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

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Abstract

67 An interlaboratory study (ILS) was conducted to test reproducibility of vitrinite and solid

68 bitumen reflectance measurements in six mudrock samples from United States

69 unconventional source-rock reservoir petroleum systems. Samples selected from the

70 Marcellus, Haynesville, Eagle Ford, Barnett, Bakken and Woodford are representative

71 of resource plays currently under exploitation in North America. All samples are from

72 marine depositional environments, are thermally mature (T_{max} >445°C) and have

73 moderate to high organic matter content (2.9 to 11.6 wt.% TOC). Their organic matter is

74 dominated by solid bitumen, which contains intraparticle nano-porosity. Visual

75 evaluation of organic nano-porosity (pore sizes < 100 nm) via SEM suggests that

76 intraparticle organic nano-pores are most abundant in dry gas maturity samples and

77 less abundant at lower wet gas/condensate and peak oil maturities. Samples were

78 distributed to ILS participants in forty laboratories in the Americas, Europe, Africa and

79 Australia; thirty-seven independent sets of results were received. Mean vitrinite

80 reflectance (VR_o) values from all ILS participants range from 0.90 to 1.83% whereas

81 mean solid bitumen reflectance (BR_o) values range from 0.85 to 2.04% (no outlying

82 values excluded), confirming the thermally mature nature of all six samples. Using

83 multiple statistical approaches to eliminate outlying values, we evaluated reproducibility

84 limit R, the maximum difference between valid mean reflectance results obtained on the

85 same sample by different operators in different laboratories using different instruments.

86 Removal of outlying values where the individual signed multiple of standard deviation

87 was >1.0 produced lowest R values, generally ≤0.5% (absolute reflectance), similar to a

88 prior ILS for similar samples. Other traditional approaches to outlier removal (outside

89 mean ± 1.5*interquartile range and outside F10 to F90 percentile range) also produced

90 similar R values. Standard deviation values <0.15*(VR$_o$ or BR$_o$) reduce R and should be

91 a requirement of dispersed organic matter reflectance analysis. After outlier removal, R

92 values were 0.1% to 0.2% for peak oil thermal maturity, about 0.3% for wet

93 gas/condensate maturity and 0.4% to 0.5% for dry gas maturity. That is, these R values

94 represent the uncertainty (in absolute reflectance) that users of vitrinite and solid

95 bitumen reflectance data should assign to any one individual reported mean reflectance

96 value from a similar thermal maturity mudrock sample. R values of this magnitude

97 indicate a need for further standardization of reflectance measurement of dispersed

98 organic matter. Furthermore, these R values quantify realistic interlaboratory

99 measurement dispersion for a difficult but critically important analytical technique

100 necessary for thermal maturity determination in the source-rock reservoirs of

101 unconventional petroleum systems.

102 **Key Words**

103 thermal maturity; shale; mudrock; interlaboratory study; standardization; resource plays;

104 vitrinite reflectance; solid bitumen reflectance; source-rock reservoir; unconventional

105 petroleum system

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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 to 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 to 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 to 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)

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129 and advent of the 'shale revolution' in the United States since about 2005 (Hackley and

130 Cardott, 2016; Wang et al., 2014), VR_o analysis now is commonly used for delineation

131 of 'sweet spots' and identification of the prime acreage in unconventional source-rock

132 reservoirs (Curiale and Curtis, 2016; Peters et al., 2016).

133 Increased need for thermal maturity information in source-rock reservoirs also has

134 sharpened focus on complementary approaches to VR_o analysis. Programmed pyrolysis

135 analysis is a cost- and time-efficient approach to determination of thermal maturity in

136 source rock reservoirs (Espitalie et al., 1985; Peters, 1986), but its interpretation may

137 suffer from contamination by drilling mud or from un-expelled oil (Carvajal-Ortiz and

138 Gentzis, 2015, 2018) as do other bulk geochemical approaches to thermal maturity

139 determination. Other workers have developed bulk and *in situ* spectroscopy-based

140 approaches to assess shale thermal maturity using, e.g., Raman measurements

141 (Hackley and Lünsdorf, 2018; Lupoi et al., 2017, 2019; Romero-Sarmiento et al., 2014;

142 Sauerer et al., 2017, among others). Wilkins et al. (2018) used the same samples of the

143 current study in an *in situ* Raman spectroscopy-based effort to determine thermal

144 maturity, acknowledging that the dry objectives used for micro-Raman spectroscopy

145 limited organic matter identification. Others have used a bulk rock Fourier transform

146 infrared spectroscopy approach (Cheshire et al., 2017; Craddock et al., 2017; Lis et al.,

147 2005), but this method cannot identify or separate compositional variability between

148 individual organic matter types. In addition, careful work has shown that chemical

149 heterogeneity in organic matter, surface quality and matrix effects may limit

150 spectroscopic approaches to thermal maturity determination, even when applied *in situ*

151 (Jubb et al., 2018; Khatibi et al., 2019). While all approaches to source-rock reservoir

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152 thermal maturity determination have merit, particularly as complementary tools, there is

153 no widely-accepted substitute for petrographic measurement of reflectance, because

154 this approach is specific to individual organic matter entities, e.g., vitrinite or solid

155 bitumen.

156 Efforts to improve and standardize reflectance measurements of organic matter

157 dispersed in sedimentary rocks have been an objective of an International Committee

158 for Coal and Organic Petrology (ICCP) working group since 2008 (ICCP, 2009). The

159 working group (currently called 'Identification of Thermal Maturity Relevant Organic

160 Matter') first produced a consensus test method for shale reflectance measurement in

161 2011 (ASTM D7708: Standard test method for microscopical determination of the

162 reflectance of vitrinite dispersed in sedimentary rocks; ASTM, 2015b). This test method

163 has since been widely adopted by the organic petrography community. For example, it

164 is used in the ICCP Dispersed Organic Matter Vitrinite Reflectance Accreditation

165 program (see https://www.iccop.org/accreditation/general-information/), and it has

166 accrued 50+ citations in peer-reviewed literature according to the Scopus citation

167 database (as of June 1, 2019).

168 An initial interlaboratory study (ILS) to develop precision statistics for ASTM D7708 was

169 conducted in 2012-2013 using a wide array of shale types. Those samples were

170 selected to present the potential range of rock materials which could be tested (Hackley

171 et al., 2015). The samples used in the ILS were immature to overmature for generation

172 of liquid hydrocarbons (0.31 to 1.53% VR_o), organic-lean to organic-rich (1 to 22 wt.%

173 total organic carbon) and from lacustrine (generally Type I kerogen), marine (generally

174 Type II kerogen) and terrigenous (carbonaceous shale from coal measures with Type III

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175 kerogen) environments. Results of the ILS showed that interlaboratory reproducibility of

176 reflectance measurement was improved by use of a common methodology (D7708)

177 compared to earlier interlaboratory exercises (e.g., Borrego, 2009; Dembicki, 1984).

178 However, the ILS also showed poor reproducibility limits (R, defined as maximum

179 difference between valid results obtained on same test material by different operators in

180 different laboratories) for certain sample types. In particular, samples with VR_o >1.0%

181 had R values of 0.41 to 0.54, compared to 0.11 to 0.33 for samples with VR_o < 1.0%. It

182 was thought that the poorer reproducibility limits for higher maturity samples might have

183 been, in part, related to low abundance of organic matter. The suggestion was then

184 made that a future ILS should consider high maturity samples with abundant organic

185 matter (Hackley et al., 2015).

186 The initial ILS looked at a range of shales from immature Eocene Green River

187 Mahogany Zone oil shale to overmature Lower Cretaceous Pearsall Formation. In the

188 present ILS, we elected to look at reproducibility of reflectance measurements in the

189 source-rock reservoir oil and gas resource plays currently under exploitation in the

190 United States, including the Marcellus, Haynesville, Eagle Ford, Barnett, Bakken and

191 Woodford. Six samples were selected on the basis of high thermal maturity and high

192 organic matter content. Samples were distributed in early 2016 to ILS participants in

193 forty laboratories in the Americas, Europe, Africa and Australia. This paper evaluates

194 the results of the ILS in the context of the interlaboratory reproducibility limit R with the

195 objective to quantify reproducibility limits of organic matter reflectance in thermally

196 mature source-rock reservoirs of unconventional petroleum systems.

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2. Methods

2.1 Basic Characterization

Samples (Table 1) were analyzed by LECO carbon analyzer 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

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220 requirements listed in Section 11 of ASTM D7708, with the intent to document

221 shortcomings and inadequacies present in the test method. Participants were given

222 their choice of reporting format, e.g., via a document, spread sheet, slide show, etc., as

223 long as the information contained in the report adhered to the requirements of D7708.

224 The instructions advised to: '*find and measure sufficient indigenous organic matter*

225 *representative of in situ thermal maturity in each of the six samples to meet the twenty*

226 *measurements requirement of ASTM D7708*'. Further, the instructions stated: '*If you*

227 *cannot find and measure vitrinite, identify what you do find and measure.*'

228 The previous ILS exercise (Hackley et al., 2015) asked participants to measure each

229 sample in duplicate to determine repeatability; the current ILS requested only one

230 analysis per sample. Not collecting measurements in duplicate preempts the possibility

231 to evaluate precision per ASTM E691: Standard practice for conducting an

232 interlaboratory study to determine the precision of a test method (ASTM, 2015c).

233 However, it was decided that one analysis per sample would boost participation in the

234 ILS.

235 *2.3 Reflectance Determination Method*

236 In brief, the D7708 reflectance determination method involves mounting a sedimentary

237 rock sample in epoxy or thermoset type resins, grinding the surface flat and polishing to

238 a final stage of 0.05 µm according to ASTM D2797 (ASTM, 2015a). Using a reflected

239 light microscope with an oil immersion objective, light reflected from sample organic

240 matter is measured at a detector which is calibrated to standards of known reflectance.

241 A wide array of microscope systems and light detection apparatus are available; use of

242 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°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°C)

obtained from analyses of the Marcellus (4 excluded values), Eagle Ford (2 excluded

values) and Barnett (1 excluded value) samples. When programmed pyrolysis data are

compiled in the modified van Krevelen Hydrogen Index (HI) vs. Oxygen Index (OI)

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266 diagram, samples are shown to have a thermally evolved Type II kerogen (Bakken) or

267 carbon-rich inert organic matter (Type IV) signature (Figure 1A), near the origin. We

268 note that the Type IV signature is due to high thermal maturity and that a Type II

269 signature would be expected from these marine shale samples at lower maturities.

270 When plotted in the HI vs. T_{max} discriminant diagram (Figure 1B), the Bakken sample

271 falls in the oil window maturity field, the Woodford sample lies at the threshold between

272 wet and dry gas thermal maturity, whereas the four remaining samples are in the dry

273 gas window. Again, all but the oil window thermal maturity Bakken sample have a

274 carbon-rich inert organic matter (Type IV) signature.

275 Mineralogical analysis (Table 3) shows that samples dominantly are composed of

276 quartz and illite, except for the Eagle Ford, which contains 54 wt.% carbonate. Two

277 samples, the Marcellus and Bakken, also contain a significant proportion of pyrite.

278 *3.2 Marcellus Shale*

279 Sample 1 from the Middle Devonian Marcellus Shale of the Appalachian Basin in West

280 Virginia contains 5.6 wt.% TOC content (on average, n=6, Table 2). Difficulties in

281 obtaining reasonable T_{max} values from this sample prompted solvent extraction, which

282 reduced average S1 and S2 by 96 and 79%, respectively. The average T_{max} of 591°C

283 reported in Table 2 is the mean of 3 analyses, two of which were on extracted sample

284 material. X-ray diffraction (XRD) analysis (Table 3) indicates sample mineralogy is

285 dominated by quartz and clays with a minor amount of pyrite. Organic content is

286 dominated by solid bitumen, which occurs disseminated between mineral grains and

287 occasionally in larger accumulations (Figure 2A). Petrographic analysis by SEM shows

288 that abundant intraparticle organic nano-porosity (e.g., Loucks et al., 2012) occurs in

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289 solid bitumen (Figure 2B). No organic fluorescence was present in this sample (or in the

290 other samples described herein), consistent with high thermal maturity. Terrigenous

291 macerals vitrinite and inertinite were rare or absent. Previous work on samples from this

292 same core indicated VR_o and BR_o values ranging from 1.6 to 2.3% (Hackley and

293 Cardott, 2016; Streib, 1981).

3.3 Haynesville Formation

295 Sample 2 from the Upper Jurassic Haynesville Formation in the Gulf Coast Basin of

296 Texas contains 2.9 wt.% TOC and has T_{max} of 526°C (Table 2). Silicate minerals quartz

297 and clays are most abundant (Table 3). The organic matter component is similar to the

298 Marcellus wherein finely disseminated solid bitumen pervades the rock matrix along

299 mineral grain boundaries or occurs in foraminifera chambers (Figure 2C). This dominant

300 solid bitumen population has high reflectance (generally >1.5%). A few sparse larger

301 accumulations of solid bitumen also are present. A second solid bitumen population

302 (rare in abundance) with lower reflectance (~0.8 to 1.0%) also occurs in thin veins and

303 vugs. Based on the T_{max} value and production of mostly dry gas in the Haynesville play

304 area (Kaiser, 2012), this second population is not representative of indigenous thermal

305 maturity. The terrigenous maceral inertinite is present whereas vitrinite is rare or absent.

306 Authigenic carbonate occurring as rhombs and spheres frequently is rimmed by solid

307 bitumen (Figure 2C). Again, solid bitumen contains abundant intraparticle organic nano-

308 pores (Figure 2D). Previous workers have reported dry gas thermal maturity VR_o and

309 BR_o values of about 1.4 to 1.7% for samples from this same core (Hackley and Cardott,

310 2016; Hammes and Frébourg, 2012).

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3.4 Eagle Ford Formation

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312 Sample 3 from the Upper Cretaceous Eagle Ford Formation in the Gulf Coast Basin of

313 Texas contains 5.5 wt.% TOC and has T_{max} of 563°C (Table 2). Unlike the other

314 samples of this study, the Eagle Ford sample contains >50 wt.% carbonate (Table 3)

315 and a much smaller quantity of silicate minerals due to distal deposition on a sediment-

316 starved carbonate platform (Eldrett et al., 2015). Solid bitumen is the dominant organic

317 matter and occurs finely disseminated in the carbonate mineral matrix (Figure 2E-F).

318 Planktic Globigerina foraminifera are common, and their chambers typically are filled

319 with solid bitumen and contemporaneous re-crystallized carbonate and/or sulfide

320 (Figure 2E). Structured terrigenous inertinite macerals are common whereas vitrinite is

321 assumed present but qualitatively less abundant (Figure 2F). Previous work reported

322 BR_o values of about 1.8% for samples from this same core (Hackley and Cardott, 2016)

323 and calculated (from T_{max}) VR_o values of about 1.2 to 1.5% were reported for nearby

324 Eagle Ford samples from similar depths (Zhang et al., 2017). Intraparticle organic nano-

325 porosity is present; preliminary work suggests it is most common in solid bitumen

326 infilling pyrite framboid clusters.

