		0.10		0.15		0.07		0.09	
	no.	32		35		36		25		45		40	
5	Ro	2.30		1.84		2.08	2.19	2.07		0.93		1.42	
	s.d.	na		na		na	0.09	0.12		0.08		n.a.	
	no.	1		1		1	16	20		6		1	
6	Ro	1.36	1.81	1.85		1.84	2.18	1.84		0.89		1.41	
	s.d.	0.09	0.11	0.06		0.06	0.06	0.08		0.03		0.06	
	no.	105	131	78		67	64	62		70		66	
7	Ro	2.30	2.18	2.00	2.09	1.89	2.28	1.76	1.99	0.98	0.88	1.41	1.63
	s.d.	0.14	0.19	0.11	0.12	0.10	0.07	0.12	0.15	0.06	0.04	0.07	0.15
	no.	27	14	19	4	21	41	28	4	31	23	24	7
8	Ro	1.51		1.88		2.03		1.42		0.90		1.07	
	s.d.	0.16		0.17		0.23		0.23		0.06		0.18	
	no.	11		17		20		20		22		21	
9	Ro	1.49	0.87	1.51	0.96	1.07	1.29	0.57	0.59	0.87	0.99	1.15	1.10
	s.d.	0.13	0.15	0.16	0.25	0.13	0.14	0.14	0.12	0.08	0.10	0.14	0.32
	no.	14	13	13	18	25	21	12	31	31	29	23	7
10	Ro	2.36		1.84		1.83		1.81		1.21		1.43	
	s.d.	0.09		0.09		0.10		0.11		0.11		0.09	
	no.	20		29		31		22		21		20	
11	Ro	1.50	1.02	1.61	1.02	1.65			1.64	1.21	0.85	1.25	0.95
	s.d.	0.17	0.13	0.25	0.16	0.16			0.25	0.15	0.13	0.06	0.11
	no.	20	12	11	13	20			32	9	13	10	5
12	Ro	2.15		1.85		1.86		1.83		1.51		1.45	
	s.d.	0.11		0.06		0.08		0.09		0.21		0.07	
	no.	38		23		12		31		24		31	
13	Ro	1.16		1.81		1.54		1.78		0.85		1.49	
	s.d.	0.11		0.12		0.14		0.13		0.06		0.11	
	no.	52		50		60		47		65		60	
14	Ro	2.10	1.89	1.99		1.97	2.20	1.78	2.00	0.92		1.40	
	s.d.	0.03	0.07	0.14		0.05	0.08	0.05	0.08	0.10		0.10	
	no.	14	11	21		11	32	21	21	19		38	
15	Ro		1.87		1.96		2.24		1.91		0.87		1.41
	s.d.		0.05		0.08		0.16		0.07		0.03		0.10
	no.		17		15		25		19		22		20
16	Ro		1.94		2.04		2.07		1.92		0.87		1.49
	s.d.		0.10		0.08		0.13		0.08		0.03		0.08
	no.		13		3		24		15		25		22
17	Ro		2.01		2.09		2.27		1.96		0.88		1.43
	s.d.		0.08		0.10		0.10		0.03		0.07		0.10
	no.		28		14		29		14		9		13
18	Ro	1.48		1.46		1.59		1.35		0.46		1.35	
	s.d.	0.14		0.17		0.19		0.12		0.10		0.26	
	no.	26		20		22		23		25		18	
19	Ro	0.92		1.34		1.59		1.21		0.70		0.80	
	s.d.	0.09		0.09		0.10		0.10		0.09		0.08	
	no.	12		15		10		10		11		16	
20	Ro	2.30		2.33		2.16		2.05		1.02		1.54	

Table 4 (Continued)

Petrographer ID	Marcellus		Haynesville		Eagle Ford		Barnett		Bakken		Woodford	
	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.
21	s.d.	0.16		0.08		0.11		0.11		0.06		0.08
	no.	59		34		22		26		33		28
	Ro	1.10		1.08		1.39		1.30		0.71		0.93
22	s.d.	0.38		0.37		0.40		0.34		0.18		0.29
	no.	26		21		41		25		31		32
	Ro		1.57	1.50	1.72	1.70	1.95	1.66	1.89	1.02	0.92	1.39
23	s.d.		0.15	0.07	0.16	0.09	0.12	0.11	0.14	0.06	0.08	0.10
	no.		72	19	27	13	15	20	35	17	94	89
	Ro	2.38	1.73	1.82	1.54	1.58	1.88		1.69	0.74		1.37
24	s.d.	0.16	0.30	0.12	0.16	0.16	0.13		0.17	0.06		0.09
	no.	38	20	30	19	9	27		30	31		30
	Ro	2.41	2.01	2.18	1.89	2.14	2.10	1.83	2.01	0.92	0.75	1.43
25	s.d.	0.11	0.41	0.15	0.08	0.11	0.12	0.09	0.11	0.04	0.09	0.09
	no.	30	32	32	30	30	22	25	20	32	31	32
	Ro	2.73		2.12		2.16		2.26		0.85		1.31
26	s.d.	0.09		0.14		0.04		0.06		0.03		0.08
	no.	9		8		2		7		5		4
	Ro	2.04		2.26		2.28		2.28		0.96		1.53
27	s.d.	0.45		0.18		0.20		0.37		0.05		0.10
	no.	70		63		25		50		100		100
	Ro	1.70	1.66	2.09	2.40	2.29	2.19	1.92	1.98	0.97	0.93	1.50
28	s.d.	0.59	0.29	0.26	0.29	0.23	0.19	0.60	0.30	0.09	0.15	0.09
	no.	3	19	10	9	3	24	5	11	20	27	5
	Ro	1.69		1.87		1.77		1.86		0.77		1.33
29	s.d.	0.34		0.15		0.10		0.20		0.06		0.05
	no.	44		20		20		35		40		40
	Ro	1.73		1.67		1.40		1.82		0.78		1.08
30	s.d.	0.17		0.24		0.19		0.26		0.07		0.10
	no.	20		20		23		20		32		31
	Ro		1.55		1.09		2.36		1.92		0.96	1.63
31	s.d.	0.09		0.12		0.08		0.12		0.06		0.09
	no.		32		21		30		30		30	30
	Ro	1.77		1.67		1.30		1.29		0.80		1.17
32	s.d.	0.17		0.21		0.18		0.14		0.06		0.17
	no.	24		33		28		21		23		24
	Ro		1.42		0.94		2.33		1.82		0.94	1.61
33	s.d.		0.13		0.09		0.06		0.09		0.05	0.05
	no.		18		30		29		30		33	31
	Ro		1.64		1.92		1.99		1.52		0.76	1.29
34	s.d.		0.11		0.26		0.15		0.19		0.14	0.13
	no.		31		54		50		40		66	33
	Ro		1.55		1.13		2.34		1.74		0.93	1.68
35	s.d.		0.19		0.28		0.10		0.15		0.06	0.14
	no.		35		21		25		31		31	34
	Ro		1.69		1.68		1.97		1.57		0.83	1.46
36	s.d.		0.16		0.15		0.23		0.18		0.09	0.14
	no.		58		33		80		70		83	98
	Ro		1.86	1.73	1.76	1.80	2.09	1.89	2.38	0.93	0.79	1.22
37	s.d.		0.51	0.08	0.616	0.07	0.05	0.09	0.51	0.05	0.19	0.08
	no.		38	20	28	15	25	18	17	21	54	22
	Ro		0.78		1.00		1.22		1.13		0.64	0.85
	s.d.		0.08		0.13		0.23		0.18		0.08	0.15
	no.		30		62		96		59		59	58