3.5 Barnett Shale

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328 Sample 4 from the Mississippian Barnett Shale in the Fort Worth Basin of Texas

329 contains 3.2% TOC with T_{max} of 533°C (Table 2). Like the other samples, solid bitumen

330 dominates the organic matter component, occurring dispersed in a matrix of quartz and

331 clays (Figure 3A). Embayment textures (euhedral mineral terminations intruding organic

332 matter, e.g., Hackley and Cardott, 2016; Hackley and Lewan, 2018; Hackley et al.,

333 2018; Hackley et al., 2017a, 2017b; Peters et al., 2018) are common and intraparticle

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334 organic nano-porosity is abundant (Figure 3B; this sample is from the same core as

335 pioneering studies of organic nano-porosity in ion-milled shale samples by Loucks et al.,

336 2009). The terrigenous maceral inertinite is rarely observed, occurring as fine-grained

337 dispersed fragments (Figure 3A), rounded char particles or in elongate lath and spindle

338 textures. Previous work on this same core has reported a wide range of VR_o and BR_o

339 values from about 1.3 to 2.0% (Hackley and Cardott, 2016; Lewan and Pawlewicz,

340 2017; Loucks et al., 2009; Romero-Sarmiento et al., 2014).

341 *3.6 Bakken Shale*

342 Sample 5 from the Devonian-Mississippian upper Bakken Shale in the Williston Basin of

343 North Dakota contains 10.7 wt.% TOC and is at peak oil thermal maturity with T_{max} of

344 447°C (Table 2), similar to previous T_{max} data reported by Fishman et al. (2015). This is

345 the lowest maturity sample studied herein with a BR_o value of about 0.9% (Hackley and

346 Cardott, 2016). Disseminated solid bitumen dominates the organic component, locally

347 occurring in accumulations >20 μm in diameter or containing inclusions of granular high

348 reflectance micrinite (?)(Figure 3C). Fine-grained inertinite char also is present. Unlike

349 the other samples of this study, intraparticle organic nano-porosity is rare to absent

350 (Figure 3D), presumably due to lower thermal maturity, and imaged porosity primarily

351 occurs as interparticle features at the margins of mineral grains.

352 *3.7 Woodford Shale*

353 Sample 6 is from the Devonian-Mississippian Woodford Shale from the Delaware Basin

354 of west Texas. The ILS sample contains 11.6 wt.% TOC with T_{max} of 476°C (Table 2)

355 and is dominated by quartz followed by a small component from illite (Table 3). Previous

356 workers reported VR_o and BR_o values of about 1.1 to 1.5% from the same Woodford

357 core (Hackley and Cardott, 2016; Harris et al., 2013; Kibria et al., 2018) indicative of wet

358 gas and condensate window thermal maturity. Similar to the previous samples, solid

359 bitumen is the dominant organic matter (Cardott et al., 2015), occurring as a network

360 groundmass finely disseminated along mineral interstices (Figure 3E). Embayment

361 textures adjacent to authigenic minerals are common. Intraparticle organic porosity is

362 present (Figure 3F) but qualitatively not as common as in samples 1-4. Fine-grained

363 inertinite is rare.

364 *3.8 Sample Summary*

365 Summarizing, samples used for this ILS are representative of the source-rock reservoirs

366 in unconventional resource plays currently under exploitation in the United States. All

367 samples represent marine depositional environments, are thermally mature, and contain

368 moderate to high organic matter content. Organic matter dominantly is solid bitumen,

369 which contains intraparticle nano-porosity. Visual appreciation of organic nano-porosity

370 via SEM suggests intraparticle organic pores are most abundant in dry gas maturity

371 samples and less abundant at lower maturities, consistent with previous studies (e.g.,

372 Chen and Xiao, 2014; Curtis et al., 2012; Klaver et al., 2015, 2016; Ko et al., 2018; Löhr

373 et al., 2015; Modica and Lapierre, 2012; Pommer and Milliken, 2015, among others).

4. Results

375 Thirty-seven independent sets of reflectance measurements were received, including

376 four instances where one set of results was the combined work of more than one

377 analyst. All analysts (except see Acknowledgments section) share co-authorship on this

378 paper and each analyst had opportunity to provide input to the paper at multiple stages

379 of writing and review. As results were submitted via email to the ILS convener (P.

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380 Hackley), each participant received immediate feedback via a chart showing

381 comparison of their result with the current group mean result for each sample. This

382 approach allowed near real-time feedback to participants and provided an immediate

383 independent check on their ability to obtain reflectance results in comparison to the

384 group mean. Such feedback is desirable to petrographic laboratories as an efficient and

385 economical quality assurance program and is thought to improve participation in ILS

386 programs. Similar to the prior ILS (Hackley et al., 2015), several analysts chose to

387 submit updated results after initial feedback, exclusively for cases where an insufficient

388 number of measurements (e.g., <5 per sample) had been collected during the first

389 analysis. Four analysts with an initial insufficient number of measurements (e.g., 0 to 2

390 measurements per sample) elected not to update their results for unknown reasons;

391 these participants also are included in authorship but their results are excluded. During

392 initial feedback, several petrographers asked for and were given information on sample

393 provenance, including age, formation name, basin and location, and total organic

394 carbon content. Again, similar to the previous ILS, in no case where updated results

395 were provided are the data considered to be 'excessively sanitized', e.g., changes to

396 reported VR_o or BR_o values were 0.1% or less in the few cases where an analyst

397 elected to provide updated results based on initial submission of an insufficient number

398 of measurements.

399 Results are compiled in Table 4 and illustrated graphically in Figure 4. The results in

400 Table 4 are not listed in the same order as the co-authorship order of this paper, which

401 is alphabetical by last name.

402 More than one-half of analysts reported solid bitumen reflectance measurements; ten

403 analysts reported only solid bitumen reflectance, i.e., these ten analysts did not identify

404 and measure any vitrinite in any sample. Thirteen analysts reported only vitrinite

405 reflectance, i.e., these analysts did not identify and measure solid bitumen in any

406 sample. We speculate these differences are due to wide variability in the specific

407 training and experience of the diverse set of analysts engaged in this ILS. Fourteen

408 analysts reported both solid bitumen and vitrinite reflectance measurements. Group

409 mean (including data from all analysts) solid bitumen and vitrinite reflectance

410 measurements are consistent with previously reported values for these samples or for

411 other samples from the same core (as presented in sections 3.2 to 3.7), ranging from

412 0.85% (Bakken, sample #5) to 2.04% (Eagle Ford, sample #3) for solid bitumen, and

413 0.90% (Bakken) to 1.83% (Marcellus, sample #1) for vitrinite (Figure 4). However, we

414 note that the group mean values reported in Figure 4 include measurements which are

415 clearly outliers according to multiple means of statistical evaluation, as will be shown

416 below. Group standard deviation (GSD) values ranged from 0.09 to 0.43 for solid

417 bitumen and from 0.19 to 0.47 for vitrinite. GSD was lowest for both vitrinite and solid

418 bitumen in the Bakken which has the lowest mean reflectance value; however, GSD did

419 not increase systematically with increasing mean R_o value as would be expected due to

420 increasing optical anisotropy of organic matter (Hackley et al., 2015). GSD was highest

421 for vitrinite in the Marcellus where the greatest dispersion in reported mean vitrinite

422 reflectance value occurred (from 0.92 to 2.73%). GSD was highest for solid bitumen in

423 the Haynesville where six analysts selected the low reflecting (rare) solid bitumen as

424 representative of thermal maturity. It is unclear why these analysts selected this

18

425 population as representative of thermal maturity as it is clearly post-diagenetic and

426 much less abundant than the pervasive pre-diagenetic solid bitumen (terms in the sense

427 of Robert, 1988). It is speculated that this population was selected based on the

428 following instruction from Jacob (1989): '[I]f several migrabitumen generations occur,

429 the generation with the lowest reflectance is representative for the degree of maturity

430 …'. However, its presence in trace amounts as fracture fill and at rock fragment margins

431 and the abundance of the higher reflecting solid bitumen population are key indicators

432 that the low reflecting population is not indicative of indigenous thermal maturity, and

433 instead represents a later stage migration, in the opinion of the majority of analysts who

434 measured solid bitumen reflectance in this study.

435 Group mean reflectance values for solid bitumen and vitrinite reflectance did not show a

436 consistent and systematic less than or greater than relationship to each other. Instead,

437 group mean values fall close to a one-to-one line, and are related by a linear regression

438 coefficient (r^2) of 0.85 (Figure 5). This result is not unexpected, as previous empirical

439 and experimental studies have shown reflectance of co-occurring solid bitumen and

440 vitrinite to be similar at VR_o and BR_o values >1.0% (Ferreiro Mählmann and Le Bayon,

441 2016; Hackley and Lewan, 2018; Jacob, 1989; Landis and Castaño, 1995; Robert,

442 1988; Schoenherr et al., 2007).

443 Participant experience in organic petrography analysis ranged from <5 years to >40

444 years, and about 30% of participants had >30 years experience (Figure 6). No

445 correlation was observed between participant years of experience and precision of

446 performance [considering average unsigned multiple of standard deviation (AUSMD) as

447 a performance measure, i.e., distance of the participant's result to the mean value

19

448 (Borrego, 2009; Borrego et al., 2006; Hackley et al., 2015; Mendonca et al., 2010)].

449 Nevertheless, participants with the most years of experience generally had lower

450 AUSMD values (Figure 7), indicating the importance of training and expertise to the

451 interpretive measurement of dispersed organic matter reflectance. However, we note

452 that the presence of outlying measurements in the data pool may unduly influence

453 evaluation with respect to AUSMD. Moreover, perhaps a better measure is the number

454 of years of experience that participants have in evaluation of marine source rocks and

455 the total number of samples evaluated, which could be recorded in a future ILS.

456 Laboratories with multiple analysts tended to return results very similar to each other,

457 indicating some level of discussion between participants or similar conceptual training.

458 For example, in the case of sample #2 from the Haynesville Formation containing a

459 secondary low reflectance solid bitumen population (Figure 4), three analysts at one

460 laboratory incorrectly selected this same non-representative population as the organic

461 matter for measurement of indigenous thermal maturity.

462 This ILS did not control for sample preparation differences. It is presumed that analysts

463 followed standard test method D7708 which specifies samples are to be prepared via

464 ASTM D2797 ending with a 0.05 µm polishing abrasive (ASTM, 2015a). If analysts used

465 a coarser polishing compound at the final stage of preparation, it is possible that lower

466 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 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 Paleozoic 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 bitumen 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

21

490 solid bitumen as vitrinite is not the only problem impacting reproducibility of reflectance

491 measurements of dispersed organic matter in sedimentary rocks.

492 To-date, there are only a few studies which have compared the range and distribution of

493 reflectance values from co-occurring vitrinite and solid bitumen (e.g., Wei et al., 2016),

494 and no studies which have done so at the peak oil to dry gas thermal maturity level of

495 the current work. That is, there is no evidence that the reflectance range of solid

496 bitumen is as narrowly defined as that of co-occurring vitrinite, although some studies

497 have noted the possibility of petroleum migration which could lead to multiple

498 populations of solid bitumen in a single sample (Kus et al., 2016; Petersen et al., 2013).

499 The previous ILS (Hackley et al., 2015) found no statistical difference between

500 measurements of mean vitrinite and solid bitumen reflectance for the samples

501 considered therein. A similar result is observed here, and it is also observed that there

502 is no systematic dispersion of measurement for one organic matter type compared to

503 the other. That is, individual mean vitrinite and solid bitumen reflectance measurements

504 reported in this study are overlapping in range and do not show consistently lower

505 standard deviation of measurement in one organic matter type than the other. This

506 suggests that misidentification of solid bitumen as vitrinite continues as an issue in the

507 petrography of source-rock reservoirs (e.g., Hackley et al., 2013), or that there is indeed

508 no difference in reflectance of these co-occurring organic matter types, particularly at

509 higher maturities. Nevertheless, if the analyst believed vitrinite was present, they would

510 have selected lower reflecting material to avoid measurement of similar-appearing

511 semifusinite. Conversely, if the analyst identified the material as solid bitumen they

512 would have selected the higher reflecting population most likely to represent the

22

513 indigenous thermal maturity of the sample and to avoid later migrated material.

514 Distinctions between vitrinite and solid bitumen of course can be made with confidence

515 in a single laboratory, particularly for lower maturity samples (e.g., Wei et al., 2016).

516 However, the observation that no systematic differences in solid bitumen and vitrinite

517 reflectance were noted here, or in the previous ILS, suggests that such distinctions are

518 not yet evident in an ILS. Again, this brings into caution the use of empirical conversions

519 to convert measurements of solid bitumen to a vitrinite reflectance equivalent (Hackley

520 et al., 2015) as the identifications and reflectance distinctions of solid bitumen and

521 vitrinite cannot be reproduced in an ILS.

522 *5.2 Evaluation of precision*

523 Reproducibility is an estimate of precision obtained from measurement results of the

524 same sample by different laboratories with different analysts using different instruments

525 (ASTM, 2015c). The reproducibility limit (R) is defined as the difference between two

526 valid results obtained under reproducibility conditions (same test material, different

527 laboratories with different analysts, different instruments). Because both results are

528 valid, R also can be thought of as the amount of uncertainty (in absolute reflectance) for

529 any one individual reflectance measurement. Herein, we use a simplified statistical

530 approach to calculate R using the formula R=2.8*GSD, where GSD=group standard

531 deviation (Ellison et al., 2009).

532 The inclusion in this ILS of a global diversity of laboratories and a broad range of

533 analyst experience contributed to high group standard deviation values (and thus high R

534 values) when all data are considered. For example, measurements of mean solid

535 bitumen reflectance in the Marcellus sample ranged from a low of 0.92 to a high of

23

536 2.73% (Table 4). This range of 1.81% absolute reflectance contributed to a high GSD of

537 0.47 and R of 1.32 (Table 5). Similar distributions of values were reported for the other

538 dry gas thermal maturity samples (Haynesville, Eagle Ford, Barnett) whereas lower

539 GSD values of 0.09 to 0.25 were found for the lower maturity Bakken and Woodford

540 samples. Thus, using all of the data results in relatively high values of R, ranging from a

541 low of 0.26 for solid bitumen in the Bakken to the high value of 1.32 for vitrinite in the

542 Marcellus. The reasons behind this dispersion are multifold. Many of the laboratories

543 participating in the current ILS are potentially unfamiliar with the typical samples of the

544 United States shale plays examined in this study. Misidentification of organic matter due

545 to operator inexperience or bias, e.g., measuring solid bitumen as vitrinite, or vice versa,

546 as discussed above, is a potential issue in these situations. This could be addressed in

547 a future ILS by limiting participation to experienced petrographers familiar with the ILS

548 samples; however, such an approach may severely restrict the number of analyses

549 returned. For certain laboratories in the current ILS, instrument calibration also appears

550 to be at issue, as discussed below. Some dispersion in results may be further explained

551 by non-linearity of the microscope detection system, particularly for older

552 photomultiplier-based analog technologies, and the choice of an inappropriate

553 calibration standard. Another instrument consideration is the ability to adjust the size of

554 the measuring aperture during measurement, such as available to laboratories with

555 Hilgers Fossil systems [Hilgers Fossil is an integrated reflectance system adaptable to

556 most microscopes which uses LED illumination (as opposed to an incandescent light

557 source) and a monochrome digital camera for light detection (as opposed to a

24

558 photomultiplier)]. This ILS did not control for microscope type or the technology used for

559 illumination or light detection.