Vit., vitrinite; S.B., solid bitumen; Ro, reflectance, s.d., standard deviation, no., number of measurements.

al., 2018; Misch et al., 2019). Many of the important source-rock reservoir petroleum systems in North America occur in Devonian to Mississippian strata (e.g., Bakken, Barnett, Marcellus, Woodford); this is early in the evolution of vascular land plants (e.g., Morris et al., 2018) and vitrinite is rare or difficult to identify in these strata (Hackley

and Lewan, 2018; Hackley and Lünsdorf, 2018; Khatibi et al., 2019). In this ILS, these two facts (i.e., dominance of solid bitumen in thermally mature mudrocks and scarcity of vitrinite in these Paleozoic strata) may have resulted in the unintended consequence of mistaken identification of solid bitumen as vitrinite, particularly in the four Pa-

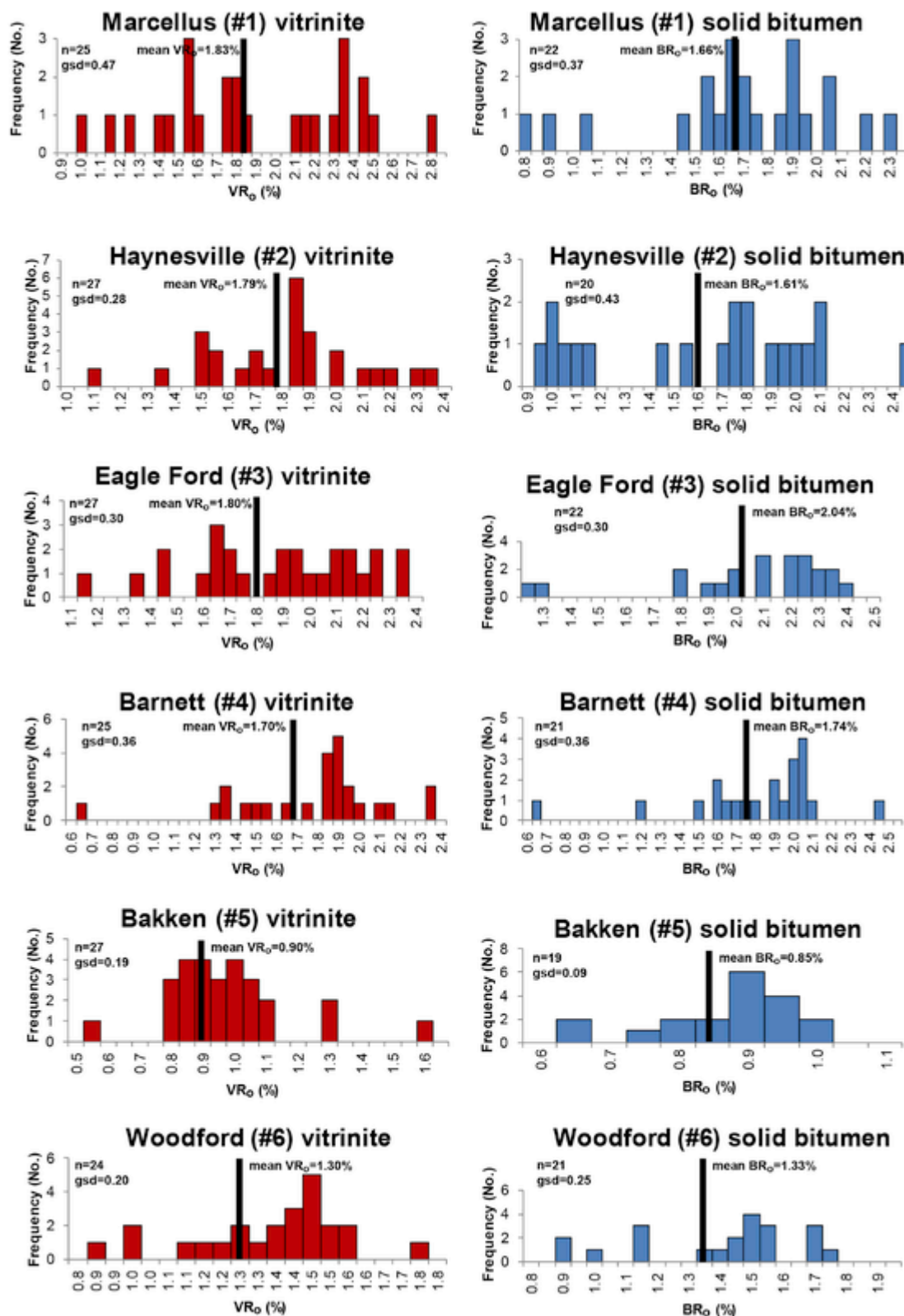


Fig. 4. Histograms of all data for mean vitrinite and solid bitumen reflectance for the six ILS samples. Note that dimensions of histogram axes are not the same in each, dependent on number of analyses and range of measurement values. Black bar shows mean value of all analysts with no outliers excluded, n = number of results, gsd = group standard deviation, VR_o = vitrinite reflectance, BR_o = solid bitumen reflectance.

leozoic samples. As noted above, thirteen analysts reported only vitrinite reflectance despite that all six samples contain abundant solid bitumen which is unmistakable in identification due to embayment-

type void-filling textures. Since all samples are vitrinite-lean, these participants may have misidentified larger accumulations of solid bitumen with clear grain boundaries as vitrinite, as most of the solid bitu-

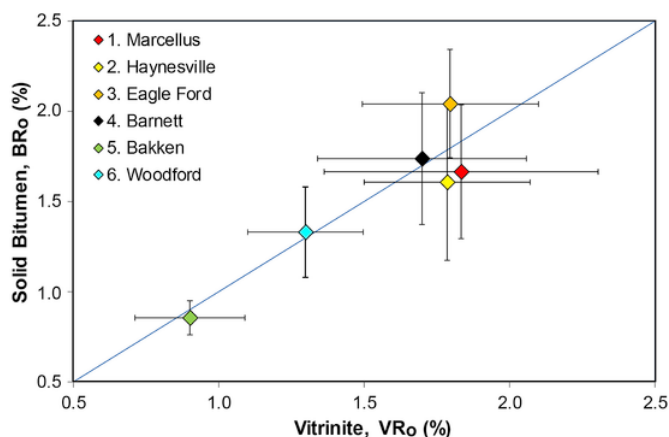


Fig. 5. Group mean solid bitumen reflectance vs group mean vitrinite reflectance for the six ILS samples. Error bars show group standard deviation.

men occurs as fine-grained disseminated intergranular material. These larger accumulations may accept a better polish (e.g., Hackley et al., 2018), and thus stand out to petrographers as somehow ‘different’ than the disseminated solid bitumen which occurs in mineral interstices. Nevertheless, the broad range in values reported by participants who only identified solid bitumen (Table 4) suggests that misidentification of solid bitumen as vitrinite is not the only problem impacting reproducibility of reflectance measurements of dispersed organic matter in sedimentary rocks.