560 Based on the wide distribution of participant results, we considered multiple traditional

561 and non-traditional ways to eliminate outlying mean reflectance values (Table 5),

562 including removal of: 1) results not using the ASTM D7708 reporting template, 2) results

563 non-compliant in any way with the reporting requirements of ASTM D7708, 3) results

564 with <20 measurements, 4) results with standard deviation >0.15*(VR$_o$ or BR$_o$), 5)

565 results with average signed multiple of standard deviation >1.5 and >1.0, 6) results

566 falling outside the mean ± 1.5*interquartile range (IQR), 7) results falling outside the F10

567 to F90 percentile range, and 8) results with individual signed multiple of standard

568 deviation >1.5 and >1.0. The removal of outlying values makes the assumption that

569 some values in the data pool, numerically distant from other values, are values arising

570 from chance phenomenon, or result from experimental or measurement errors.

571 Several of these approaches to elimination of outlying values can be taken without a

572 pool of data to work from, i.e., the elimination of a particular value can be applied for

573 reasons other than the value lying far outside the group mean. For example, methods 1-

574 4 from the list given in the preceding paragraph can be applied to any individual result.

575 We considered that petrographers not adhering to the ASTM D7708 reporting template

576 or not following reporting requirements of ASTM D7708 may provide imprecise data.

577 However, elimination of these results did not consistently reduce R; for example,

578 removing results where the ASTM reporting template was not used reduced R in only 7

579 of 12 cases (Table 5). On the other hand, removing results where the reporting

580 requirements were not met increased R in 10 of 12 cases. This occurred because of

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581 cases where a petrographer had returned results close to the group mean, but, for

582 example, had provided a table of results without the other reporting requirements

583 specified by ASTM D7708 section 11, e.g., descriptions of fluorescence, sample organic

584 matter types, polish quality, etc. These observations suggest that adherence to D7708

585 reporting requirements or use of the reporting template don't necessarily improve data

586 quality, or, in this case, measurement reproducibility. Removal of results with <20

587 measurements resulted in reductions to R in only 5 of 12 cases, whereas removal of

588 results with standard deviation >0.15*(VR_o or BR_o) reduced R in 10 of 12 cases (Table

589 5). ASTM D7708 requires that reports of mean reflectance backed by fewer than 20

590 measurements are to be flagged as 'qualitative'. However, the observation that R is not

591 always reduced by removal of results with <20 measurements suggests that

592 measurement reproducibility is not necessarily impacted by the number of

593 measurements. On the other hand, the consistent reduction of R observed by removal

594 of results with standard deviation >0.15*(VR_o or BR_o) suggests that this screening

595 technique should be applied for all measurements of dispersed organic reflectance. The

596 rationale is that requiring standard deviation to be <0.15*(VR_o or BR_o) influences the

597 petrographer to preferentially select and measure one type of organic matter as

598 representative of indigenous thermal maturity, as opposed to measuring and averaging

599 the reflectance values of all organic matter present. Therefore, we recommend that

600 reported measurements of mean dispersed organic matter reflectance meet the

601 requirement that standard deviation is <0.15*(VR_o or BR_o).

602 Removal of results with average signed multiple of standard deviation (ASMSD) >1.5 is

603 the criterion used by ICCP for pass/fail status in their accreditation programs (Borrego

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604 et al., 2006; Hackley et al., 2015; Mendonca et al., 2010). In Figure 7 we show absolute

605 values of ASMSD versus average unsigned multiple of standard deviation (AUMSD) for

606 vitrinite and solid bitumen measurements. The red circle (Fig. 7A) and ellipse (Fig. 7B)

607 indicate failing petrographers based on the ICCP criterion. Microscope calibration

608 problems appear to be at issue in these cases where distances to the mean value are

609 high and SMSD consistently has the same sign. Removal of these results from the data

610 pool results in consistent improvement to R values and R values are further improved

611 by restricting the data pool to results with ASMSD<1.0. Restricting the data pool to

612 results with ASMSD<1.0 produced the lowest R value for solid bitumen in the Eagle

613 Ford sample (Table 5).

614 Another approach to outlier removal is to eliminate results for individual samples where

615 the SMSD is > 1.5 or >1.0. That is, the results from an analyst would be removed only

616 when the reported mean reflectance value of an individual sample had a SMSD > 1.5 or

617 >1.0, as opposed to considering the ASMSD for all samples from an analyst. In general,

618 this approach produces the lowest R values because it excludes mistakes, such as

619 selection of the low reflecting solid bitumen population in the Haynesville sample, while

620 keeping results from other samples where the analyst performed well in comparison to

621 the group mean. With the exception of vitrinite in the Marcellus sample, R values range

622 0.14 to 0.52 (Table 5) with higher values occurring in higher maturity samples.

623 Summarizing, R values were about 0.1 to 0.2 for the peak oil thermal maturity Bakken

624 sample, about 0.2 to 0.3 for the wet gas and condensate thermal maturity Woodford

625 sample, and about 0.4 to 0.5 for Marcellus, Haynesville, Eagle Ford and Barnett

626 samples of dry gas maturity. These R values represent the approximate uncertainty (in

27

627 absolute reflectance) that users of vitrinite and solid bitumen reflectance data could

628 assign to any one individual reported mean reflectance value from a similar thermal

629 maturity mudrock sample. We note that these R values are similar to R values obtained

630 for similar maturity samples in the previous ILS (Hackley et al., 2015) and an

631 improvement over historical ILS exercises which contained similar diversity of source-

632 rock reservoir samples (Borrego, 2009; Dembicki, 1984).

633 Traditional means of outlier elimination remove results falling outside the mean ±

634 1.5*interquartile range and outside the F10 to F90 percentile range. Using the

635 interquartile range approach resulted in R values of 0.10 to 1.32. In 3 of 12 cases, this

636 approach produced the lowest R values of all approaches used for outlier elimination.

637 However, in cases where the interquartile range was high, this approach found no

638 outlying values, resulting in no improvement to R for 3 of the 12 cases (Table 5).

639 Removal of results outside the F10 to F90 percentile range consistently improved R and

640 produced the lowest R values in 2 of 12 cases. In general, these traditional approaches

641 to outlier removal found R to be similar to or slightly higher than the result obtained

642 when removing individual samples where the SMSD was > 1.5 or >1.0.

643 *5.3 Future directions*

644 This ILS found that R of 0.1 to 0.5 was obtainable for vitrinite and solid bitumen

645 reflectance measurements in thermally mature source rocks typical of the North

646 American resource plays. This level of uncertainty in interlaboratory reproducibility

647 suggests that further work is necessary to standardize and improve measurement of

648 dispersed organic matter reflectance. Discussions amongst ILS participants at the 2016,

649 2017 and 2018 meetings of ICCP in Houston, Bucharest and Brisbane, respectively,

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650 settled on several future directions for the ILS working group, beginning with a name

651 change to 'Identification of Thermal Maturity Relevant Organic Matter'. Previously, the

652 working group was named 'Identification of Primary Vitrinite' and it was thought by some

653 that including the word 'vitrinite' in the working group title may potentially have led some

654 ILS participants to emphasize vitrinite measurements where little is present. Towards

655 this end, a future ILS may ask participants to assign a 'confidence of identification'

656 criterion for each measurement, allowing removal of individual measurements of poorly-

657 identified organic matter. A similar approach was used in the ILS of Borrego et al.

658 (2006), in which a 'reliability index' was established using the number of measurements

659 and coefficient of variation. In addition, a future ILS may consider giving specialized

660 instructions for organic matter identification in difficult samples, as recommended by

661 Borrego et al. (2006). For example, provision with ILS samples of the basic

662 programmed pyrolysis information contained in Table 2 would have helped participants

663 to avoid the low reflectance solid bitumen population contained in the Haynesville

664 sample. It is long known that polish quality impacts reflectance measurement (e.g.,

665 Stach et al., 1982). As mentioned above, it is presumed ILS participants polished to a

666 final 0.05 μm stage per the requirements of ASTM D7708. However, a future ILS may

667 eliminate variations in polish quality by using samples prepared in one laboratory, rather

668 than allowing each participant to finish the preparation.

669 Another idea put forth by ILS participants was a new ILS in which the emphasis is

670 placed on measurement of solid bitumen reflectance rather than vitrinite. Despite some

671 studies de-emphasizing solid bitumen reflectance as a poor thermal maturity proxy (Kus

672 et al., 2016; Petersen et al., 2013), other works have relied on this parameter in part

29

673 due to its dominance in the organic assemblage of source-rock reservoirs (Borrego et

674 al., 2018; Gonçalves et al., 2014; Juliao et al., 2015; Mastalerz et al., 2018; Misch et al.,

675 2019; Valentine et al., 2014, among others). Therefore, a future ILS to examine

676 reflectance measurement of dispersed organic matter in source-rock reservoirs should

677 consider that solid bitumen is the targeted organic matter type.

678 In preparation for another ILS focused on solid bitumen, it was considered that an

679 exercise which used images, rather than physical samples, would be appropriate to

680 educate petrographers whom are perhaps not as familiar with unconventional source-

681 rock reservoirs. Towards that end, images of organic matter from the six samples of the

682 current ILS are being collated, with regions of interest for organic matter identification

683 indicated on each image. It is considered that an initial ILS using images of source rock

684 reservoirs could better prepare participants for a future ILS with physical samples.

685 Further, the use of Hilgers Fossil reflectance systems in many laboratories opens the

686 possibility for an ILS which uses calibrated images. Hilgers Fossil software contains a

687 'Student' module intended for offline (without a microscope) measurement of calibrated

688 images. That is, one laboratory with the Hilgers Fossil system could create sets of

689 calibrated images which could be then shared to other Hilgers Fossil users for an

690 image-based ILS where the images are measured instead of physical samples. The

691 Hilgers Fossil system relies on modern solid-state technology including LED illumination

692 and CCD light detection, resulting in an ultra-stable configuration relative to older

693 analog-based systems which use tungsten halogen illumination and photomultipliers. In

694 addition, the Hilgers Fossil Student approach to an ILS would have the benefit of an

695 image record of measurement location from each participant. However, such an ILS

696 would be limited to only those laboratories with Hilgers Fossil systems or to those with

697 access to the Hilgers Fossil Student software. An additional limitation or advantage of

698 this approach would be that a single petrographer, or group thereof, would make the

699 initial identifications of organic matter which the participants would then accept as given

700 or dispute.

6. Summary and conclusions

702 An interlaboratory study (ILS) was conducted using six thermally mature mudrock

703 samples to test reproducibility of vitrinite and solid bitumen reflectance measurements in

704 North American unconventional source-rock reservoir petroleum systems. Organic-rich

705 (2.87 to 11.60 wt.% total organic carbon content) samples were used from the

706 Marcellus, Haynesville, Eagle Ford, Barnett, Bakken and Woodford shales which

707 ranged from peak oil to dry gas thermal maturity conditions (T_{max} 447 to 591°C). The

708 samples contain solid bitumen as the dominant organic matter with minor inertinite;

709 vitrinite is rare or absent according to the majority of analysts, and liptinite is absent due

710 to thermal conversion to petroleum and non-liptinite residues (e.g., solid bitumen).

711 Intraparticle organic nano-porosity occurs in solid bitumen and is visually less abundant

712 in the lower maturity samples. Forty laboratories in the Americas, Europe, Africa and

713 Australia received the samples and thirty-seven independent sets of results were

714 produced. Mean vitrinite reflectance values ranged from 0.90 to 1.83% and mean solid

715 bitumen reflectance values ranged from 0.85 to 2.04% when all results are considered

716 (including outlying values). Multiple statistical approaches were used to eliminate

717 outlying values and obtain a precision estimate: reproducibility limit R defined as the

718 maximum difference between valid results obtained on the same test material by

31

719 different analysts in different laboratories using different instruments. After outlier

720 removal, R values generally were 0.1 to ≤0.5% (absolute reflectance), similar to

721 previous results for similar samples. It was observed that standard deviation values

722 <$0.15*(VR_o$ or BR_o) reduce R; therefore, this specification should be required for

723 dispersed organic matter reflectance analysis. The results provide users of reflectance

724 data a realistic expectation of uncertainty which can be used to assign uncertainty to

725 any one reflectance analysis and demonstrate that further work is necessary in

726 standardization of dispersed organic matter reflectance measurement.

727 **Author Contributions**

728 PCH conceived this research and designed the study with input from co-authors. All co-

729 authors contributed data which was analyzed and interpreted by PCH in consultation

730 with co-authors. PCH wrote the manuscript with input from co-authors.

742 Program. All of the data used are contained in tables herein or available from the

743 associated data release: https://doi.org/10.5066/P9LB8IJ4. Any use of trade, firm, or

744 product names is for descriptive purposes only and does not imply endorsement by the

745 U.S. Government.

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784 Figure 4. Histograms of all data for mean vitrinite and solid bitumen reflectance for the

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795 The red circle (A) and ellipse (B) indicate failing petrographers based on the ICCP

796 criterion of AUMSD>1.5.

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1 **Testing reproducibility of vitrinite and solid bitumen reflectance measurements in**

2 **North American unconventional source-rock reservoir petroleum systems**

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Abstract

68 An interlaboratory study (ILS) was conducted to test reproducibility of vitrinite and solid

69 bitumen reflectance measurements in six mudrock samples from United States

70 unconventional source-rock reservoir petroleum systems. Samples selected from the

71 Marcellus, Haynesville, Eagle Ford, Barnett, Bakken and Woodford are representative

72 of resource plays currently under exploitation in North America. All samples are from

73 marine depositional environments, are thermally mature (T_{max} >445°C) and have

74 moderate to high organic matter content (2.9 to 11.6 wt.% TOC). Their organic matter is

75 dominated by solid bitumen, which contains intraparticle nano-porosity. Visual

76 evaluation of organic nano-porosity (pore sizes < 100 nm) via SEM suggests that

77 intraparticle organic nano-pores are most abundant in dry gas maturity samples and

78 less abundant at lower wet gas/condensate and peak oil maturities. Samples were

79 distributed to ILS participants in forty laboratories in the Americas, Europe, Africa and

80 Australia; thirty-seven independent sets of results were received. Mean vitrinite

81 reflectance (VR_o) values from all ILS participants range from 0.90 to 1.83% whereas

82 mean solid bitumen reflectance (BR_o) values range from 0.85 to 2.04% (no outlying

83 values excluded), confirming the thermally mature nature of all six samples. Using

84 multiple statistical approaches to eliminate outlying values, we evaluated reproducibility

3

85   limit R, the maximum difference between valid mean reflectance results obtained on the

86   same sample by different operators in different laboratories using different instruments.

87   Removal of outlying values where the individual signed multiple of standard deviation

88   was >1.0 produced lowest R values, generally ≤0.5% (absolute reflectance), similar to a

89   prior ILS for similar samples. Other traditional approaches to outlier removal (outside

90   mean ± 1.5*interquartile range and outside F10 to F90 percentile range) also produced

91   similar R values. Standard deviation values <0.15*(VR_o or BR_o) reduce R and should be

92   a requirement of dispersed organic matter reflectance analysis. After outlier removal, R

93   values were 0.1% to 0.2% for peak oil thermal maturity, about 0.3% for wet

94   gas/condensate maturity and 0.4% to 0.5% for dry gas maturity. That is, these R values

95   represent the uncertainty (in absolute reflectance) that users of vitrinite and solid

96   bitumen reflectance data should assign to any one individual reported mean reflectance

97   value from a similar thermal maturity mudrock sample. R values of this magnitude

98   indicate a need for further standardization of reflectance measurement of dispersed

99   organic matter. Furthermore, these R values quantify realistic interlaboratory

100   measurement dispersion for a difficult but critically important analytical technique

101   necessary for thermal maturity determination in the source-rock reservoirs of

102   unconventional petroleum systems.

103   **Key Words**

104   thermal maturity; shale; mudrock; interlaboratory study; standardization; resource plays;

105   vitrinite reflectance; solid bitumen reflectance; source-rock reservoir; unconventional

106   petroleum system

4

1. Introduction and background

Determination of the reflectance of vitrinite in sedimentary rocks by optical microscopy has been long regarded as the ~~'gold standard'~~standard technique for ~~prediction~~ 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 to 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 to 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 to 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

130 (Curtis, 2002) and advent of the 'shale revolution' in the United States since about 2005

131 (Hackley and Cardott, 2016; Wang et al., 2014), VR_o analysis now is commonly used for

132 delineation of 'sweet spots' and identification of the prime acreage in unconventional

133 source-rock reservoirs (Curiale and Curtis, 2016; Peters et al., 2016).

134 Increased need for thermal maturity information in ~~unconventional~~ source-rock

135 reservoirs also has sharpened focus on complementary approaches to VR_o analysis.

136 Programmed pyrolysis analysis is a cost- and time-efficient approach to determination

137 of thermal maturity in source rock reservoirs (Espitalie et al., 1985; Peters, 1986), but its

138 interpretation may suffer from contamination by drilling mud or from un-expelled oil

139 (Carvajal-Ortiz and Gentzis, 2015, 2018) as do other bulk geochemical approaches to

140 thermal maturity determination. Other workers have ~~tried to~~ developed bulk and *in situ*

141 spectroscopy-based approaches to assess shale thermal maturity using, e.g., Raman

142 measurements (Hackley and Lünsdorf, 2018; Lupoi et al., 2017, 2019; Romero-

143 Sarmiento et al., 2014; Sauerer et al., 2017, among others). Wilkins et al. (2018) used

144 the same samples of the current study in an *in situ* Raman spectroscopy-based effort to

145 determine thermal maturity, acknowledging~~, however,~~ that the dry objectives used for

146 micro-Raman spectroscopy limited organic matter identification. Others have used a

147 bulk rock Fourier transform infrared spectroscopy approach (Cheshire et al., 2017;

148 Craddock et al., 2017; Lis et al., 2005), but this method cannot identify or separate

149 compositional variability between individual organic matter types. In addition, careful

150 work has shown that chemical heterogeneity in organic matter, surface quality and

151 matrix effects may limit spectroscopic approaches to thermal maturity determination,

152 even when applied *in situ* (Jubb et al., 2018; Khatibi et al., 2019). While all approaches

6

153 to ~~unconventional~~ source-rock reservoir thermal maturity determination have merit,

154 particularly as complementary tools, there is no ~~current~~ widely-accepted substitute for

155 petrographic measurement of reflectance, ~~which~~ because this approach is specific to

156 individual organic matter entities, e.g., vitrinite or solid bitumen.

157 Efforts to improve and standardize reflectance measurements of organic matter

158 dispersed in sedimentary rocks have been an objective of an International Committee

159 for Coal and Organic Petrology (ICCP) working group since 2008 (ICCP, 2009). The

160 working group (currently called 'Identification of Thermal Maturity Relevant Organic

161 Matter') first produced a consensus test method for shale reflectance measurement in

162 2011 (ASTM D7708: Standard test method for microscopical determination of the

163 reflectance of vitrinite dispersed in sedimentary rocks; ASTM, 2015b). This test method

164 has since been widely adopted by the organic petrography community~~,~~. For example,

165 ~~e.g.,~~ it is used in the ICCP Dispersed Organic Matter Vitrinite Reflectance Accreditation

166 program (see https://www.iccop.org/accreditation/general-information/), and it has

167 accrued 50+ citations in peer-reviewed literature according to the Scopus citation

168 database (as of June 1, 2019).

169 An initial interlaboratory study (ILS) to develop precision statistics for ASTM D7708 was

170 conducted in 2012-2013 using a wide array of shale types. Those samples were

171 selected to present the potential range of rock materials which could be tested (Hackley

172 et al., 2015). The samples used in the ILS were immature to overmature for generation

173 of liquid hydrocarbons (0.31 to 1.53% VR_o), organic-lean to organic-rich (1 to 22 wt.%

174 total organic carbon) and from lacustrine (generally Type I kerogen), marine (generally

175 Type II kerogen) and ~~terrestrial~~ terrigenous (carbonaceous shale from coal measures

7

176 with Type III kerogen) environments. Results of the ILS showed that interlaboratory

177 ~~precision (~~reproducibility of reflectance measurement~~)~~ was improved by use of a

178 common methodology (D7708) compared to earlier interlaboratory exercises (e.g.,

179 Borrego, 2009; Dembicki, 1984). However, the ILS also showed poor reproducibility

180 limits (R, defined as maximum difference between valid results obtained on same test

181 material by different operators in different laboratories) for certain sample types. In

182 particular, samples with VR_o >1.0% had R values of 0.41 to 0.54, compared to 0.11 to

183 0.33 for samples with VR_o < 1.0%. It was thought that the poorer reproducibility limits for

184 higher maturity samples might have been, in part, related to low abundance of organic

185 matter. The suggestion was then made that a future ILS should consider high maturity

186 samples with abundant organic matter (Hackley et al., 2015).

187 The initial ILS looked at a range of shales ~~materials~~ from immature Eocene Green River

188 Mahogany Zone oil shale to overmature Lower Cretaceous Pearsall Formation. In the

189 present ILS, we elected to look at reproducibility of reflectance measurements in the

190 ~~unconventional~~ source-rock reservoir oil and gas resource plays currently under

191 exploitation in the United States, including the Marcellus, Haynesville, Eagle Ford,

192 Barnett, Bakken and Woodford. Six samples were selected on the basis of high thermal

193 maturity and high organic matter content. Samples were distributed in early 2016 to ILS

194 participants in forty laboratories in the Americas, Europe, Africa and Australia. This

195 paper evaluates the results of the ILS in the context of the interlaboratory reproducibility

196 limit R with the objective to quantify reproducibility limits of organic matter reflectance in

197 thermally mature source-rock reservoirs of unconventional petroleum systems.

2. Methods

2.1 Basic Characterization

Samples (Table 1) were analyzed by LECO carbon analyzer 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

221 requirements listed in Section 11 of ASTM D7708, with the intent to document

222 shortcomings and inadequacies present in the test method. Participants were given

223 their choice of reporting format, e.g., via a document, spread sheet, slide show, etc., as

224 long as the information contained in the report adhered to the requirements of D7708.

225 The instructions advised to: '*find and measure sufficient indigenous organic matter*

226 *representative of in situ thermal maturity in each of the six samples to meet the twenty*

227 *measurements requirement of ASTM D7708*'. Further, the instructions stated: '*If you*

228 *cannot find and measure vitrinite, identify what you do find and measure.*'

229 The previous ILS exercise (Hackley et al., 2015) asked participants to measure each

230 sample in duplicate to determine repeatability; the current ILS requested only one

231 analysis per sample. Not collecting measurements in duplicate preempts the possibility

232 to evaluate precision per ASTM E691: Standard practice for conducting an

233 interlaboratory study to determine the precision of a test method (ASTM, 2015c).

234 However, it was decided that one analysis per sample would boost participation in the

235 ILS.

236 *2.3 Reflectance Determination Method*

237 In brief, the D7708 reflectance determination method involves mounting a sedimentary

238 rock sample in epoxy or thermoset type resins, grinding the surface flat and polishing to

239 a final stage of 0.05 µm according to ASTM D2797 (ASTM, 2015a). Using a reflected

240 light microscope with an oil immersion objective, light reflected from sample organic

241 matter is measured at a detector which is calibrated to standards of known reflectance.

242 A wide array of microscope systems and light detection apparatus are available; use of

243 ASTM D7708 is not limited to a certain type of equipment.

10

3. Samples

244

245   Six samples were used for this study. All samples were from collections of the U.S.

246   Geological Survey, previously characterized for another study (Hackley and Cardott,

247   2016), and representative of the ~~unconventional~~ source-rock reservoir petroleum

248   systems currently exploited in North America (Table 1). In all cases, the samples were

249   from conventional oil and gas exploration cores and were selected because they are

250   organic-rich and from thermally mature peak oil to dry gas conditions. Because of

251   advanced thermal maturity, oil-prone macerals alginite and bituminite (which are

252   common in immature marine source rocks) are not recognizable as such due to their

253   conversion to petroleum (e.g., Hackley and Lewan, 2018) or due to the loss of their

254   distinguishing optical properties (Pickel et al., 2017).

3.1 Geochemical Screening and Mineralogy

255

256   Geochemical data compiled from the samples in Table 2 shows total organic carbon

257   (TOC) content ranges from 2.9 to 11.6 wt.%, whereas T_{max} values range from 447 to

258   591°C. These data confirm the organic-rich, thermally mature nature of the sample set

259   (e.g., Baskin, 1997; Peters, 1986; Peters and Cassa, 1994). Production index (PI)

260   values ranging from 0.14 to 0.74 also confirm mature to postmature conditions (Peters

261   and Cassa, 1994). Note that the average programmed pyrolysis parameters in Table 2

262   exclude results from extracted samples, whereas the average T_{max} values do include

263   results from extracted samples but exclude unreasonable low values (e.g., <400°C)

264   obtained from analyses of the Marcellus (4 excluded values), Eagle Ford (2 excluded

265   values) and Barnett (1 excluded value) samples. When programmed pyrolysis data are

266   compiled in the ~~pseudo~~ modified van Krevelen Hydrogen Index (HI) vs. Oxygen Index

11

267 (OI) diagram, samples are shown to have a thermally evolved Type II kerogen (Bakken)

268 or carbon-rich inert organic matter (Type IV) signature (Figure 1A), near the origin. We

269 note that the Type IV signature is due to high thermal maturity and that a Type II

270 signature would be expected from these marine shale samples at lower maturities.

271 When plotted in the HI vs. T_{max} discriminant diagram (Figure 1B), the Bakken sample

272 falls in the oil window maturity field, the Woodford sample lies at the threshold between

273 wet and dry gas thermal maturity, whereas the four remaining samples are in the dry

274 gas window. Again, all but the oil window thermal maturity Bakken sample have a

275 carbon-rich inert organic matter (Type IV) signature.

276 Mineralogical analysis (Table 3) shows that samples dominantly are composed of

277 quartz and illite, except for the Eagle Ford, which contains 54 wt.% carbonate. Two

278 samples, the Marcellus and Bakken, also contain a significant proportion of pyrite.

3.2 Marcellus Shale

280 Sample 1 from the Middle Devonian Marcellus Shale of the Appalachian Basin in West

281 Virginia contains 5.6 wt.% TOC content (on average, n=6, Table 2). Difficulties in

282 obtaining reasonable T_{max} values from this sample prompted solvent extraction, which

283 reduced average S1 and S2 by 96 and 79%, respectively. The average T_{max} of 591°C

284 reported in Table 2 is the mean of 3 analyses, two of which were on extracted sample

285 material. X-ray diffraction (XRD) analysis (Table 3) indicates sample mineralogy is

286 dominated by quartz and clays with a minor amount of pyrite. Organic content is

287 dominated by solid bitumen, which occurs disseminated between mineral grains and

288 occasionally in larger accumulations (Figure 2A). Petrographic analysis by SEM shows

289 that abundant intraparticle organic nano-porosity (e.g., Loucks et al., 2012) occurs in

12

290 solid bitumen (Figure 2B). No organic fluorescence was present in this sample (or in the

291 other samples described herein), ~~indicative of~~consistent with high thermal maturity.

292 ~~Terrestrial~~ Terrigenous macerals vitrinite and inertinite were rare or absent. Previous

293 work on samples from this same core indicated VR_o and BR_o values ranging from 1.6 to

294 2.3% (Hackley and Cardott, 2016; Streib, 1981).

3.3 Haynesville Formation

296 Sample 2 from the Upper Jurassic Haynesville Formation in the Gulf Coast Basin of

297 Texas contains 2.9 wt.% TOC and has T_{max} of 526°C (Table 2). Silicate minerals quartz

298 and clays are most abundant (Table 3). The organic matter component is similar to the

299 Marcellus wherein finely disseminated solid bitumen pervades the rock matrix along

300 mineral grain boundaries or occurs in foraminifera chambers (Figure 2C). This dominant

301 solid bitumen population has high reflectance (generally >1.5%). A few sparse larger

302 accumulations of solid bitumen also are present. A second solid bitumen population

303 (rare in abundance) with lower reflectance (~0.8 to 1.0%) also occurs in thin veins and

304 vugs. Based on the T_{max} value and production of mostly dry gas in the Haynesville play

305 area (Kaiser, 2012), this second population is not representative of indigenous thermal

306 maturity. ~~Terrestrial~~ The terrigenous maceral inertinite is present whereas vitrinite is rare

307 or absent. Authigenic carbonate occurring as rhombs and spheres frequently is rimmed

308 by solid bitumen (Figure 2C). Again, solid bitumen contains abundant intraparticle

309 organic nano-pores (Figure 2D). Previous workers have reported dry gas thermal

310 maturity VR_o and BR_o values of about 1.4 to 1.7% for samples from this same core

311 (Hackley and Cardott, 2016; Hammes and Frébourg, 2012).

13

3.4 Eagle Ford Formation

312

313 Sample 3 from the Upper Cretaceous Eagle Ford Formation in the Gulf Coast Basin of

314 Texas contains 5.5 wt.% TOC and has T_{max} of 563°C (Table 2). Unlike the other

315 samples of this study, the Eagle Ford sample contains >50 wt.% carbonate (Table 3)

316 and a much smaller quantity of silicate minerals due to distal deposition on a sediment-

317 starved carbonate platform (Eldrett et al., 2015). Solid bitumen is the dominant organic

318 matter and occurs finely disseminated in the carbonate mineral matrix (Figure 2E-F).