To-date, there are only a few studies which have compared the range and distribution of reflectance values from co-occurring vitrinite and solid bitumen (e.g., Wei et al., 2016), and no studies which have done so at the peak oil to dry gas thermal maturity level of the current work. That is, there is no evidence that the reflectance range of solid bitumen is as narrowly defined as that of co-occurring vitrinite, although some studies have noted the possibility of petroleum migration which could lead to multiple populations of solid bitumen in a single sample (Kus et al., 2016; Petersen et al., 2013). The previous ILS (Hackley et al., 2015) found no statistical difference between measurements of mean vitrinite and solid bitumen reflectance for the samples considered therein. A similar result is observed here, and it is also observed that there is no systematic dispersion of measurement for one organic matter type compared to the other. That is, individual mean vitrinite and solid bitumen reflectance measurements reported in this study are overlapping in range and do not show consistently lower standard deviation of measurement in one organic matter type than the other. This suggests that misidentification of solid bitumen as vitrinite continues as an issue in the petrography of source-rock reservoirs (e.g., Hackley et al., 2013), or that there is indeed no difference in reflectance of these co-occurring organic matter types, particularly at higher maturities. Nevertheless, if the analyst believed vitrinite was present, they would have selected lower reflecting material to avoid measurement of similar-appearing semifusinite. Conversely, if the analyst identified the material as solid bitumen they would have selected the higher reflecting population most likely to represent the indigenous thermal maturity of the sample and to avoid later migrated material. Distinctions between vitrinite and solid bitumen of course can be made with confidence in a single laboratory, particularly for lower maturity samples (e.g., Wei et al., 2016). However, the observation that no systematic differences in solid bitumen and vitrinite reflectance were noted here, or in the previous ILS, suggests that such distinctions

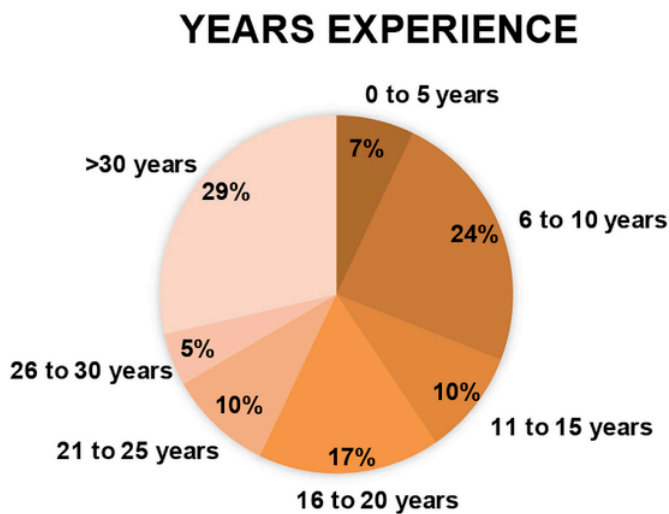


Fig. 6. Participants years of experience.

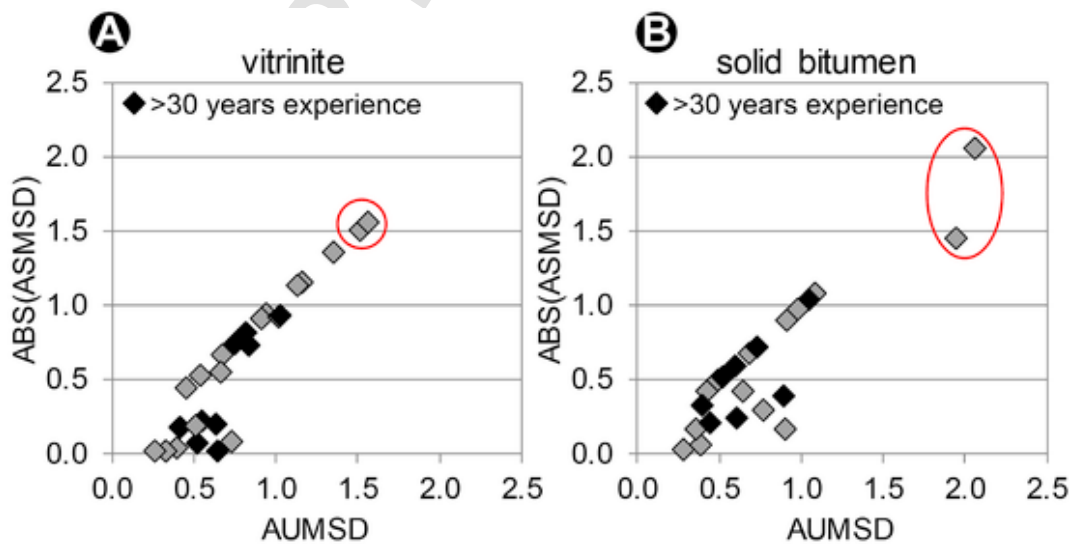


Fig. 7. Absolute values of average signed multiple of standard deviation (ASMSD) vs average unsigned multiple of standard deviation (AUMSD) values for (A) vitrinite and (B) solid bitumen, showing participants with 30 + years of experience by black diamonds. The red circle (A) and ellipse (B) indicate failing petrographers based on the ICCP criterion of AUMSD > 1.5.

are not yet evident in an ILS. Again, this brings into caution the use of empirical conversions to convert measurements of solid bitumen to a vitrinite reflectance equivalent (Hackley et al., 2015) as the identifications and reflectance distinctions of solid bitumen and vitrinite cannot be reproduced in an ILS.

5.2. Evaluation of precision

Reproducibility is an estimate of precision obtained from measurement results of the same sample by different laboratories with different analysts using different instruments (ASTM, 2015c). The reproducibility limit (R) is defined as the difference between two valid results obtained under reproducibility conditions (same test material, different laboratories with different analysts, different instruments). Because both results are valid, R also can be thought of as the amount of uncertainty (in absolute reflectance) for any one individual reflectance measurement. Herein, we use a simplified statistical approach to calculate R using formula $R = 2.8 \times \text{GSD}$, where GSD = group standard deviation (Elison et al., 2009).

The inclusion in this ILS of a global diversity of laboratories and a broad range of analyst experience contributed to high group standard deviation values (and thus high R values) when all data are considered. For example, measurements of mean solid bitumen reflectance in the Marcellus sample ranged from a low of 0.92 to a high of 2.73% (Table 4). This range of 1.81% absolute reflectance contributed to a high GSD of 0.47 and R of 1.32 (Table 5). Similar distributions of values were reported for the other dry gas thermal maturity samples (Haynesville, Eagle Ford, Barnett) whereas lower GSD values of 0.09–0.25 were found for the lower maturity Bakken and Woodford samples. Thus, using all of the data results in relatively high values of R, ranging from a low of 0.26 for solid bitumen in the Bakken to the high value of 1.32 for vitrinite in the Marcellus. The reasons behind this dispersion are multifold. Many of the laboratories participating in the current ILS are potentially unfamiliar with the typical samples of the United States shale plays examined in this study. Misidentification of organic matter due to operator inexperience or bias, e.g., measuring solid bitumen as vitrinite, or vice versa, as discussed above, is a potential issue in these situations. This could be addressed in a future ILS by limiting participation to experienced petrographers familiar with the ILS samples; however, such an approach may severely restrict the number of analyses returned. For certain laboratories in the current ILS, instrument calibration also appears to be at issue, as discussed below. Some dispersion in results may be further explained by non-linearity of the microscope de-

tection system, particularly for older photomultiplier-based analog technologies, and the choice of an inappropriate calibration standard. Another instrument consideration is the ability to adjust the size of the measuring aperture during measurement, such as available to laboratories with Hilgers Fossil systems [Hilgers Fossil is an integrated reflectance system adaptable to most microscopes which uses LED illumination (as opposed to an incandescent light source) and a monochrome digital camera for light detection (as opposed to a photomultiplier)]. This ILS did not control for microscope type or the technology used for illumination or light detection.