319 Planktic Globigerina foraminifera are common, and their chambers typically are filled

320 with solid bitumen and contemporaneous re-crystallized carbonate and/or sulfide

321 (Figure 2E). Structured ~~terrestrial~~ terrigenous inertinite macerals are common whereas

322 vitrinite is assumed present but qualitatively less abundant (Figure 2F). Previous work

323 reported BR_o values of about 1.8% for samples from this same core (Hackley and

324 Cardott, 2016) and calculated (from T_{max}) VR_o values of about 1.2 to 1.5% were

325 reported for nearby Eagle Ford samples from similar depths (Zhang et al., 2017).

326 Intraparticle organic nano-porosity is present; preliminary work suggests it is most

327 common in solid bitumen infilling pyrite framboid clusters.

3.5 Barnett Shale

328

329 Sample 4 from the Mississippian Barnett Shale in the Fort Worth Basin of Texas

330 contains 3.2% TOC with T_{max} of 533°C (Table 2). Like the other samples, solid bitumen

331 dominates the organic matter component, occurring dispersed in a matrix of quartz and

332 clays (Figure 3A). Embayment textures (euhedral mineral terminations intruding organic

333 matter, e.g., Hackley and Cardott, 2016; Hackley and Lewan, 2018; Hackley et al.,

334 2018; Hackley et al., 2017a, 2017b; Peters et al., 2018) are common and intraparticle

14

335 organic nano-porosity is abundant (Figure 3B; this sample is from the same core as

336 ~~landmark description~~pioneering studies of organic nano-porosity in ion-milled shale

337 samples by Loucks et al., 2009). ~~Terrestrial~~ The terrigenous maceral inertinite is rarely

338 observed, occurring as fine-grained dispersed fragments (Figure 3A), rounded char

339 particles or in elongate lath and spindle textures. Previous work on this same core has

340 reported a wide range of VR_o and BR_o values from about 1.3 to 2.0% (Hackley and

341 Cardott, 2016; Lewan and Pawlewicz, 2017; Loucks et al., 2009; Romero-Sarmiento et

342 al., 2014).

3.6 Bakken Shale

344 Sample 5 from the Devonian-Mississippian upper Bakken Shale in the Williston Basin of

345 North Dakota contains 10.7 wt.% TOC and is ~~from~~ at peak oil thermal maturity with T_{max}

346 of 447°C (Table 2), similar to previous T_{max} data reported by Fishman et al. (2015). This

347 is the lowest maturity sample studied herein with a BR_o value of about 0.9% (Hackley

348 and Cardott, 2016). ~~A groundmass of~~ Disseminated solid bitumen dominates the

349 organic component, locally occurring in accumulations >20 μm in diameter or containing

350 inclusions of granular high reflectance micrinite (?) ~~residue~~ (Figure 3C). Fine-grained

351 inertinite char also is present. Unlike the other samples of this study, intraparticle

352 organic nano-porosity is rare to absent (Figure 3D), presumably due to lower thermal

353 maturity, and imaged porosity primarily occurs as interparticle features at the margins of

354 mineral grains.

3.7 Woodford ~~Formation~~Shale

356 Sample 6 is from the Devonian-Mississippian Woodford ~~Formation~~ Shale from the

357 Delaware Basin of west Texas. The ILS sample contains 11.6 wt.% TOC with T_{max} of

15

358 476°C (Table 2) and is dominated by quartz followed by a small component from illite

359 (Table 3). Previous workers reported VR_o and BR_o values of about 1.1 to 1.5% from the

360 same Woodford core (Hackley and Cardott, 2016; Harris et al., 2013; Kibria et al., 2018)

361 indicative of wet gas and condensate window thermal maturity. Similar to the previous

362 samples, solid bitumen is the dominant organic matter (Cardott et al., 2015), occurring

363 as a network groundmass finely disseminated along mineral interstices (Figure 3E).

364 Embayment textures adjacent to authigenic minerals are common. Intraparticle organic

365 porosity is present (Figure 3F) but qualitatively not as common as in samples 1-4. Fine-

366 grained inertinite is rare.

367 *3.8 Sample Summary*

368 Summarizing, samples used for this ILS are representative of the source-rock reservoirs

369 in unconventional resource plays currently under exploitation in the United States. All

370 samples represent marine depositional environments, are thermally mature, and contain

371 moderate to high organic matter content. Organic matter dominantly is solid bitumen,

372 which contains intraparticle nano-porosity. Visual appreciation of organic nano-porosity

373 via SEM suggests intraparticle organic pores are most abundant in dry gas maturity

374 samples and less abundant at lower maturities, consistent with previous studies (e.g.,

375 Chen and Xiao, 2014; Curtis et al., 2012; Klaver et al., 2015, 2016; Ko et al., 2018; Löhr

376 et al., 2015; Modica and Lapierre, 2012; Pommer and Milliken, 2015, among others).

4. Results

378 Thirty-seven independent sets of reflectance measurements were received, including

379 four instances where one set of results was the combined work of more than one

380 analyst. All analysts (except see Acknowledgments section) share co-authorship on this

16

381 paper and each analyst had opportunity to provide input to the paper at multiple stages

382 of writing and review. As results were submitted via email to the ILS convener (P.

383 Hackley), each participant received immediate feedback via a chart showing

384 comparison of their result compared towith the current group mean result for each

385 sample. This approach allowed near real-time feedback to participants and provided an

386 immediate independent check on their ability to obtain reflectance results in comparison

387 to the group mean. Such feedback is desirable to petrographic laboratories as an

388 efficient and economical quality assurance program and is thought to improve

389 participation in ILS programs. Similar to the prior ILS (Hackley et al., 2015), several

390 analysts chose to submit updated results after initial feedback, primarily exclusively for

391 cases where an insufficient number of measurements (e.g., <5 per sample) had been

392 collected during the first analysis. Four analysts with an initial insufficient number of

393 measurements (e.g., 0 to 2 measurements per sample) elected not to update their

394 results for unknown reasons; these participants also are included in authorship but their

395 results are excluded. During initial feedback, several petrographers asked for and were

396 given information on sample provenance, including age, formation name, basin and

397 location, and total organic carbon content. Again, similar to the previous ILS, in no case

398 where updated results were provided are the data considered to be 'excessively

399 sanitized', e.g., changes to reported VR_o or BR_o values were 0.1% or less in the few

400 cases where an analyst elected to provide updated results based on initial submission

401 of an insufficient number of measurements.

402 Results are compiled in Table 4 and illustrated graphically in Figure 4. The results in

403 Table 4 are not listed in the same order as the co-authorship order of this paper, which

404 is alphabetical by last name.

405 More than one-half of analysts reported solid bitumen reflectance measurements; ten

406 analysts reported only solid bitumen reflectance, i.e., these ten analysts refused did not

407 to identify and measure any vitrinite in any sample. Thirteen analysts reported only

408 vitrinite reflectance, i.e., these analysts refused did not to identify and measure solid

409 bitumen in any sample. We speculate these differences are due to wide variability in the

410 specific training and experience of the diverse set of analysts engaged in this ILS.

411 Fourteen analysts reported both solid bitumen and vitrinite reflectance measurements.

412 Group mean (including data from all analysts) solid bitumen and vitrinite reflectance

413 measurements are consistent with previously reported values for these samples or for

414 other samples from the same core (as presented in sections 3.2 to 3.7), ranging from

415 0.85% (Bakken, sample #5) to 2.04% (Eagle Ford, sample #3) for solid bitumen, and

416 0.90% (Bakken) to 1.83% (Marcellus, sample #1) for vitrinite (Figure 4). However, we

417 note that the group mean values reported in Figure 4 include measurements which are

418 clearly outliers according to multiple means of statistical evaluation, as will be shown

419 below. Group standard deviation (GSD) values ranged from 0.09 to 0.43 for solid

420 bitumen and from 0.19 to 0.47 for vitrinite. GSD was lowest for both vitrinite and solid

421 bitumen in the Bakken which has the lowest mean reflectance value; however, GSD did

422 not increase systematically with increasing mean R_o value as would be expected due to

423 increasing optical anisotropy of organic matter (Hackley et al., 2015). GSD was highest

424 for vitrinite in the Marcellus where the greatest dispersion in reported mean vitrinite

18

425 reflectance value occurred (from 0.92 to 2.73%). GSD was highest for solid bitumen in

426 the Haynesville where six analysts selected the low reflecting (rare) solid bitumen as

427 representative of thermal maturity. It is unclear why these analysts selected this

428 population as representative of thermal maturity as it is clearly post-diagenetic and

429 much less abundant than the pervasive pre-diagenetic solid bitumen (terms in the sense

430 of Robert, 1988). It is speculated that this population was selected based on the

431 following instruction from Jacob (1989): '[I]f several migrabitumen generations occur,

432 the generation with the lowest reflectance is representative for the degree of maturity

433 …'. However, its presence in trace amounts as fracture fill and at rock fragment margins

434 and the abundance of the higher reflecting solid bitumen population are key indicators

435 that the low reflecting population is not indicative of indigenous thermal maturity, and

436 instead represents a later stage migration, in the opinion of the majority of analysts who

437 measured solid bitumen reflectance in this study.

438 Group mean reflectance values for solid bitumen and vitrinite reflectance did not show a

439 consistent and systematic less than or greater than relationship to each other. Instead,

440 group mean values fall close to a one-to-one line, and are related by a linear regression

441 coefficient (r^2) of 0.85 (Figure 5). This result is not unexpected, as previous empirical

442 and experimental studies have shown reflectance of co-occurring solid bitumen and

443 vitrinite to be similar at VR_o and BR_o values >1.0% (Ferreiro Mählmann and Le Bayon,

444 2016; Hackley and Lewan, 2018; Jacob, 1989; Landis and Castaño, 1995; Robert,

445 1988; Schoenherr et al., 2007).

446 Participant experience in organic petrography analysis ranged from <5 years to >40

447 years, and about 30% of participants had >30 years experience (Figure 6). No

19

448 correlation was observed between participant years of experience and precision of

449 performance [considering average unsigned multiple of standard deviation (AUSMD) as

450 a performance measure, i.e., distance of the participant's result to the mean value

451 (Borrego, 2009; Borrego et al., 2006; Hackley et al., 2015; Mendonca et al., 2010)].

452 Nevertheless, participants with the most years of experience generally had lower

453 AUSMD values (Figure 7), indicating the importance of training and expertise to the

454 interpretive measurement of dispersed organic matter reflectance. However, we note

455 that the presence of outlying measurements in the data pool may unduly influence

456 evaluation with respect to AUSMD. Moreover, perhaps a better measure is the number

457 of years of experience that participants have in evaluation of marine source rocks and

458 the total number of samples evaluated, which could be recorded in a future ILS.

459 Laboratories with multiple analysts tended to return results very similar to each other,

460 indicating some level of discussion between participants or similar conceptual training.

461 For example, in the case of sample #2 from the Haynesville Formation containing a

462 secondary low reflectance solid bitumen population (Figure 4), three analysts at one

463 laboratory incorrectly selected this same non-representative population as the organic

464 matter for measurement of indigenous thermal maturity.

465 This ILS did not control for sample preparation differences. It is presumed that analysts

466 followed standard test method D7708 which specifies samples are to be prepared via

467 ASTM D2797 ending with a 0.05 μm polishing abrasive (ASTM, 2015a). If analysts used

468 a coarser polishing compound at the final stage of preparation, it is possible that lower

469 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 ~~unconventional~~ 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 al., 2018; Misch et al., 2019). Many of the important ~~unconventional~~ 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 Paleozoic 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 bitumen 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

493 participants who only identified solid bitumen (Table 4) suggests that misidentification of

494 solid bitumen as vitrinite is not the only problem impacting reproducibility of reflectance

495 measurements of dispersed organic matter in sedimentary rocks.

496 To-date, there are only a few studies which have compared the range and distribution of

497 reflectance values from co-occurring vitrinite and solid bitumen (e.g., Wei et al., 2016),

498 and no studies which have done so at the peak oil to dry gas thermal maturity level of

499 the current work. That is, there is no evidence that the reflectance range of solid

500 bitumen is as narrowly defined as that of co-occurring vitrinite, although some studies

501 have noted the possibility of petroleum migration which could lead to multiple

502 populations of solid bitumen in a single sample (Kus et al., 2016; Petersen et al., 2013).

503 The previous ILS (Hackley et al., 2015) found no statistical difference between

504 measurements of mean vitrinite and solid bitumen reflectance for the samples

505 considered therein. A similar result is observed here, and it is also observed that there

506 is no systematic dispersion of measurement for one organic matter type compared to

507 the other. That is, individual mean vitrinite and solid bitumen reflectance measurements

508 reported in this study are overlapping in range and do not show consistently lower

509 standard deviation of measurement in one organic matter type than the other. This

510 suggests that misidentification of solid bitumen as vitrinite continues as an issue in the

511 petrography of source-rock reservoirs (e.g., Hackley et al., 2013), or that there is indeed

512 no difference in reflectance of these co-occurring organic matter types, particularly at

513 higher maturities. Nevertheless, if the analyst believed vitrinite was present, they would

514 have selected lower reflecting material to avoid measurement of similar-appearing

515 semifusinite. Conversely, if the analyst identified the material as solid bitumen they

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516 would have selected the higher reflecting population most likely to represent the

517 indigenous thermal maturity of the sample and to avoid later migrated material.

518 Distinctions between vitrinite and solid bitumen of course can be made with confidence

519 in a single laboratory, particularly for lower maturity samples (e.g., Wei et al., 2016).

520 However, the observation that no systematic differences in solid bitumen and vitrinite

521 reflectance were noted here, or in the previous ILS, suggests that such distinctions are

522 not yet ~~reproducible~~ evident in an ILS. Again, this brings into caution the use of

523 empirical conversions to convert measurements of solid bitumen to a vitrinite

524 reflectance equivalent (Hackley et al., 2015) as the identifications and reflectance

525 distinctions of solid bitumen and vitrinite cannot be reproduced in an ILS.

5.2 Evaluation of precision

527 Reproducibility is an estimate of precision obtained from measurement results of the

528 same sample by different laboratories with different analysts using different instruments

529 (ASTM, 2015c). The reproducibility limit (R) is defined as the difference between two

530 valid results obtained under reproducibility conditions (same test material, different

531 laboratories with different analysts, different instruments). Because both results are

532 valid, R also can be thought of as the amount of uncertainty (in absolute reflectance) for

533 any one individual reflectance measurement. Herein, we use a simplified statistical

534 approach to calculate R using the formula R=2.8*GSD, where GSD=group standard

535 deviation (Ellison et al., 2009).

536 The inclusion in this ILS of a global diversity of laboratories and a broad range of

537 analyst experience contributed to high group standard deviation values (and thus high R

538 values) when all data are considered. For example, measurements of mean solid

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539 bitumen reflectance in the Marcellus sample ranged from a low of 0.92 to a high of

540 2.73% (Table 4). This range of 1.81% absolute reflectance contributed to a high GSD of

541 0.47 and R of 1.32 (Table 5). Similar distributions of values were reported for the other

542 dry gas thermal maturity samples (Haynesville, Eagle Ford, Barnett) whereas lower

543 GSD values of 0.09 to 0.25 were found for the lower maturity Bakken and Woodford

544 samples. Thus, using all of the data results in relatively high values of R, ranging from a

545 low of 0.26 for solid bitumen in the Bakken to the high value of 1.32 for vitrinite in the

546 Marcellus. The reasons behind this dispersion are multifold. Many of the laboratories

547 participating in the current ILS are potentially unfamiliar with the typical samples of the

548 United States shale plays examined in this study. Misidentification of organic matter due

549 to operator inexperience or bias, e.g., measuring solid bitumen as vitrinite, or vice versa,

550 as discussed above, is a potential issue in these situations. This could be addressed in

551 a future ILS by limiting participation to experienced petrographers whom are familiar

552 with the ILS samples; however, such an approach may severely restrict the number of

553 analyses returned. For certain laboratories in the current ILS, instrument calibration also

554 appears to be at issue, as discussed below. Some dispersion in results may be further

555 explained by non-linearity of the microscope detection system, particularly for older

556 photomultiplier-based analog technologies, and the choice of an inappropriate

557 calibration standard. Another instrument consideration is the ability to adjust the size of

558 the measuring aperture during measurement, such as available to laboratories with

559 Hilgers Fossil systems [Hilgers Fossil is an integrated reflectance system adaptable to

560 most microscopes which uses LED illumination (as opposed to an incandescent light

561 source) and a monochrome digital camera for light detection (as opposed to a

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562 photomultiplier)]. This ILS did not control for microscope type or the technology used for

563 illumination or light detection.

564 Based on the wide distribution of participant results, we considered multiple traditional

565 and non-traditional ways to eliminate outlying mean reflectance values (Table 5),

566 including removal of: 1) results not using the ASTM D7708 reporting template, 2) results

567 non-compliant in any way with the reporting requirements of ASTM D7708, 3) results

568 with <20 measurements, 4) results with standard deviation >0.15*(VR$_o$ or BR$_o$), 5)

569 results with average signed multiple of standard deviation >1.5 and >1.0, 6) results

570 falling outside the mean ± 1.5*interquartile range (IQR), 7) results falling outside the F10

571 to F90 percentile range, and 8) results with individual signed multiple of standard

572 deviation >1.5 and >1.0. The removal of outlying values makes the assumption that

573 some values in the data pool, numerically distant from other values, are values arising

574 from chance phenomenon, or result from experimental or measurement errors.

575 Several of these approaches to elimination of outlying values can be taken without a

576 pool of data to work from, i.e., the elimination of a particular value can be applied for

577 reasons other than the value lying far outside the group mean. For example, methods 1-

578 4 from the list given in the preceding paragraph can be applied to any individual result.

579 We considered that petrographers not adhering to the ASTM D7708 reporting template

580 or not following reporting requirements of ASTM D7708 may provide imprecise data.

581 However, elimination of these results did not consistently reduce R; for example,

582 removing results where the ASTM reporting template was not used reduced R in only 7

583 of 12 cases (Table 5). On the other hand, removing results where the reporting

584 requirements were not met increased R in 10 of 12 cases. This occurred because of

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585   cases where a petrographer had returned results close to the group mean, but, for

586   example, had provided a table of results without the other reporting requirements

587   specified by ASTM D7708 section 11, e.g., descriptions of fluorescence, sample organic

588   matter types, polish quality, etc. These observations suggest that adherence to D7708

589   reporting requirements or use of the reporting template don't necessarily improve data

590   quality, or, in this case, measurement ~~precision~~reproducibility. Removal of results with

591   <20 measurements resulted in reductions to R in only 5 of 12 cases, whereas removal

592   of results with standard deviation >$0.15*(VR_o$ or BR_o) reduced R in 10 of 12 cases

593   (Table 5). ASTM D7708 requires that reports of mean reflectance backed by fewer than

594   20 measurements are to be flagged as 'qualitative'. However, the observation that R is

595   not always reduced by removal of results with <20 measurements suggests that

596   measurement ~~precision~~ reproducibility is not necessarily impacted by the number of

597   measurements. On the other hand, the consistent reduction of R observed by removal

598   of results with standard deviation >$0.15*(VR_o$ or BR_o) suggests that this screening

599   technique should be applied for all measurements of dispersed organic reflectance. The

600   rationale is that requiring standard deviation to be <$0.15*(VR_o$ or BR_o) influences the

601   petrographer to preferentially select and measure one type of organic matter as

602   representative of indigenous thermal maturity, as opposed to measuring and averaging

603   the reflectance values of all organic matter present. Therefore, we recommend that

604   reported measurements of mean dispersed organic matter reflectance meet the

605   requirement that standard deviation is <$0.15*(VR_o$ or BR_o).

606   Removal of results with average signed multiple of standard deviation (ASMSD) >1.5 is

607   the criterion used by ICCP for pass/fail status in their accreditation programs (Borrego

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608 et al., 2006; Hackley et al., 2015; Mendonca et al., 2010). In Figure 7 we show absolute

609 values of ASMSD versus average unsigned multiple of standard deviation (AUMSD) for

610 vitrinite and solid bitumen measurements. The red circle (Fig. 7A) and ellipse (Fig. 7B)

611 indicate failing petrographers based on the ICCP criterion. Microscope calibration

612 problems appear to be at issue in these cases where distances to the mean value are

613 high and SMSD consistently has the same sign. Removal of these results from the data

614 pool results in consistent improvement to R values and R values are further improved

615 by restricting the data pool to results with ASMSD<1.0. Restricting the data pool to

616 results with ASMSD<1.0 produced the lowest R value for solid bitumen in the Eagle

617 Ford sample (Table 5).

618 Another approach to outlier removal considered elimination ofis to eliminate results for

619 individual samples where the SMSD was is > 1.5 or >1.0. That is, the results from an

620 analyst were would be removed only when the reported mean reflectance value of an

621 individual sample had a SMSD > 1.5 or >1.0, as opposed to considering the ASMSD for

622 all samples from an analyst. In general, this approach produces the lowest R values

623 because it excludes mistakes, such as selection of the low reflecting solid bitumen

624 population in the Haynesville sample, while keeping results from other samples where

625 the analyst performed well in comparison to the group mean. With the exception of

626 vitrinite in the Marcellus sample, R values range 0.14 to 0.52 (Table 5) with higher

627 values occurring in higher maturity samples. Summarizing, R values were about 0.1 to

628 0.2 for the peak oil thermal maturity Bakken sample, about 0.2 to 0.3 for the wet gas

629 and condensate thermal maturity Woodford sample, and about 0.4 to 0.5 for Marcellus,

630 Haynesville, Eagle Ford and Barnett samples of dry gas maturity. These R values

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631 represent the approximate uncertainty (in absolute reflectance) that users of vitrinite and

632 solid bitumen reflectance data ~~should~~ could assign to any one individual reported mean

633 reflectance value from a similar thermal maturity mudrock sample. We note that these R

634 values are similar to R values obtained for similar maturity samples in the previous ILS

635 (Hackley et al., 2015) and an improvement over historical ILS exercises which

636 contained similar diversity of source-rock reservoir samples (Borrego, 2009; Dembicki,

637 1984).

638 Traditional means of outlier elimination ~~considered removal of~~remove results falling

639 outside the mean ± 1.5*interquartile range and outside the F10 to F90 percentile range.

640 Using the interquartile range approach resulted in R values of 0.10 to 1.32. In 3 of 12

641 cases, this approach produced the lowest R values of all approaches used for outlier

642 elimination. However, in cases where the interquartile range was high, this approach

643 found no outlying values, resulting in no improvement to R for 3 of the 12 cases (Table

644 5). Removal of results outside the F10 to F90 percentile range consistently improved R

645 and produced the lowest R values in 2 of 12 cases. In general, these traditional

646 approaches to outlier removal found R to be similar to or slightly higher than the result

647 obtained when removing individual samples where the SMSD was > 1.5 or >1.0.

648 *5.3 Future directions*

649 This ILS found that R of 0.1 to 0.5 was obtainable for vitrinite and solid bitumen

650 reflectance measurements in thermally mature source rocks typical of the North

651 American resource plays. This level of uncertainty in interlaboratory reproducibility

652 suggests that further work is necessary to standardize and improve measurement of

653 dispersed organic matter reflectance. Discussions amongst ILS participants at the 2016,

654   2017 and 2018 meetings of ICCP in Houston, Bucharest and Brisbane, respectively,

655   settled on several future directions for the ILS working group, beginning with a name

656   change to 'Identification of Thermal Maturity Relevant Organic Matter'. Previously, the

657   working group was named 'Identification of Primary Vitrinite' and it was thought by some

658   that including the word 'vitrinite' in the working group title may potentially have led some

659   ILS participants to ~~identify~~ emphasize vitrinite measurements where little ~~or no vitrinite~~ is

660   present. Towards this end, a future ILS may ask participants to assign a 'confidence of

661   identification' criterion for each measurement, allowing removal of individual

662   measurements of poorly-identified organic matter. A similar approach was used in the

663   ILS of Borrego et al. (2006), in which a 'reliability index' was established using the

664   number of measurements and coefficient of variation. In addition, a future ILS may

665   consider giving specialized instructions for organic matter identification in difficult

666   samples, as recommended by Borrego et al. (2006). For example, provision with ILS

667   samples of the basic programmed pyrolysis information contained in Table 2 would

668   have helped participants to avoid the low reflectance solid bitumen population contained

669   in the Haynesville sample. It is long known that polish quality impacts reflectance

670   measurement (e.g., Stach et al., 1982). As mentioned above, it is presumed ILS

671   participants polished to a final 0.05 µm stage per the requirements of ASTM D7708.

672   However, a future ILS may eliminate variations in polish quality by using samples

673   prepared in one laboratory, rather than allowing each participant to finish the

674   preparation.

675   Another idea put forth by ILS participants was a new ILS in which the emphasis is

676   placed on measurement of solid bitumen reflectance rather than vitrinite. Despite ~~that~~

29

677 some studies ~~have~~ de-~~emphasized~~ emphasizing solid bitumen reflectance as a poor

678 thermal maturity proxy (Kus et al., 2016; Petersen et al., 2013), other works have relied

679 on this parameter in part due to its dominance in the organic assemblage of source-rock

680 reservoirs (Borrego et al., 2018; Gonçalves et al., 2014; Juliao et al., 2015; Mastalerz et

681 al., 2018; Misch et al., 2019; Valentine et al., 2014, among others). Therefore, a future

682 ILS to examine reflectance measurement of dispersed organic matter in ~~unconventional~~

683 source-rock reservoirs should consider that solid bitumen is the targeted organic matter

684 type.

685 In preparation for another ILS focused on solid bitumen, it was considered that an

686 exercise which used images, rather than physical samples, would be appropriate to

687 educate petrographers whom are perhaps not as familiar with unconventional source-

688 rock reservoirs. Towards that end, images of organic matter from the six samples of the

689 current ILS are being collated, with regions of interest for organic matter identification

690 indicated on each image. It is considered that an initial ILS using images of source rock

691 reservoirs could better prepare participants for a future ILS with physical samples.

692 Further, the use of Hilgers Fossil reflectance systems in many laboratories opens the

693 possibility for an ILS which uses calibrated images. Hilgers Fossil software contains a

694 'Student' module intended for offline (without a microscope) measurement of calibrated

695 images. That is, one laboratory with the Hilgers Fossil system could create sets of

696 calibrated images which could be then shared to other Hilgers Fossil users for an

697 image-based ILS where the images are measured instead of physical samples. The

698 Hilgers Fossil system relies on modern solid-state technology including LED illumination

699 and CCD light detection, resulting in an ultra-stable configuration relative to older

700 analog-based systems which use tungsten halogen illumination and photomultipliers. In

701 addition, the Hilgers Fossil Student approach to an ILS would have the benefit of an

702 image record of measurement location from each participant. However, such an ILS

703 would be limited to only those laboratories with Hilgers Fossil systems or to those with

704 access to the Hilgers Fossil Student software. An additional limitation or advantage of

705 this approach would be that a single petrographer, or group thereof, would make the

706 initial identifications of organic matter which the participants would then accept as given

707 or dispute.

6. Summary and conclusions

709 An interlaboratory study (ILS) was conducted using six thermally mature mudrock

710 samples to test reproducibility of vitrinite and solid bitumen reflectance measurements in

711 North American unconventional source-rock reservoir petroleum systems. Organic-rich

712 (2.87 to 11.60 wt.% total organic carbon content) samples were used from the

713 Marcellus, Haynesville, Eagle Ford, Barnett, Bakken and Woodford shales which

714 ranged from peak oil to dry gas thermal maturity conditions (T_{max} 447 to 591°C). The

715 samples contain solid bitumen as the dominant organic matter with minor inertinite;

716 vitrinite is rare or absent according to the majority of analysts, and liptinite is absent due

717 to thermal conversion to petroleum and non-liptinite residues (e.g., solid bitumen).

718 Intraparticle organic nano-porosity occurs in solid bitumen and is visually less abundant

719 in the lower maturity samples. Forty laboratories in the Americas, Europe, Africa and

720 Australia received the samples and thirty-seven independent sets of results were

721 produced. Mean vitrinite reflectance values ranged from 0.90 to 1.83% and mean solid

722 bitumen reflectance values ranged from 0.85 to 2.04% when all results are considered

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723 (including outlying values). Multiple statistical approaches were used to eliminate

724 outlying values and obtain a precision estimate: reproducibility limit R defined as the

725 maximum difference between valid results obtained on the same test material by

726 different analysts in different laboratories using different instruments. After outlier

727 removal, R values generally were 0.1 to ≤0.5% (absolute reflectance), similar to

728 previous results for similar samples. It was observed that standard deviation values

729 $<0.15*(VR_o$ or $BR_o)$ reduce R; therefore, this specification should be required for

730 dispersed organic matter reflectance analysis. The results provide users of reflectance

731 data a realistic expectation of uncertainty which can be used to assign uncertainty to

732 any one reflectance ~~measurement~~ analysis and demonstrate that further work is

733 necessary in standardization of dispersed organic matter reflectance measurement.

Author Contributions

735 PCH conceived this research and designed the study with input from co-authors. All co-

736 authors contributed data which was analyzed and interpreted by PCH in consultation

737 with co-authors. PCH wrote the manuscript with input from co-authors.

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767 boundaries are based on Peters and Cassa (1994) and Baskin (1997). The kerogen

768 type evolution lines are based on Espitalie et al. (1985) and Hart and Steen (2015).

769 Figure 2. A. Photomicrograph of large (~30 μm) solid bitumen accumulation and

770 disseminated solid bitumen in Marcellus Shale sample 1 under oil immersion in white

771 incident light. B. Scanning electron microscopy (SEM) micrograph of Marcellus Shale

772 sample 1 showing intraparticle organic nano-porosity in solid bitumen. C.