Based on the wide distribution of participant results, we considered multiple traditional and non-traditional ways to eliminate outlying mean reflectance values (Table 5), including removal of: 1) results not using the ASTM D7708 reporting template, 2) results non-compliant in any way with the reporting requirements of ASTM D7708, 3) results with <20 measurements, 4) results with standard deviation $> 0.15 \times (\text{VR}_o \text{ or } \text{BR}_o)$, 5) results with average signed multiple of standard deviation > 1.5 and > 1.0 , 6) results falling outside the mean $\pm 1.5 \times$ interquartile range (IQR), 7) results falling outside the F10 to F90 percentile range, and 8) results with individual signed multiple of standard deviation > 1.5 and > 1.0 . The removal of outlying values makes the assumption that some values in the data pool, numerically distant from other values, are values arising from chance phenomenon, or result from experimental or measurement errors.

Several of these approaches to elimination of outlying values can be taken without a pool of data to work from, i.e., the elimination of a particular value can be applied for reasons other than the value lying far outside the group mean. For example, methods 1–4 from the list given in the preceding paragraph can be applied to any individual result. We considered that petrographers not adhering to the ASTM D7708 reporting template or not following reporting requirements of ASTM D7708 may provide imprecise data. However, elimination of these results did not consistently reduce R; for example, removing results where the ASTM reporting template was not used reduced R in only 7 of 12 cases (Table 5). On the other hand, removing results where the reporting requirements were not met increased R in 10 of 12 cases. This occurred because of cases where a petrographer had returned results close to the group mean, but, for example, had provided a table of results without the other reporting requirements specified by ASTM D7708 section 11, e.g., descriptions of fluorescence, sample organic matter types, polish quality, etc. These observations suggest that adherence to D7708 reporting requirements or use of the reporting template don't necessarily improve data quality, or, in this case, mea-

Table 5
Values for reproducibility limit (R) from ILS results. See text for additional explanation.

Method of removing outlying values	Marcellus		Haynesville		Eagle Ford		Barnett		Bakken		Woodford	
	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.
all data (no outliers removed)	1.32	1.04	0.80	1.22	0.85	0.84	1.01	1.02	0.53	0.26	0.55	0.70
ASTM template	1.00	1.05	0.74	1.30	0.80	0.61	0.65	0.56	0.63	0.24	0.55	0.78
non-compliant with D7708	1.20	1.22	0.79	1.26	0.90	1.02	1.15	1.20	0.65	0.30	0.59	0.80
<20 measurements	1.22	0.91	0.80	1.02	0.90	0.87	0.73	1.03	0.56	0.28	0.52	0.72
standard deviation $> 1.5 \times (\text{VR}_o \text{ or } \text{BR}_o)$	1.35	1.04	0.71	1.13	0.84	0.70	0.71	0.52	0.48	0.23	0.53	0.54
remove ASMSD > 1.5	1.18	0.78	0.67	1.12	0.84	0.50	0.98	0.63	0.53	0.22	0.43	0.64
remove ASMSD > 1.0	1.11	0.79	0.54	1.14	0.68	0.45	0.56	0.58	0.57	0.17	0.42	0.51
IQR	1.32	0.47	0.54	1.22	0.76	0.49	0.11	0.52	0.26	0.10	0.19	0.70
F10–F90	1.07	0.65	0.58	0.97	0.64	0.46	0.63	0.51	0.23	0.26	0.55	0.50
remove ISMSD > 1.5	1.09	0.54	0.58	1.08	0.64	0.49	0.68	0.52	0.26	0.18	0.56	0.35
remove ISMSD > 1.0	0.91	0.47	0.42	0.48	0.47	0.47	0.52	0.52	0.24	0.14	0.36	0.28

Vit., vitrinite; S.B., solid bitumen; ASMSD, average signed multiple of standard deviation; IQR, interquartile range; F10–F-90, excluding values outside of 10–90 percentile range; ISMSD, individual signed multiple of standard deviation.

surement reproducibility. Removal of results with <20 measurements resulted in reductions to R in only 5 of 12 cases, whereas removal of results with standard deviation $> 0.15 \cdot (VR_o \text{ or } BR_o)$ reduced R in 10 of 12 cases (Table 5). ASTM D7708 requires that reports of mean reflectance backed by fewer than 20 measurements are to be flagged as 'qualitative'. However, the observation that R is not always reduced by removal of results with <20 measurements suggests that measurement reproducibility is not necessarily impacted by the number of measurements. On the other hand, the consistent reduction of R observed by removal of results with standard deviation $> 0.15 \cdot (VR_o \text{ or } BR_o)$ suggests that this screening technique should be applied for all measurements of dispersed organic reflectance. The rationale is that requiring standard deviation to be $< 0.15 \cdot (VR_o \text{ or } BR_o)$ influences the petrographer to preferentially select and measure one type of organic matter as representative of indigenous thermal maturity, as opposed to measuring and averaging the reflectance values of all organic matter present. Therefore, we recommend that reported measurements of mean dispersed organic matter reflectance meet the requirement that standard deviation is $< 0.15 \cdot (VR_o \text{ or } BR_o)$.

Removal of results with average signed multiple of standard deviation (ASMSD) > 1.5 is the criterion used by ICCP for pass/fail status in their accreditation programs (Borrego et al., 2006; Hackley et al., 2015; Mendonca et al., 2010). In Fig. 7 we show absolute values of ASMSD versus average unsigned multiple of standard deviation (AUMSD) for vitrinite and solid bitumen measurements. The red circle (Fig. 7A) and ellipse (Fig. 7B) indicate failing petrographers based on the ICCP criterion. Microscope calibration problems appear to be at issue in these cases where distances to the mean value are high and SMSD consistently has the same sign. Removal of these results from the data pool results in consistent improvement to R values and R values are further improved by restricting the data pool to results with ASMSD < 1.0 . Restricting the data pool to results with ASMSD < 1.0 produced the lowest R value for solid bitumen in the Eagle Ford sample (Table 5).

Another approach to outlier removal is to eliminate results for individual samples where the SMSD is > 1.5 or > 1.0 . That is, the results from an analyst would be removed only when the reported mean reflectance value of an individual sample had a SMSD > 1.5 or > 1.0 , as opposed to considering the ASMSD for all samples from an analyst. In general, this approach produces the lowest R values because it excludes mistakes, such as selection of the low reflecting solid bitumen population in the Haynesville sample, while keeping results from other samples where the analyst performed well in comparison to the group mean. With the exception of vitrinite in the Marcellus sample, R values range 0.14–0.52 (Table 5) with higher values occurring in higher maturity samples. Summarizing, R values were about 0.1–0.2 for the peak oil thermal maturity Bakken sample, about 0.2–0.3 for the wet gas and condensate thermal maturity Woodford sample, and about 0.4–0.5 for Marcellus, Haynesville, Eagle Ford and Barnett samples of dry gas maturity. These R values represent the approximate uncertainty (in absolute reflectance) that users of vitrinite and solid bitumen reflectance data could assign to any one individual reported mean reflectance value from a similar thermal maturity mudrock sample. We note that these R values are similar to R values obtained for similar maturity samples in the previous ILS (Hackley et al., 2015) and an improvement over historical ILS exercises which contained similar diversity of source-rock reservoir samples (Borrego, 2009; Dembicki, 1984).

Traditional means of outlier elimination remove results falling outside the mean $\pm 1.5 \cdot$ interquartile range and outside the F10 to F90 percentile range. Using the interquartile range approach resulted in R values of 0.10–1.32. In 3 of 12 cases, this approach produced the lowest R values of all approaches used for outlier elimination. However, in cases where the interquartile range was high, this approach found no outlying values, resulting in no improvement to R for 3 of the 12

cases (Table 5). Removal of results outside the F10 to F90 percentile range consistently improved R and produced the lowest R values in 2 of 12 cases. In general, these traditional approaches to outlier removal found R to be similar to or slightly higher than the result obtained when removing individual samples where the SMSD was > 1.5 or > 1.0 .

5.3. Future directions

This ILS found that R of 0.1–0.5 was obtainable for vitrinite and solid bitumen reflectance measurements in thermally mature source rocks typical of the North American resource plays. This level of uncertainty in interlaboratory reproducibility suggests that further work is necessary to standardize and improve measurement of dispersed organic matter reflectance. Discussions amongst ILS participants at the 2016, 2017 and 2018 meetings of ICCP in Houston, Bucharest and Brisbane, respectively, settled on several future directions for the ILS working group, beginning with a name change to 'Identification of Thermal Maturity Relevant Organic Matter'. Previously, the working group was named 'Identification of Primary Vitrinite' and it was thought by some that including the word 'vitrinite' in the working group title may potentially have led some ILS participants to emphasize vitrinite measurements where little is present. Towards this end, a future ILS may ask participants to assign a 'confidence of identification' criterion for each measurement, allowing removal of individual measurements of poorly-identified organic matter. A similar approach was used in the ILS of Borrego et al. (2006), in which a 'reliability index' was established using the number of measurements and coefficient of variation. In addition, a future ILS may consider giving specialized instructions for organic matter identification in difficult samples, as recommended by Borrego et al. (2006). For example, provision with ILS samples of the basic programmed pyrolysis information contained in Table 2 would have helped participants to avoid the low reflectance solid bitumen population contained in the Haynesville sample. It is long known that polish quality impacts reflectance measurement (e.g., Stach et al., 1982). As mentioned above, it is presumed ILS participants polished to a final 0.05 μm stage per the requirements of ASTM D7708. However, a future ILS may eliminate variations in polish quality by using samples prepared in one laboratory, rather than allowing each participant to finish the preparation.

Another idea put forth by ILS participants was a new ILS in which the emphasis is placed on measurement of solid bitumen reflectance rather than vitrinite. Despite some studies de-emphasizing solid bitumen reflectance as a poor thermal maturity proxy (Kus et al., 2016; Petersen et al., 2013), other works have relied on this parameter in part due to its dominance in the organic assemblage of source-rock reservoirs (Borrego et al., 2018; Gonçalves et al., 2014; Juliao et al., 2015; Mastalerz et al., 2018; Misch et al., 2019; Valentine et al., 2014, among others). Therefore, a future ILS to examine reflectance measurement of dispersed organic matter in source-rock reservoirs should consider that solid bitumen is the targeted organic matter type.

In preparation for another ILS focused on solid bitumen, it was considered that an exercise which used images, rather than physical samples, would be appropriate to educate petrographers whom are perhaps not as familiar with unconventional source-rock reservoirs. Towards that end, images of organic matter from the six samples of the current ILS are being collated, with regions of interest for organic matter identification indicated on each image. It is considered that an initial ILS using images of source rock reservoirs could better prepare participants for a future ILS with physical samples. Further, the use of Hilgers Fossil reflectance systems in many laboratories opens the possibility for an ILS which uses calibrated images. Hilgers Fossil software contains a 'Student' module intended for offline (without a microscope) measurement of calibrated images. That is, one laboratory with the Hilgers Fos-

sil system could create sets of calibrated images which could be then shared to other Hilgers Fossil users for an image-based ILS where the images are measured instead of physical samples. The Hilgers Fossil system relies on modern solid-state technology including LED illumination and CCD light detection, resulting in an ultra-stable configuration relative to older analog-based systems which use tungsten halogen illumination and photomultipliers. In addition, the Hilgers Fossil Student approach to an ILS would have the benefit of an image record of measurement location from each participant. However, such an ILS would be limited to only those laboratories with Hilgers Fossil systems or to those with access to the Hilgers Fossil Student software. An additional limitation or advantage of this approach would be that a single petrographer, or group thereof, would make the initial identifications of organic matter which the participants would then accept as given or dispute.

6. Summary and conclusions

An interlaboratory study (ILS) was conducted using six thermally mature mudrock samples to test reproducibility of vitrinite and solid bitumen reflectance measurements in North American unconventional source-rock reservoir petroleum systems. Organic-rich (2.87–11.60 wt% total organic carbon content) samples were used from the Marcellus, Haynesville, Eagle Ford, Barnett, Bakken and Woodford shales which ranged from peak oil to dry gas thermal maturity conditions (T_{\max} 447–591 °C). The samples contain solid bitumen as the dominant organic matter with minor inertinite; vitrinite is rare or absent according to the majority of analysts, and liptinite is absent due to thermal conversion to petroleum and non-liptinite residues (e.g., solid bitumen). Intraparticle organic nano-porosity occurs in solid bitumen and is visually less abundant in the lower maturity samples. Forty laboratories in the Americas, Europe, Africa and Australia received the samples and thirty-seven independent sets of results were produced. Mean vitrinite reflectance values ranged from 0.90 to 1.83% and mean solid bitumen reflectance values ranged from 0.85 to 2.04% when all results are considered (including outlying values). Multiple statistical approaches were used to eliminate outlying values and obtain a precision estimate: reproducibility limit R defined as the maximum difference between valid results obtained on the same test material by different analysts in different laboratories using different instruments. After outlier removal, R values generally were 0.1 to $\leq 0.5\%$ (absolute reflectance), similar to previous results for similar samples. It was observed that standard deviation values $< 0.15 \cdot (VR_o \text{ or } BR_o)$ reduce R; therefore, this specification should be required for dispersed organic matter reflectance analysis. The results provide users of reflectance data a realistic expectation of uncertainty which can be used to assign uncertainty to any one reflectance analysis and demonstrate that further work is necessary in standardization of dispersed organic matter reflectance measurement.

Author contributions

PCH conceived this research and designed the study with input from co-authors. All co-authors contributed data which was analyzed and interpreted by PCH in consultation with co-authors. PCH wrote the manuscript with input from co-authors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpetgeo.2019.104172>.