773 Photomicrograph of solid bitumen in Haynesville Formation sample 2 under oil

774 immersion in white incident light, showing disseminated solid bitumen and solid bitumen

775 in foraminifera chambers and along dolomite mineral grain boundaries. D. SEM

776 micrograph of Haynesville Formation sample 2 showing intraparticle organic nano-

777 porosity in solid bitumen with inorganic inclusions. E. Photomicrograph of solid bitumen

778 in foraminifera chamber in Eagle Ford Formation sample 3 under oil immersion in white

779 incident light. F. Photomicrograph of inertinite and vitrinite (?) with disseminated solid

780 bitumen in Eagle Ford Formation sample 3 under oil immersion in white incident light.

781 Figure 3. A. Photomicrograph of disseminated and solid bitumen occurring at mineral

782 grain boundaries in Barnett Shale sample 4 under oil immersion in white incident light.

783 B. Scanning electron microscopy (SEM) micrograph of Barnett Shale sample 4 showing

784 intraparticle organic nano-porosity in solid bitumen. C. Photomicrograph of

785 disseminated and larger accumulations of solid bitumen in Bakken Shale sample 5

786 under oil immersion in white incident light. D. SEM micrograph of Bakken Shale sample

787 5 showing interparticle nano-porosity at the contact between solid bitumen and the

788 inorganic matrix. E. Photomicrograph of disseminated solid bitumen in Woodford

789 Formation Shale sample 6 under oil immersion in white incident light. F. SEM

34

790 micrograph of Woodford ~~Formation~~ Shale sample 6 showing intraparticle organic nano-

791 porosity in solid bitumen.

792 Figure 4. Histograms of all data for mean vitrinite and solid bitumen reflectance for the

793 six ILS samples. Note that dimensions of histogram axes are not the same in each,

794 dependent on number of analyses and range of measurement values. Black bar shows

795 mean value of all analysts with no outliers excluded, n = number of results, gsd = group

796 standard deviation, VR_o = vitrinite reflectance, BR_o = solid bitumen reflectance.

797 Figure 5. Group mean solid bitumen reflectance vs group mean vitrinite reflectance for

798 the six ILS samples. Error bars show group standard deviation.

799 Figure 6. Participants years of experience.

800 Figure 7. Absolute values of average signed multiple of standard deviation (ASMSD) vs

801 average unsigned multiple of standard deviation (AUMSD) values for (A) vitrinite and

802 (B) solid bitumen, showing participants with 30+ years of experience by black diamonds.

803 The red circle (A) and ellipse (B) indicate failing petrographers based on the ICCP

804 criterion of AUMSD>1.5.

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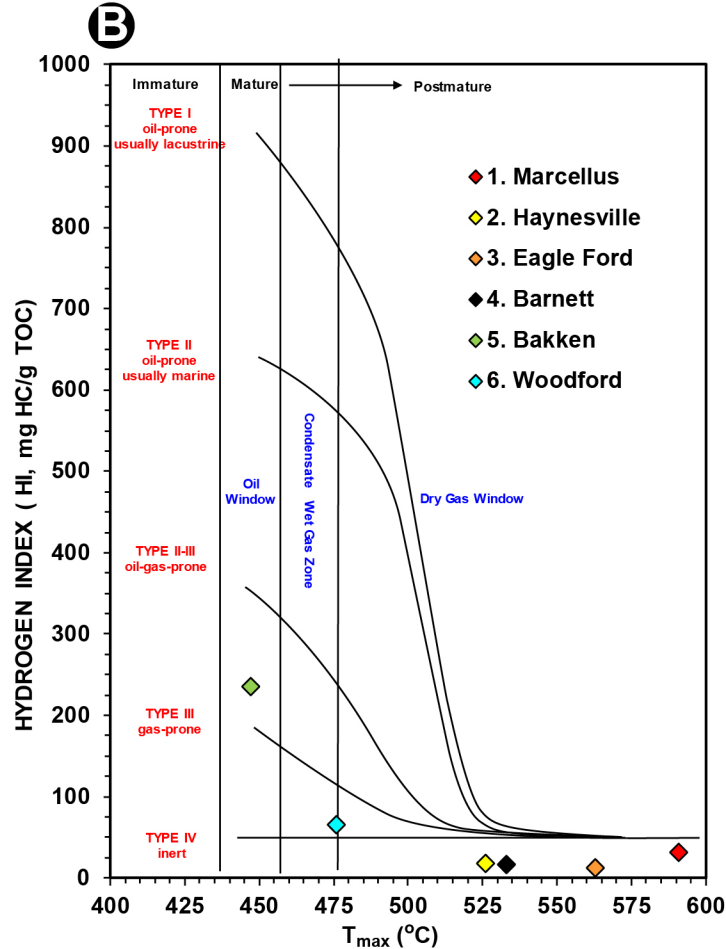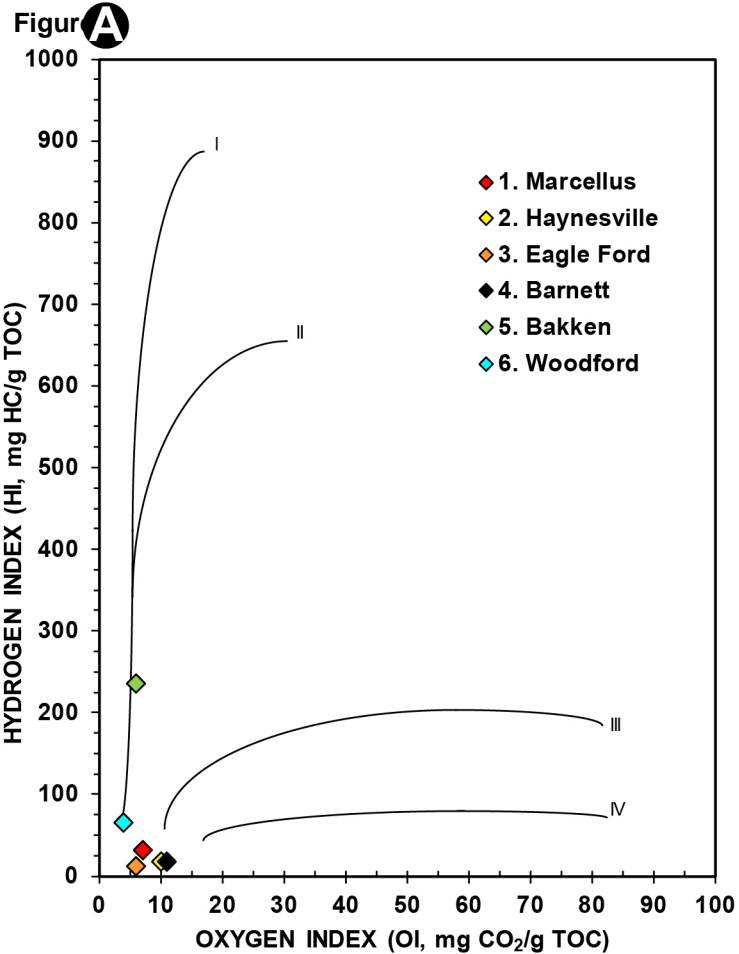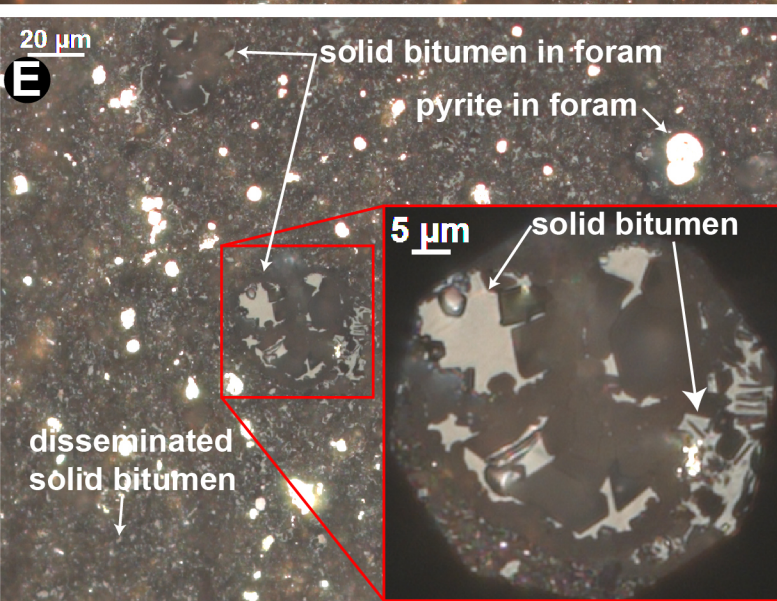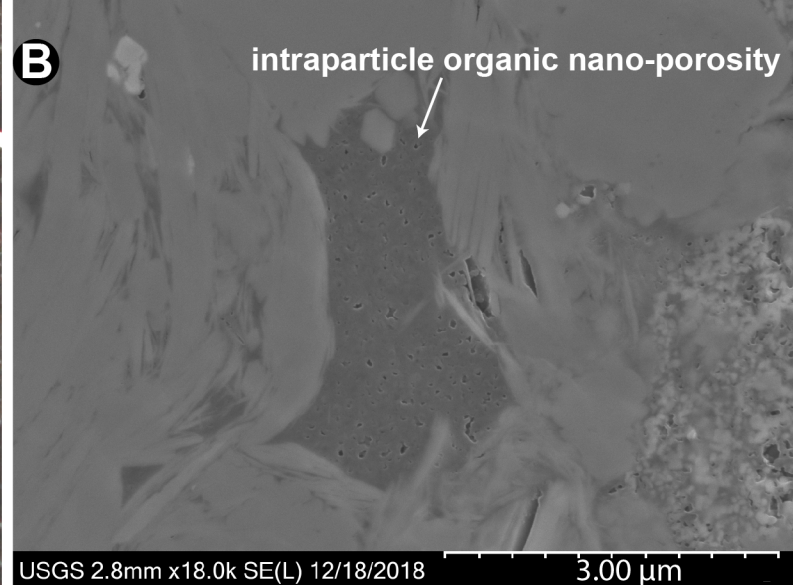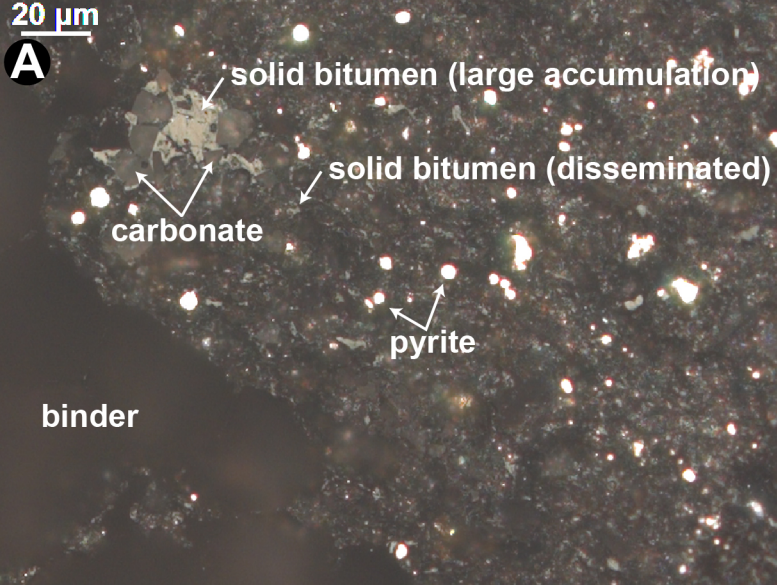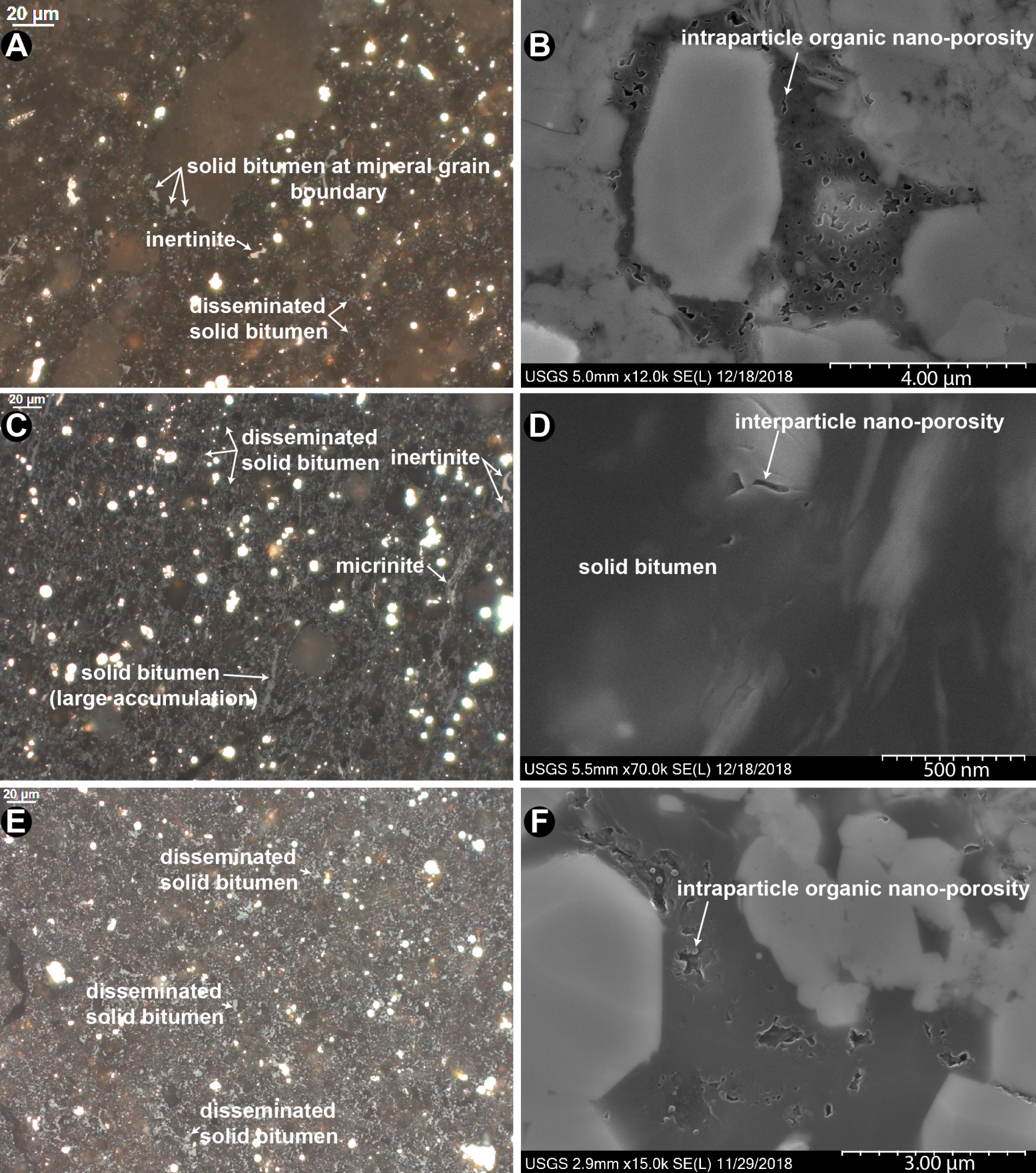
Figure 1