References

- ASTM, 2015. D2797 Standard Practice for Preparing Coal Samples for Microscopical Analysis by Reflected Light, Petroleum Products, Lubricants, and Fossil Fuels; Gaseous Fuels; Coal and Coke, Sec. 5, V. 05.06. ASTM International, West Conshohocken, PA.
- ASTM, 2015. D7708 Standard Test Method for Microscopical Determination of the Reflectance of Vitrinite Dispersed in Sedimentary Rocks, Petroleum Products, Lubricants, and Fossil Fuels; Gaseous Fuels; Coal and Coke, Sec. 5, V. 05.06. ASTM International, West Conshohocken, PA.
- ASTM, 2015. E691 Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method, Annual Book of ASTM Standards: General Test Methods; Forensic Psychophysiology; Forensic Sciences; Terminology; Conformity Assessment; Statistical Methods; Nanotechnology; Forensic Engineering; Manufacture of Pharmaceutical Products. ASTM International, West Conshohocken, PA, p. 21.
- Baskin, D.K., 1997. Atomic H/C ratio of kerogen as an estimate of thermal maturity and organic matter conversion. AAPG (Am. Assoc. Pet. Geol.) Bull. 81, 1437–1450.
- Borrego, A.G., 2009. Precision of vitrinite reflectance measurements in dispersed organic matter: reappraisal of the information from past commission II activities working group of the ICCP. ICCP News 48, 50–58.
- Borrego, A.G., 2017. A dry polishing technique for the petrographic examination of mudrocks: Discussion. Int. J. Coal Geol. 183, 136–137.
- 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., Mész, 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.
- Borrego, A.G., López García, A., Merino-Tomé, O., 2018. Petrographic and geochemical characterization of organic-rich Mississippian black shales in the north of Spain: vegamián formation, Cantabrian zone. Int. J. Coal Geol. 190, 126–145.
- Cardott, B.J., Landis, C.R., Curtis, M.E., 2015. Post-oil solid bitumen network in the Woodford Shale, USA: a potential primary migration pathway. Int. J. Coal Geol. 139, 106–113.
- Carvajal-Ortiz, H., Gentzis, T., 2015. Critical considerations when assessing hydrocarbon plays using Rock-Eval pyrolysis and organic petrology data: data quality revisited. Int. J. Coal Geol. 152, 113–122.
- Carvajal-Ortiz, H., Gentzis, T., 2018. Geochemical screening of source rocks and reservoirs: the importance of using the proper analytical program. Int. J. Coal Geol. 190, 56–69.
- Chen, J., Xiao, X., 2014. Evolution of nanoporosity in organic-rich shales during thermal maturation. Fuel 129, 173–181.
- Cheshire, S., Craddock, P.R., Xu, G., Sauerer, B., Pomerantz, A.E., McCormick, D., Abdallah, W., 2017. Assessing thermal maturity beyond the reaches of vitrinite reflectance and Rock-Eval pyrolysis: a case study from the Silurian Qusaiba formation. Int. J. Coal Geol. 180, 29–45.
- Craddock, P.R., Prange, M.D., Pomerantz, A.E., 2017. Kerogen thermal maturity and content of organic-rich mudrocks determined using stochastic linear regression models applied to diffuse reflectance IR Fourier transform spectroscopy (DRIFTS). Org. Geochem. 110, 122–133.
- Curiale, J.A., Curtis, J.B., 2016. Organic geochemical applications to the exploration for source-rock reservoirs – a review. J. Unconv. Oil Gas Resour. 13, 1–31.
- Curtis, J.B., 2002. Fractured shale-gas systems. AAPG (Am. Assoc. Pet. Geol.) Bull. 86, 1921–1938.
- Curtis, M.E., Cardott, B.J., Sondergeld, C.H., Rai, C.S., 2012. Development of organic porosity in the Woodford Shale with increasing thermal maturity. Int. J. Coal Geol. 103, 26–31.
- Demaision, G., 1984. The generative basin concept. In: Demaison, G., Murriss, R.J. (Eds.), Petroleum Geochemistry and Basin Evaluation, 35. AAPG Memoir, pp. 1–14.
- Dembicki, H., 1984. An interlaboratory comparison of source rock data. Geochim. Cosmochim. Acta 48, 2641–2649.
- Dembicki, H., Meinschein, W.G., Hattin, D.E., 1976. Possible ecological and environmental significance of the predominance of even-carbon number C_{20} – C_{30} n-alkanes. Geochim. Cosmochim. Acta 40, 203–208.
- Dow, W.G., 1977. Kerogen studies and geological interpretations. J. Geochem. Explor. 7, 79–99.
- Eldrett, J.S., Ma, C., Bergman, S.C., Ozkan, A., Minisini, D., Lutz, B., Jackett, S.-J., Macaulay, C., Kelly, A.E., 2015. Origin of limestone-marlstone cycles: astro-

- nommic forcing of organic-rich sedimentary rocks from the Cenomanian to early Coniacian of the Cretaceous Western Interior Seaway, USA. *Earth Planet. Sci. Lett.* 423, 98–113.
- Ellison, S.L.R., Barwick, V.J., Farrant, T.J.D., 2009. Validation and method performance. In: Ellison, S.L.R., Barwick, V.J., Farrant, T.J.D. (Eds.), *Practical Statistics for the Analytical Scientist: A Bench Guide*. Edition 2. Royal Society of Chemistry, pp. 144–160.
- Espitalié, J., Deroo, G., Marquis, F., 1985. La pyrolyse Rock-Eval et ses applications. Deuxième partie. 40. *Revue De L Institut Français Du Pétrole*, pp. 755–784.
- Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., 1977. Méthode rapide de caractérisation des roches, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pet.* 32, 23–43.
- Ferreiro Mählmann, R., Le Bayon, R., 2016. Vitrinite and vitrinite like solid bitumen reflectance in thermal maturity studies: correlations from diagenesis to incipient metamorphism in different geodynamic settings. *Int. J. Coal Geol.* 157, 52–73.
- Fishman, N.S., Egenhoff, S.O., Boehlke, A.R., Lowers, H.A., 2015. Petrology and diagenetic history of the upper shale member of the late devonian-early mississippian bakken formation, Williston Basin, north Dakota. In: Larsen, D., Egenhoff, S.O., Fishman, N.S. (Eds.), *Paying Attention to Mudrocks: Priceless!*. Geological Society of America, Boulder, Colorado, pp. 125–151.
- Gonçalves, P.A., Mendonça Filho, J.G., da Silva, F.S., Flores, D., 2014. Solid bitumen occurrences in the ardua sub-basin (Lusitanian basin, Portugal): petrographic features. *Int. J. Coal Geol.* 131, 239–249.
- Hackley, P.C., 2017. Application of organic petrology in high maturity shale gas systems. In: Suárez-Ruiz, I., Mendonça Filho, J.G. (Eds.), *Geology: Current and Future Developments*. Bentham, United Arab Emirates, pp. 206–236.
- Hackley, P.C., Araújo, C.V., Borrego, A.G., Bouzinos, A., Cardott, B.J., Cook, A.C., Eble, C., Flores, D., Gentzsis, 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.
- 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.
- Hackley, P.C., Lewan, M.D., 2018. Understanding and distinguishing reflectance measurements of solid bitumen and vitrinite using hydrous pyrolysis: implications to petroleum assessment. *AAPG (Am. Assoc. Pet. Geol.) Bull.* 102, 1119–1140.
- Hackley, P.C., Lünsdorf, N.K., 2018. Application of Raman spectroscopy as thermal maturity probe in shale petroleum systems: insights from natural and artificial maturation sequences. *Energy Fuels* 32, 11190–11202.
- 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.
- Hackley, P.C., Valentine, B.J., Hatcherian, J.J., 2018. On the petrographic distinction of bituminite from solid bitumen in immature to early mature source rocks. *Int. J. Coal Geol.* 196, 232–245.
- Hackley, P.C., Valentine, B.J., Voortman, L.M., Van Oosten Slingeland, D.S.B., Hatcherian, J., 2017. Utilization of integrated correlative light and electron microscopy (iCLEM) for imaging sedimentary organic matter. *J. Microsc.* 267, 371–383.
- Hackley, P.C., Zhang, L., Zhang, T., 2017. Organic petrology of peak oil maturity Triassic Yanchang Formation lacustrine mudrocks, Ordos Basin, China. *Interpretation* 5, SF211-SF223.
- Hackley, P.C., Zhang, T., Jubb, A.M., Valentine, B.J., Dulong, F.T., Hatcherian, J.J., 2019. Organic petrography and diagenesis of Leonardian (Wolfcamp A) mudrocks and carbonates, midland basin, Texas. *Mar. Pet. Geol.* X, X-X.
- Hammes, U., Frébourg, G., 2012. Haynesville and Bossier mudrocks: a facies and sequence stratigraphic investigation, east Texas and Louisiana, USA. *Mar. Pet. Geol.* 31, 8–26.
- Harris, N.B., Mnich, C.A., Selby, D., Korn, D., 2013. Minor and trace element and Re-Os chemistry of the Upper Devonian Woodford Shale, Permian Basin, west Texas: insights into metal abundance and basin processes. *Chem. Geol.* 356, 76–93.
- Hart, B.S., Steen, A.S., 2015. Programmed pyrolysis (Rock-Eval) data and shale paleoenvironmental analyses: a review. *Interpretation* 3, SH41-SH58.
- Hartkopf-Fröder, C., Königshof, P., Littke, R., Schwarzbauer, J., 2015. Optical thermal maturity parameters and organic geochemical alteration at low grade diagenesis to anchimetamorphism: a review. *Int. J. Coal Geol.* 150–151, 74–119.
- Hosterman, J.W., Dulong, F.T., 1989. A computer program for semi-quantitative mineral analysis by X-ray powder diffraction. In: Pevear, D.R., Mumpton, F.A. (Eds.), *Quantitative Mineral Analysis of Clays*. Clay Minerals Society Workshop Lectures, pp. 38–50.
- Hunt, J.M., 1996. *Petroleum Geochemistry and Geology*. second ed. W.H. Freeman and Company, New York.
- ICCP, 2009. *ICCP working group identification of primary vitrinite in shale: 2009 report*. *ICCP News* 48, 62–70.
- Jacob, H., 1989. Classification, structure, genesis and practical importance of natural solid oil bitumen (“migrabitumen”). *Int. J. Coal Geol.* 11, 65–79.
- Jubb, A.M., Botterell, P.J., Birdwell, J.E., Burruss, R.C., Hackley, P.C., Valentine, B.J., Hatcherian, J.J., Wilson, S.A., 2018. High microscale variability in Raman thermal maturity estimates from shale organic matter. *Int. J. Coal Geol.* 1–9, 2018.
- Juliao, T., Suárez-Ruiz, I., Marquez, R., Ruiz, B., 2015. The role of solid bitumen in the development of porosity in shale oil reservoir rocks of the Upper Cretaceous in Colombia. *Int. J. Coal Geol.* 147–148, 126–144.
- Kaiser, M.J., 2012. Profitability assessment of Haynesville shale gas wells. *Energy* 38, 315–330.
- Khatibi, S., Ostadhassan, M., Hackley, P.C., Tuschel, D., Abarghani, A., Bubach, B., 2019. Understanding organic matter heterogeneity and maturation rate by Raman spectroscopy. *Int. J. Coal Geol.* 206, 46–64.
- Kibria, M.G., Hu, Q., Liu, H., Zhang, Y., Kang, J., 2018. Pore structure, wettability, and spontaneous imbibition of Woodford shale, Permian basin, west Texas. *Mar. Pet. Geol.* 91, 735–748.
- Klaver, J., Desbois, G., Littke, R., Urai, J.L., 2015. BIB-SEM characterization of pore space morphology and distribution in postmaturation to overmature samples from the Haynesville and Bossier Shales. *Mar. Pet. Geol.* 59, 451–466.
- Klaver, J., Desbois, G., Littke, R., Urai, J.L., 2016. BIB-SEM pore characterization of mature and post mature Posidonia Shale samples from the Hils area, Germany. *Int. J. Coal Geol.* 158, 78–89.
- Ko, L.T., Ruppel, S.C., Loucks, R.G., Hackley, P.C., Zhang, T., Shao, D., 2018. Pore-types and pore-network evolution in Upper Devonian-Lower Mississippian Woodford and Mississippian Barnett mudstones: insights from laboratory thermal maturation and organic petrology. *Int. J. Coal Geol.* 190, 3–28.
- Kus, J., Khanaqa, P., Mohialdeen, I.M.J., Kaufhold, S., Babies, H.G., Meßner, J., Blumenberg, M., 2016. Solid bitumen, bituminite and thermal maturity of the upper jurassic-lower cretaceous chia gara formation, kirkuk oil field, zagros fold belt, kurdistan, Iraq. *Int. J. Coal Geol.* 165, 28–48.
- Landis, C.R., Castaño, J.R., 1995. Maturation and bulk chemical properties of a suite of solid hydrocarbons. *Org. Geochem.* 22, 137–149.
- Lewan, M.D., Pawlewicz, M.J., 2017. Reevaluation of thermal maturity and stages of petroleum formation of the mississippian Barnett shale, Fort Worth Basin, Texas. *AAPG (Am. Assoc. Pet. Geol.) Bull.* 101, 1945–1970.
- Lis, G.P., Mastalerz, M., Schimmelmann, A., Lewan, M., Stankiewicz, B.A., 2005. FTIR absorption indices for thermal maturity in comparison with vitrinite reflectance R_o in type-II kerogens from Devonian black shales. *Org. Geochem.* 36, 1533–1552.
- Löhr, S.C., Baruch, E.T., Hall, P.A., Kennedy, M.J., 2015. Is organic pore development in gas shales influenced by the primary porosity and structure of thermally immature organic matter? *Org. Geochem.* 87, 119–132.
- Loucks, R.G., Reed, R.M., Ruppel, S.C., Hammes, U., 2012. Spectrum of pore types and networks in mudrocks and a descriptive classification for matrix-related mudrock pores. *AAPG (Am. Assoc. Pet. Geol.) Bull.* 96, 1071–1098.
- Loucks, R.G., Reed, R.M., Ruppel, S.C., Jarvie, D.M., 2009. Morphology, genesis, and distribution of nanometer-scale pores in siliceous mudstones of the mississippian Barnett shale. *J. Sediment. Res.* 79, 848–861.
- Lupoi, J.S., Fritz, L.P., Parris, T.M., Hackley, P.C., Solotky, L., Eble, C.F., Schlaegle, S., 2017. Assessment of thermal maturity trends in Devonian–Mississippian source rocks using Raman spectroscopy: limitations of peak-fitting method. *Front. Energy Res.* 5.
- Lupoi, J.S., Hackley, P.C., Birsic, E., Fritz, L.P., Solotky, L., Weislogel, A., Schlaegle, S., 2019. Quantitative evaluation of vitrinite reflectance in shale using Raman spectroscopy and multivariate analysis. *Fuel* 254, 115573.
- Magoon, L.B., Dow, W.G., 1994. The petroleum system. In: Magoon, L.B., Dow, W.G. (Eds.), *The Petroleum System: from Source to Trap*. AAPG Memoir 60, pp. 3–24.
- Mastalerz, M., Drobniak, A., Stankiewicz, A.B., 2018. Origin, properties, and implications of solid bitumen in source-rock reservoirs: a review. *Int. J. Coal Geol.* 195, 14–36.
- Mendonca, J.G., Araújo, C.V., Borrego, A.G., Cook, A., Flores, D., Hackley, P., Hower, J.C., Kern, M.L., Kommeren, K., Kus, J., Mastalerz, M., Mendonca, J.O., Menezes, T.R., Newman, J., Ranasinghe, P., Souza, I., Suarez-Ruiz, I., Ujje, Y., 2010. Effect of concentration of dispersed organic matter on optical maturity parameters: interlaboratory results of the organic matter concentration working group of the ICCP. *Int. J. Coal Geol.* 84, 154–165.
- Misch, D., Gross, D., Hawranek, G., Horsfield, B., Klaver, J., Mendez-Martin, F., Urai, J.L., Vranjes-Wessely, S., Sachsenhofer, R.F., Schmatz, J., Li, J., Zou, C., 2019. Solid bitumen in shales: petrographic characteristics and implications for reservoir characterization. *Int. J. Coal Geol.* 205, 14–31.
- Modica, C.J., Lapiere, S.G., 2012. Estimation of kerogen porosity in source rocks as a function of thermal transformation: example from the Mowry Shale in the Powder River Basin of Wyoming. *AAPG (Am. Assoc. Pet. Geol.) Bull.* 96, 87–108.
- Morris, J.L., Puttick, M.N., Clark, J.W., Edwards, D., Kenrick, P., Pressel, S., Wellman, C.H., Yang, Z., Schneider, H., Donoghue, P.C.J., 2018. The timescale of early land plant evolution. *Proc. Natl. Acad. Sci.* 110, E2274–E2283.
- Peters, K.E., 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. *AAPG (Am. Assoc. Pet. Geol.) Bull.* 70, 318–329.
- 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, pp. 93–120.
- Peters, K.E., Hackley, P.C., Thomas, J.J., Pomerantz, A.E., 2018. Experimental evidence for suppression of vitrinite reflectance by lypintite during hydrous pyrolysis of artificial source rock. *Org. Geochem.* 125, 220–228.
- Peters, K.E., Xia, X., Pomerantz, A., Mullins, O.C., 2016. Geochemistry applied to evaluation of unconventional resources. In: Ma, Y.Z., Holditch, S.A. (Eds.), *Unconventional Oil and Gas Resources Handbook: Evaluation and Development*. Elsevier, Waltham, Massachusetts, pp. 71–126.
- 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.
- Pickel, W., Kus, J., Flores, D., Kalatzidis, S., Christianis, K., Cardott, B.J., Misz-Kennan, M., Rodrigues, S., Hentschel, A., Hamor-Vido, M., Crosdale, P., Wagner, N., ICCP, 2017. Classification of lypintite—ICCP system 1994. *Int. J. Coal Geol.* 169, 40–61.
- Pommer, M., Milliken, K.L., 2015. Pore types and pore-size distributions across thermal maturity, Eagle Ford Formation, southern Texas. *AAPG (Am. Assoc. Pet. Geol.) Bull.* 99, 1713–1744.
- Robert, P., 1988. *Organic Metamorphism and Geothermal History: Microscopic Study of Organic Matter and Thermal Evolution of Sedimentary Basins*. Elf-Aquitaine and Reidel Publishing Company, Dordrecht, p. 311.
- Romero-Sarmiento, M.-F., Rouzaud, J.-N., Bernard, S., Deldicque, D., Thomas, M., Littke, R., 2014. Evolution of Barnett Shale organic carbon structure and nanostructure with increasing maturation. *Org. Geochem.* 71, 7–16.
- Sauerer, B., Craddock, P.R., AlJohani, M.D., Alsamadony, K.L., Abdallah, W., 2017. Fast and accurate shale maturity determination by Raman spectroscopy measurement with minimal sample preparation. *Int. J. Coal Geol.* 173, 150–157.
- 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.

- Stach, E., Mackowsky, M.-T., Teichmüller, M., Taylor, G.H., Chandra, D., Teichmüller, R., Murchison, D.G., Zierke, F., 1982. *Stach's Textbook of Coal Petrology*. Gebrüder Borntraeger, Berlin, p. 535.
- Streib, D.L., 1981. Distribution of Gas, Organic Carbon and Vitrinite Reflectance in the Eastern Devonian Gas Shales and Their Relationship to the Geologic Framework. U.S. Department of Energy, Morgantown, WV, p. 273. Morgantown Technology Center Report DOE/MC/08216-1276.
- Suárez-Ruiz, I., Flores, D., Mendonça Filho, J.G., Hackley, P.C., 2012. Review and update of the applications of organic petrology: Part 1, geological applications. *Int. J. Coal Geol.* 99, 54–112.
- Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Robert, P., 1998. *Organic Petrology*. Gebrüder Borntraeger, Berlin and Stuttgart.
- Teichmüller, M., 1987. Organic material and very low-grade metamorphism. In: Frey, M. (Ed.), *Low Temperature Metamorphism*. Blackie, Glasgow, pp. 114–161.
- Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence*. second ed. Springer-Verlag, Berlin, p. 699.
- Valentine, B.J., Hackley, P.C., Enomoto, C.B., Bove, A.M., Dulong, F.T., Lohr, C.D., Scott, K.R., 2014. Organic petrology of the Aptian-age section in the downdip Mississippi Interior Salt Basin, Mississippi, USA: observations and preliminary implications for thermal maturation history. *Int. J. Coal Geol.* 131, 378–391.
- Wang, Q., Chen, X., Jha, A.N., Rogers, H., 2014. Natural gas from shale formation – the evolution, evidences and challenges of shale gas revolution in United States. *Renew. Sustain. Energy Rev.* 30, 1–28.
- Wei, L., Wang, Y., Mastalerz, M., 2016. Comparative optical properties of vitrinite and other macerals from Upper Devonian – lower Mississippian New Albany Shale: implications for thermal maturity. *Int. J. Coal Geol.* 168, 222–236.
- Wilkins, R.W.T., Sherwood, N., Li, Z., 2018. RaMM (Raman maturity method) study of samples used in an interlaboratory exercise on a standard test method for determination of vitrinite reflectance on dispersed organic matter in rocks. *Mar. Pet. Geol.* 91, 236–250.
- Zagorski, W.A., Wrightstone, G.R., Bowman, D.C., 2012. The Appalachian Basin Marcellus gas play: its history of development, geologic controls on production, and future potential as a world-class reservoir. In: Breyer, J.A. (Ed.), *Shale Reservoirs: Giant Resources for the 21st Century: AAPG Memoir 97*. pp. 172–200.
- Zhang, T., Sun, X., Milliken, K.L., Ruppel, S.C., Enriquez, D., 2017. Empirical relationship between gas composition and thermal maturity in Eagle Ford Shale, south Texas. *AAPG (Am. Assoc. Pet. Geol.) Bull.* 101, 1277–1307.

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