Figure 2

Figure 3
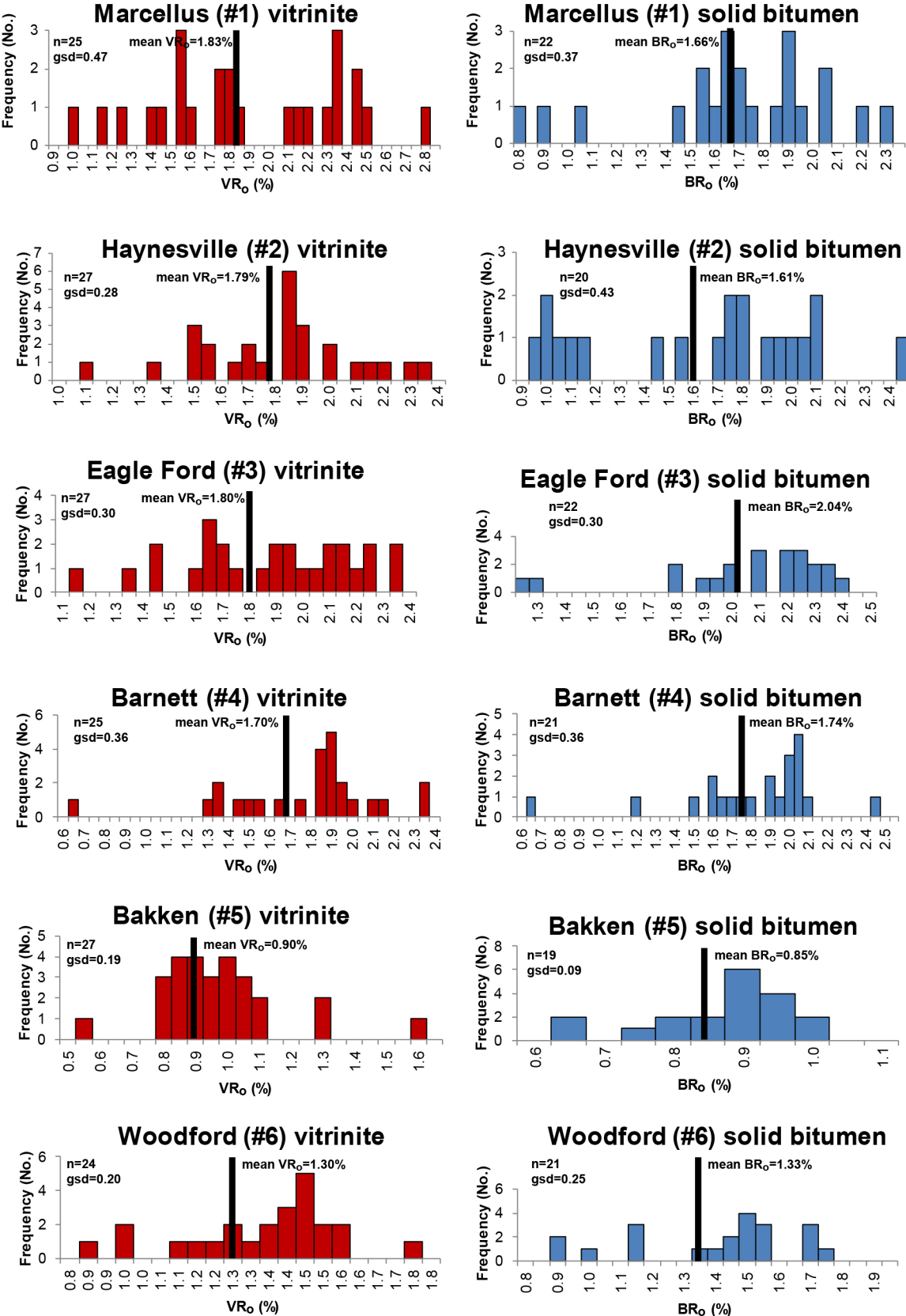
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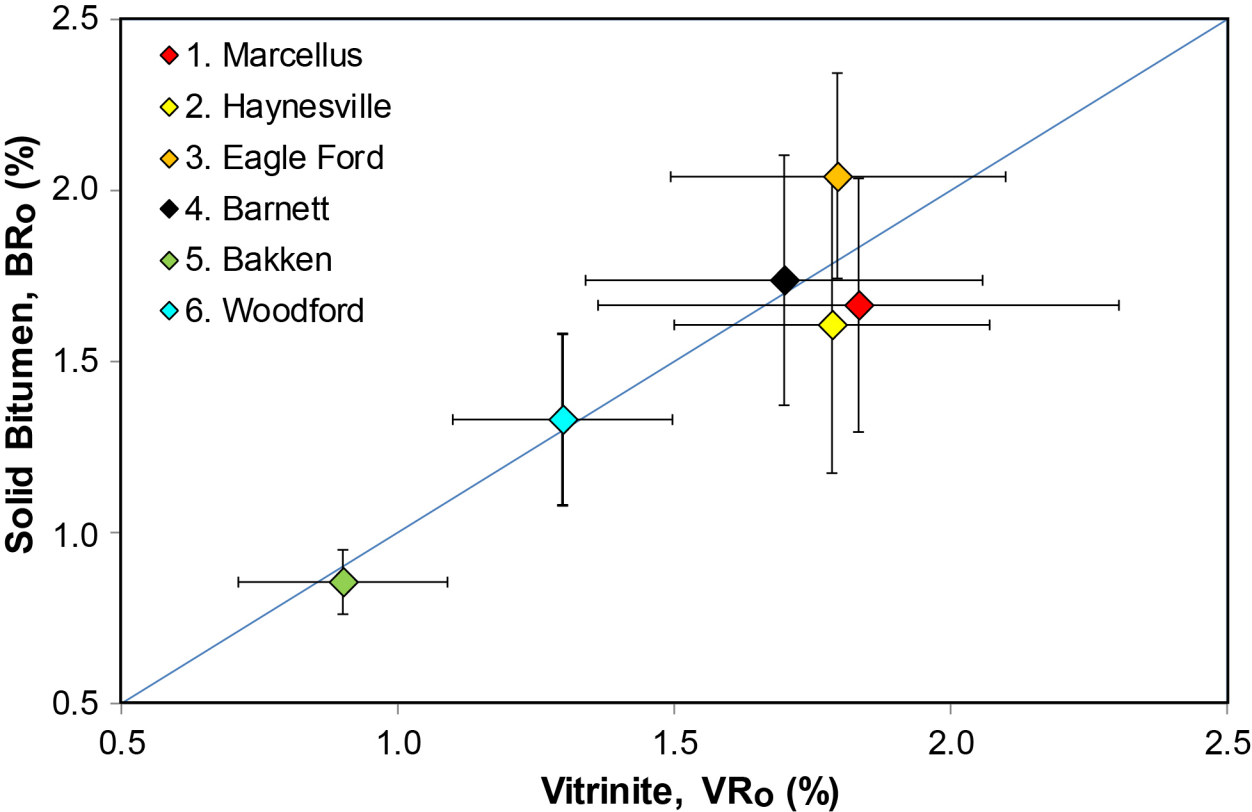
Figure 5

YEARS EXPERIENCE
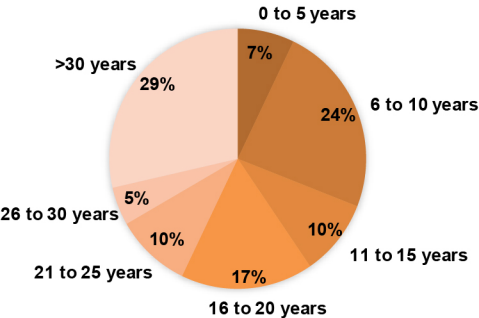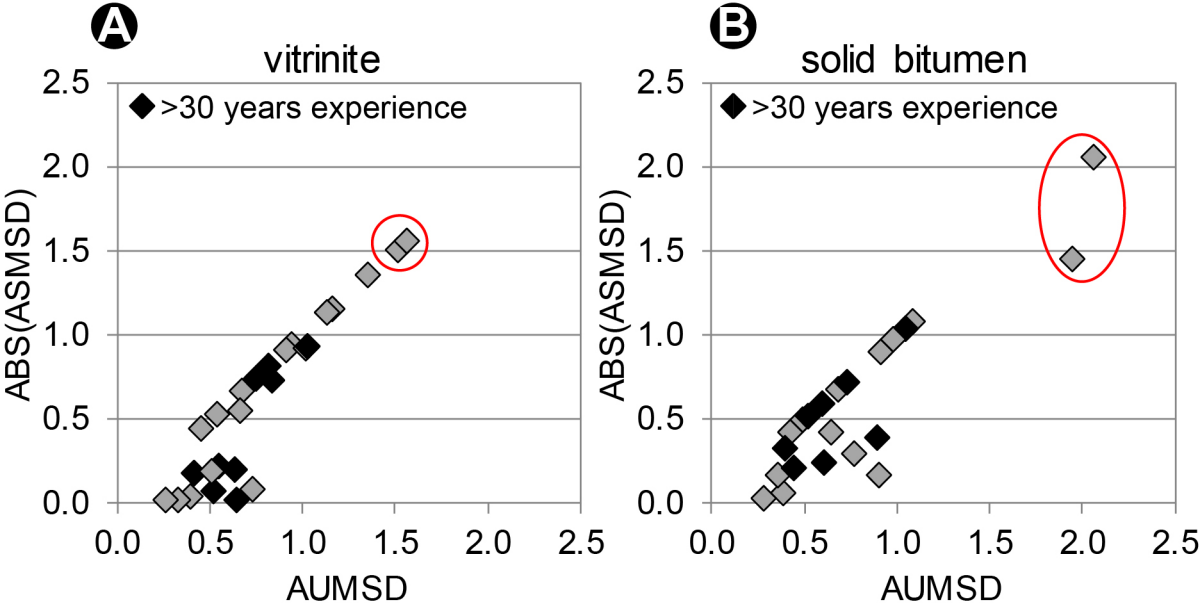
Figure 6

Figure 7

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.

Table 2. Summary organic carbon and programmed pyrolysis data.

Code	Formation	TOC	S1	S2	S3	T_{max}	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; T_{max} in °C; HI = hydrogen Index (S2*100/TOC); OI = Oxygen Index (S3*100/TOC); PI = Production Index (S1/(S1+S2)). 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 T_{max} values include extracted samples and exclude unreasonable low values; all other reported average parameters exclude values from extracted samples.

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.%.

Table 4. Reflectance data from ILS participants

Petrographer ID		Marcellus Sample 1		Haynesville Sample 2		Eagle Ford Sample 3		Barnett Sample 4		Bakken Sample 5		Woodford Sample 6	
		Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.	Vit.	S.B.
1	R_o		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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o	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	R_o		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	R_o		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	R_o		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	R_o	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	R_o	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	R_o	2.30		2.33		2.16		2.05		1.02		1.54	

	s.d.	0.16		0.08		0.11		0.11		0.06		0.08	
	no.	59		34		22		26		33		28	
21	R_o	1.10		1.08		1.39		1.30		0.71		0.93	
	s.d.	0.38		0.37		0.40		0.34		0.18		0.29	
	no.	26		21		41		25		31		32	
22	R_o		1.57	1.50	1.72	1.70	1.95	1.66	1.89	1.02	0.92		1.39
	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
23	R_o	2.38	1.73	1.82	1.54	1.58	1.88		1.69	0.74		1.37	1.08
	s.d.	0.16	0.30	0.12	0.16	0.16	0.13		0.17	0.06		0.09	0.08
	no.	38	20	30	19	9	27		30	31		30	30
24	R_o	2.41	2.01	2.18	1.89	2.14	2.10	1.83	2.01	0.92	0.75	1.43	1.34
	s.d.	0.11	0.41	0.15	0.08	0.11	0.12	0.09	0.11	0.04	0.09	0.09	0.08
	no.	30	32	32	30	30	22	25	20	32	31	32	20
25	R_o	2.73		2.12		2.16		2.26		0.85		1.31	
	s.d.	0.09		0.14		0.04		0.06		0.03		0.08	
	no.	9		8		2		7		5		4	
26	R_o	2.04		2.26		2.28		2.28		0.96		1.53	
	s.d.	0.45		0.18		0.20		0.37		0.05		0.10	
	no.	70		63		25		50		100		100	
27	R_o	1.70	1.66	2.09	2.40	2.29	2.19	1.92	1.98	0.97	0.93	1.50	1.48
	s.d.	0.59	0.29	0.26	0.29	0.23	0.19	0.60	0.30	0.09	0.15	0.09	0.23
	no.	3	19	10	9	3	24	5	11	20	27	5	12
28	R_o	1.69		1.87		1.77		1.86		0.77		1.33	
	s.d.	0.34		0.15		0.10		0.20		0.06		0.05	
	no.	44		20		20		35		40		40	
29	R_o	1.73		1.67		1.40		1.82		0.78		1.08	
	s.d.	0.17		0.24		0.19		0.26		0.07		0.10	
	no.	20		20		23		20		32		31	
30	R_o		1.55		1.09		2.36		1.92		0.96		1.63
	s.d.		0.09		0.12		0.08		0.12		0.06		0.09
	no.		32		21		30		30		30		30
31	R_o	1.77		1.67		1.30		1.29		0.80		1.17	
	s.d.	0.17		0.21		0.18		0.14		0.06		0.17	
	no.	24		33		28		21		23		24	
32	R_o		1.42		0.94		2.33		1.82		0.94		1.61
	s.d.		0.13		0.09		0.06		0.09		0.05		0.05
	no.		18		30		29		30		33		31
33	R_o		1.64		1.92		1.99		1.52		0.76		1.29
	s.d.		0.11		0.26		0.15		0.19		0.14		0.13
	no.		31		54		50		40		66		33
34	R_o		1.55		1.13		2.34		1.74		0.93		1.68
	s.d.		0.19		0.28		0.10		0.15		0.06		0.14
	no.		35		21		25		31		31		34
35	R_o		1.69		1.68		1.97		1.57		0.83		1.46
	s.d.		0.16		0.15		0.23		0.18		0.09		0.14
	no.		58		33		80		70		83		98
36	R_o		1.86	1.73	1.76	1.80	2.09	1.89	2.38	0.93	0.79	1.22	1.44
	s.d.		0.51	0.08	0.616	0.07	0.05	0.09	0.51	0.05	0.19	0.08	0.31
	no.		38	20	28	15	25	18	17	21	54	22	10
37	R_o		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; R_o, reflectance, s.d., standard deviation, no., number of measurements.

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

Method of removing outlying values	Marcellus Sample 1		Haynesville Sample 2		Eagle Ford Sample 3		Barnett Sample 4		Bakken Sample 5		Woodford 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*(VR$_o$ or 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 ouside of 10-90 percentile range; ISMSD, individual signed multiple of standard deviation.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: