



Assessing the thermal maturity of black shales using vitrinite reflectance: Insights from Devonian black shales in the eastern United States



Bei Liu^a, Juan Teng^{b,c,*}, Maria Mastalerz^c, Juergen Schieber^a

^a Department of Earth and Atmospheric Sciences, Indiana University, Bloomington, IN 47405, USA

^b College of Energy, Chengdu University of Technology, Chengdu, Sichuan 610059, China

^c Indiana Geological and Water Survey, Indiana University, Bloomington, IN 47405-2208, USA

ARTICLE INFO

Keywords:

Vitrinite reflectance
Thermal maturity
Black shale
Dispersed organic matter
Coal
Vitrinite-like particles
Zooclast fragments

ABSTRACT

Thermal maturity of source rocks indicated by vitrinite reflectance (R_o) is an important and reliable parameter to determine the petroleum potential of sedimentary basins. Originally, R_o was used to characterize the degree of coalification of coals and thus works well for coal seams, but it has limitations when used to determine the thermal maturity of black shale successions. A suite of six coal-shale pairs from the Upper Devonian black shale formations in the eastern United States (New Albany Shale, Ohio Shale, Dunkirk Shale, and Rhinestreet Shale) was selected to study the applicability of R_o in assessing the thermal maturity of black shale successions. The results show that vitrinite in the studied coal samples is dominated by collotelinite, whereas vitrinite in black shales occurs as small dispersed particles ($\sim 5 \mu\text{m}$) in the mineral matrix. When comparing the size and morphology of dispersed vitrinite particles in shales and collotelinite fragments in coals, vitrinite in shales and adjacent coals should have the same origin. The measured mean random R_o of vitrinite in coals ranges from 0.51–0.68%, and is 0.04–0.11% (average 0.07%) lower than that of dispersed vitrinite particles in enclosing shales. This observation contrasts with previously reported R_o suppression in liptinite-rich black shales. A high standard deviation of R_o measurements indicates a highly heterogeneous nature of vitrinite in black shales.

Three mechanisms can be envisioned to contribute to the higher R_o of dispersed vitrinite particles in black shales relative to enclosed coals. First, small vitrinite particles may become more oxidized because small particles are more frequently suspended during transport to the site of deposition and reworking of bottom sediments after deposition than large pieces of driftwood that will turn into enclosed coal lenses during burial diagenesis. Second, misidentification of zooclast (e.g., chitinozoan) fragments as vitrinite due to loss of diagnostic morphology. Third, various macerals in the vitrinite group (e.g., corpogelinite and collotelinite) may have had different original reflectance values. Based on the petrographic characteristics of vitrinite and vitrinite-like particles, caution should be applied when using the R_o values of dispersed vitrinite and vitrinite-like particles in black shales as indicators of thermal maturity.

1. Introduction

Vitrinite reflectance (R_o) is the most widely used proxy to indicate the thermal maturity of sedimentary organic matter (OM) in post-Silurian sediments (Buchardt and Lewan, 1990; Mukhopadhyay, 1994; Taylor et al., 1998). The reflectance of vitrinite increases with increasing thermal maturity (i.e., temperature) due to increasing degree of aromatization and condensation of the molecular structure that results in elevated ordered stacking of aromatic units (McCartney and Teichmüller, 1972). R_o has been successfully applied to reconstruct the thermal history of sedimentary basins because of this irreversible chemical reactions (e.g., Hood et al., 1975; Tissot and Welte, 1984; Tissot

et al., 1987; Mukhopadhyay, 1994), and is one of the most important parameters in source rock evaluation and shale oil/gas exploration (Tissot and Welte, 1984; Wang and Gale, 2009; Jarvie, 2012a, 2012b). Because of the scarcity and heterogeneity of vitrinite in black shales and pre-Devonian rocks, however, R_o at times fails to serve as an effective thermal maturity indicator. Therefore, documenting R_o and its equivalents of black shales accurately and precisely is of great significance for the evaluation of both conventional and unconventional petroleum systems.

Vitrinite comprises multiple macerals that are derived from the gelification of ligno-cellulosic tissues of terrestrial higher plants (Stach et al., 1982; ICCP, 1998; Taylor et al., 1998). The reflectance of one of

* Corresponding author at: College of Energy, Chengdu University of Technology, Chengdu, Sichuan 610059, China.

E-mail address: Tengjuancugb@outlook.com (J. Teng).

<https://doi.org/10.1016/j.coal.2020.103426>

Received 19 December 2019; Received in revised form 6 February 2020; Accepted 8 February 2020

Available online 08 February 2020

0166-5162/ © 2020 Elsevier B.V. All rights reserved.

these macerals (collotelinite) is generally measured and documented as the R_o of samples (ICCP, 1998). In practice, any terrestrial OM in black shales that has a reflectance higher than the liptinite group and lower than the inertinite group is likely vitrinite, and its reflectance can be measured. When vitrinite particles are very small, it is difficult to distinguish vitrinite from vitrinite-like particles (Buchardt and Lewan, 1990; Petersen et al., 2013) and solid bitumen (Hackley et al., 2015; Mählmann and Le Bayon, 2016; Wei et al., 2016; Hackley and Lewan, 2018).

Vitrinite-like particles are OM particles that resemble vitrinite in carbonaceous rocks, and their reflectance has been used to assess thermal maturity (Buchardt and Lewan, 1990; Schleicher et al., 1998; Xiao et al., 2000; Petersen et al., 2013; Reyes et al., 2018), particularly in Lower Paleozoic rocks (Buchardt and Lewan, 1990; Schleicher et al., 1998; Xiao et al., 2000; Petersen et al., 2013; Reyes et al., 2018) that lack organic debris from land-derived vascular plants (Kenrick and Crane, 1997). Petersen et al. (2013) measured the reflectance of zooclast and vitrinite-like particles in Middle Cambrian to Upper Silurian shales from central and southern Sweden and the Danish island of Bornholm (Baltic Sea), and found that the reflectance distribution of graptolite and vitrinite-like particles is almost identical. Based on this observation, they interpreted the vitrinite-like particles in these Lower Paleozoic shales to be graptolite fragments that lacked diagnostic morphological features.

One of the problems that is commonly mentioned in connection with R_o values is the so-called R_o suppression, a common phenomenon in black shales that refers to situations where the R_o is lower than the value predicted from the R_o -depth profile (Price and Baker, 1985; Wenger and Baker, 1987; Raymond and Murchison, 1991; Goodarzi et al., 1993; Lo, 1993). Multiple mechanisms have been proposed to explain R_o suppression in black shales (McTavish, 1978, 1998; Hutton and Cook, 1980; Price and Baker, 1985; Wenger and Baker, 1987; Raymond and Murchison, 1991; Hao and Chen, 1992; Goodarzi et al., 1993; Lewan, 1993; Hao et al., 1995, 2007; Carr, 2000a, 2000b; Ujjié et al., 2004; Barker et al., 2007; Hackley and Lewan, 2018; Peters et al., 2018), such as (1) a free radical reaction mechanism by which free radicals generated from bitumen and associated volatile products contribute to termination reactions and slow the aromatization process of co-occurring vitrinite (Peters et al., 2018); (2) misidentification of solid bitumen for vitrinite (Hackley and Lewan, 2018); (3) impregnation of vitrinite with liptinite macerals, bitumen, or aliphatic compounds (Jones and Edison, 1978; Hutton and Cook, 1980; Kalkreuth, 1982; Raymond and Murchison, 1991; Petersen and Vosgerau, 1999; Carr, 2000a); (4) diagenetic enrichment of hydrogen in vitrinite (Price and Baker, 1985; Wenger and Baker, 1987; Hao and Chen, 1992; Carr, 2000a); and (5) overpressured conditions that prevent forward reactions of vitrinite maturation (McTavish, 1978, 1998; Hao et al., 1995, 2007; Carr, 2000a).

In this study, we compared the R_o of dispersed vitrinite particles in black shales with that of vitrinite from associated coals (compressed tree trunks or branches) for a suite of six coal-shale pairs from Devonian black shales in the eastern United States. Because the coal is contained within shale samples, coal and shale had the same thermal history and theoretically the R_o values of coal and vitrinite in enclosing shales should be the same. We observed distinct differences in reflectance between vitrinite in coals and enclosing shales and discussed possible reasons for these differences and implications for thermal maturity assessments of black shale successions.

2. Samples and methods

Six pairs of black shales and enclosed coal lenses were collected from the eastern United States (Fig. 1). All the black shales are from Upper Devonian formations, including the New Albany Shale of the Illinois Basin, and the Ohio Shale, Dunkirk Shale, and Rhinestreet Shale of the Appalachian Basin. The Illinois Basin and the Appalachian Basin

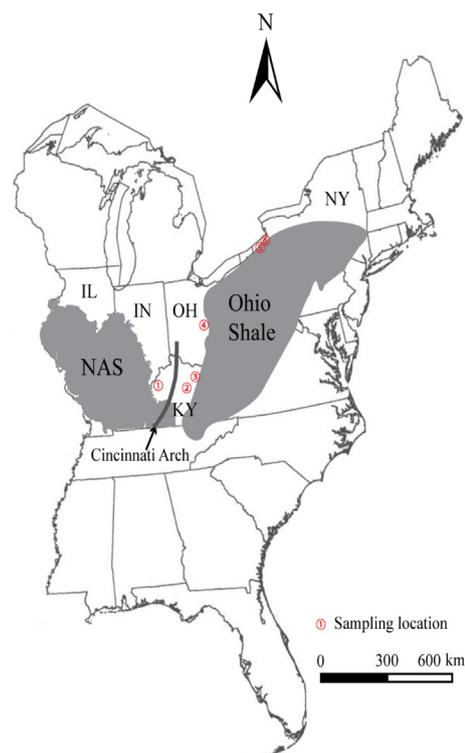


Fig. 1. Map showing the locations of sampling sites and the extent of the New Albany Shale (Illinois Basin) and Ohio Shale (Appalachian Basin). Modified from McFarlan (1943), Curtis (2002), and Mastalerz et al. (2013). NAS = New Albany Shale. ① = New Albany Shale from Shepherdsville, KY; ② = Ohio Shale from Irvine, KY; ③ = Ohio Shale from Morehead, KY; ④ = Ohio Shale from Columbus, OH; ⑤ = Dunkirk Shale from Dunkirk, NY; ⑥ = Rhinestreet Shale from Derby, NY.

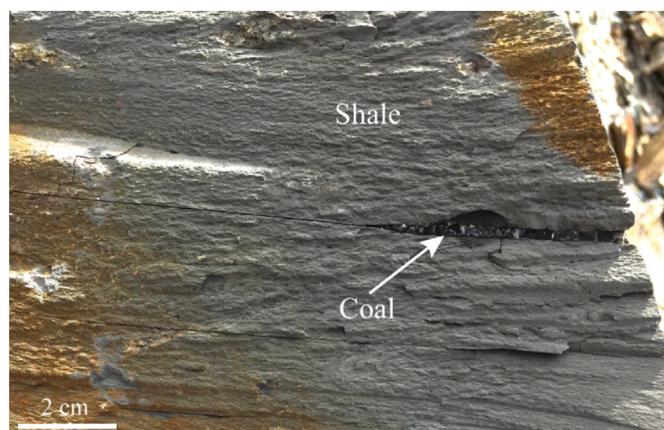


Fig. 2. Photo of a thin coal layer embedded within black shales. New Albany Shale from Shepherdsville, Kentucky, USA.

are separated by the Cincinnati Arch (Buschbach and Kolata, 1990) (Fig. 1). The coal lenses embedded within black shales are about 1–2 mm thick and 10–20 cm long in outcrop (Fig. 2). Coal samples were hand-picked from the rock surface, and the directly associated shales were collected at the same time. Coal and shale samples were sealed immediately with Ziplock bags to prevent contamination.

Coal and shale samples were crushed to rock chips of < 1 mm and made into whole-rock petrographic pellets following standard coal petrography procedures (ICCP, 1963). The mean random R_o values of coal and shale samples were measured using a Zeiss Photoscope III microscope with more than 100 measurements per sample on coal

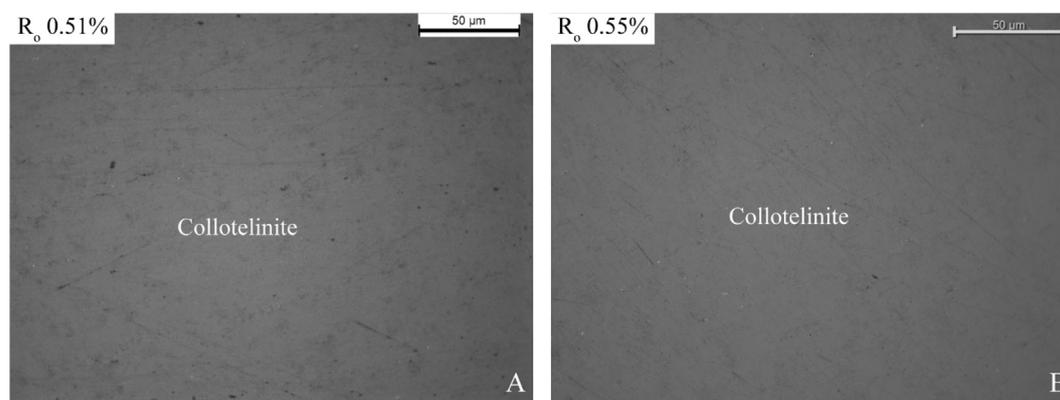


Fig. 3. Photomicrographs of collotelinite in coal samples in reflected white light and oil immersion. (A) Coal sample in New Albany Shale from Shepherdsville, KY. (B) Coal sample in the Ohio Shale from Morehead, KY.

samples and more than 25 measurements per sample on shale samples. A reflected-light microscope (Leica DM2500 P) was used to document the organic petrographic characteristics of macerals in coals and shales in reflected white light and oil immersion as well as under blue light.

3. Results

Organic matter in the coal portion of these samples is dominated by collotelinite of the vitrinite maceral group (Fig. 3). Cellular structures can still be observed in places (Fig. 4). No inertinite or liptinite group macerals were observed.

Primary OM in black shales that enclosed the coal lenses consists of amorphous organic matter, alginite, liptodetrinite, vitrinite, and inertinite (Fig. 5), common primary macerals in Devonian black shales of the eastern United States (Robl et al., 1992; Mastalerz et al., 2012b, 2013; Hackley and Cardott, 2016; Hackley et al., 2017, 2018; Liu et al., 2017, 2019a, 2019b, 2020; Teng et al., 2020). Vitrinite occurs as small dispersed particles (~5 µm) in the mineral matrix, and is similar to the broken vitrinite fragments in coals in size and morphology (Fig. 6), suggesting that the dispersed vitrinite particles in the black shale matrix have the same source as the woody materials of the enclosed coal lenses. Alginite derived from *Tasmanites* cysts in the New Albany Shale and Ohio Shale samples shows greenish-yellow fluorescence under blue light irradiation and shows yellowish fluorescence in the Dunkirk and Rhinestreet Shale samples (Fig. 7). Solid bitumen is very rare in the New Albany Shale and Ohio Shale samples, but common in the Dunkirk and Rhinestreet Shale samples (Fig. 8) because the latter two samples have higher thermal maturities and some amorphous organic matter has been converted into hydrocarbons and solid bitumen (Hackley et al., 2018; Liu et al., 2019a).

The measured mean random R_o of vitrinite in coals ranges from 0.51–0.68%, whereas the R_o of vitrinite in enclosing shales ranges from 0.55–0.73% (Fig. 9; Table 1). Thus the R_o of vitrinite in coals is 0.04–0.11% (average 0.07%) lower than the R_o of dispersed vitrinite particles in enclosing shales. The standard deviation of R_o measurements of coals varies from 0.01–0.02, whereas the standard deviation of R_o measurements of dispersed vitrinite particles in shales ranges from 0.06–0.07, indicating that vitrinite in coals is more homogeneous than that in surrounding shales.

4. Discussion

Statistically, more than 70% of the R_o values of small dispersed vitrinite particles in shales are higher than the mean R_o of enclosed coals (Fig. 10). This can be explained by the oxidation of small dispersed vitrinite precursor particles during transport to the site of deposition and reworking of bottom sediments after deposition, because small particles can easily be suspended, compared to large driftwood pieces that will turn into enclosed coal lenses embedded within black shales during burial diagenesis. Some vitrinite particles were oxidized to such a degree that they have much higher reflectance than others, making them almost indistinguishable from semifusinite (Fig. 11). Previous studies have reported that oxidation of vitrinite can cause higher R_o (Goodarzi and Murchison, 1973; Castaño and Sparks, 1974; Buiskool Toxopeus, 1983). Wenger and Baker (1987) reported that gray shales deposited in oxic environments tend to have hydrogen-poor vitrinite that shows a higher R_o than that of nearby coals. Similarly, Hao and Chen (1992) reported that vitrinite formed in oxic environments has a lower hydrogen and a higher R_o than that formed in anoxic environments. Because dispersed vitrinite particles in black shales that are

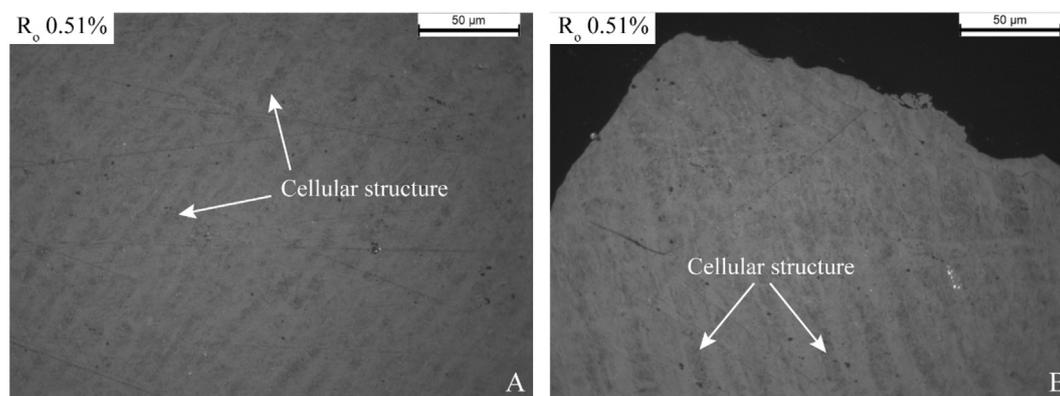


Fig. 4. Photomicrographs of vitrinite with preserved cellular structures in coal samples in reflected white light and oil immersion. Coal sample in the New Albany Shale from Shepherdsville, KY.

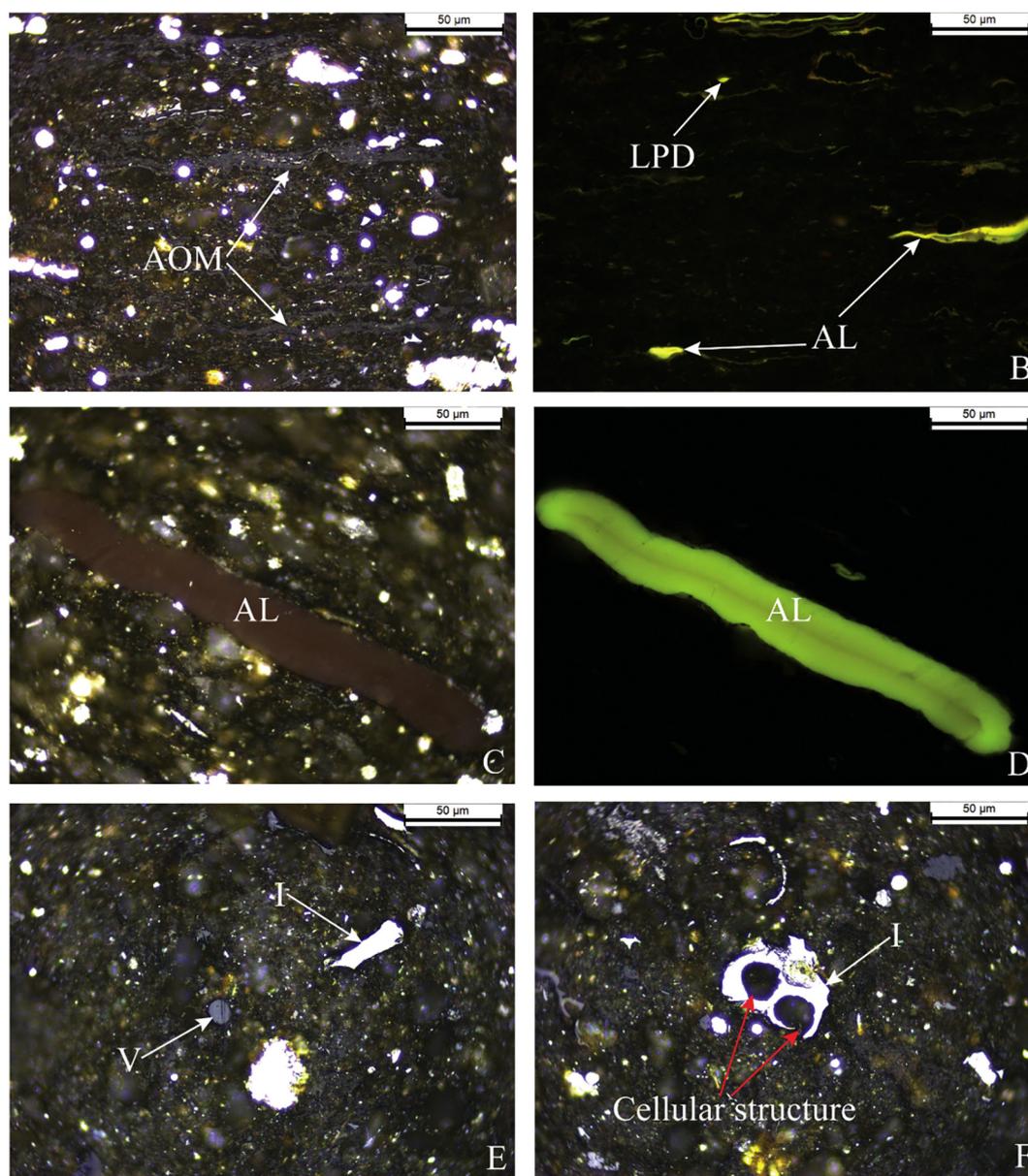


Fig. 5. Photomicrographs of primary macerals in black shales in reflected white light and oil immersion (A, C, E, F) and in fluorescence mode (B, D). Panels B and D show the same field of view as panels A and C in fluorescence mode, respectively. Note that the cellular pores in inertinite in panel F are filled with mineral matter, probably diagenetic silica. New Albany Shale sample from Shepherdsville, KY. AOM = amorphous organic matter; AL = alginite; LPD = liptodetrinite; V = vitrinite; I = inertinite.

used to measure reflectance are typically very small (Mastalerz et al., 2018), caution should be applied when measuring the R_o of small dispersed vitrinite particles in shales. Researchers should try to include as many measurements as possible (25 at least) to get an average value, as recommended by ASTM (2014) and Barker and Pawlewicz (1993).

The reflectance of zooclasts such as graptolites (Bustin et al., 1989; Goodarzi and Norford, 1985, 1987, 1989; Goodarzi et al., 1992; Petersen et al., 2013; Luo et al., 2017, 2018, 2020; Wang et al., 2019) and chitinozoans (Goodarzi, 1985; Bertrand and Héroux, 1987; Bertrand, 1990; Tricker et al., 1992; Reyes et al., 2018) also increases with progressive heating and has been successfully used to determine the thermal maturity of vitrinite-poor source rocks. Graptolite fragments without any recognizable morphology can resemble vitrinite particles (Petersen et al., 2013; Cardott and Curtis, 2018) and could be mistaken for vitrinite. For example, the vitrinite-like particles (interpreted as graptolite fragments) in the Middle Cambrian to Lower Ordovician Alum Shale (Petersen et al., 2013; their Fig. 8C1) and

nongranular graptolite fragments in the Upper Ordovician Wufeng Formation and the Lower Silurian Longmaxi Formation shales (Luo et al., 2018; their Fig. 5) are almost identical (in morphology) to some of the observed dispersed vitrinite particles in black shales in this study (Figs. 5E, 6B). However, graptolites are very rare in late Devonian and at best could make a very minimal contribution to the population of vitrinite-like particles in the studied shale samples. In contrast, chitinozoans are common, although not abundant, in the studied Upper Devonian black shales (Fig. 12). Because the reflectance of graptolites and chitinozoans is generally higher than that of vitrinite subjected to the same thermal history (Tricker et al., 1992; Petersen et al., 2013), misidentification of fragments of chitinozoan derived zooclasts as dispersed vitrinite particles could possibly cause the higher R_o of shales relative to enclosed coals (Fig. 9; Table 1).

Vitrinite in the studied shale samples appears highly heterogeneous, as suggested by the high standard deviation of R_o (Table 1). Some vitrinite particles have sharp edges, suggesting that they could be

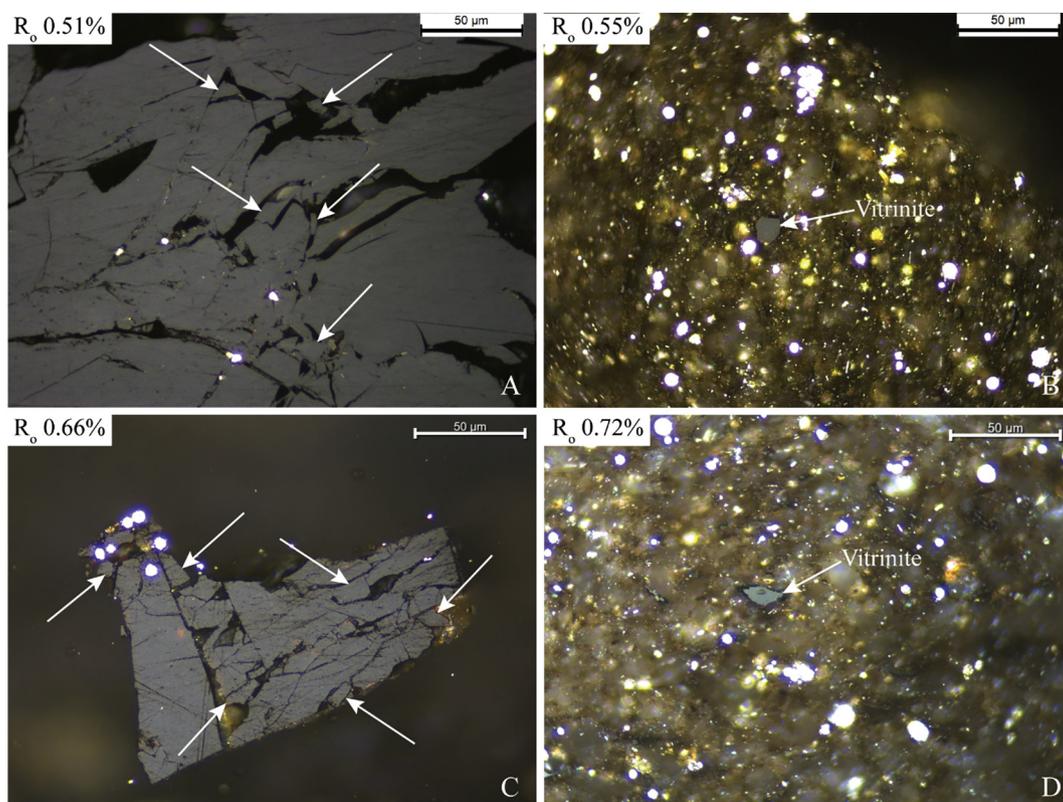


Fig. 6. Photomicrographs of vitrinite fragments (white arrows) in coals (A, C) and dispersed vitrinite particles in shales (B, D) that enclosed the coal samples in reflected white light and oil immersion. (A – B) Coal and shale samples from the New Albany Shale from Shepherdsville, KY. (C – D) Coal and shale samples from the Dunkirk Shale from Dunkirk, NY.

fragments of collotelinite, whereas others are rounded and could possibly be corpogelinite (Fig. 13). Corpogelinite commonly occurs as discrete bodies that fill cellular pores of plant tissues (ICCP, 1998), and looks very similar to the rounded vitrinite particles observed in shales in this study (Fig. 13A). Corpogelinite typically has a higher and wider range of R_o measurements than co-occurring collotelinite (ICCP, 1998), and therefore averaging R_o measurements from collotelinite and corpogelinite particles in black shales may be another reason why the R_o values of shales are higher than those of enclosed coals.

Previous studies reported that the R_o of black shales is often lower than that of interbedded coals (Wenger and Baker, 1987; Raymond and Murchison, 1991; Goodarzi et al., 1993), which contrasts with the findings from this study. Impregnation of bitumen and aliphatic compounds within vitrinite was previously proposed to explain R_o suppression in black shales, because liptinite macerals in black shales are

often oil-prone. For example, Hutton and Cook (1980) reported an inverse relationship between mean maximum R_o and alginite content in the Joadja oil shale and interbedded coals. However, there is some evidence against the influence of bitumen saturation on R_o suppression. Specifically, Barker et al. (2007) compared the R_o values of black shale (including the New Albany Shale) and coal samples before and after organic solvent extraction and found that the R_o values were almost identical. Indeed, it is difficult for large bitumen molecules to enter vitrinite particles (surface coating is possible) in black shales that do not show detectable pores under SEM (Liu et al., 2017). However, we do not exclude the possibility that light hydrocarbons impregnate vitrinite particles initially and solidify later through thermal or microbial degradation, because vitrinite hosts large amounts of micropores (< 2 nm) and small mesopores (2–50 nm) (Rouquerol et al., 1994) detected by low-pressure CO_2 and N_2 adsorption analysis (Mastalerz

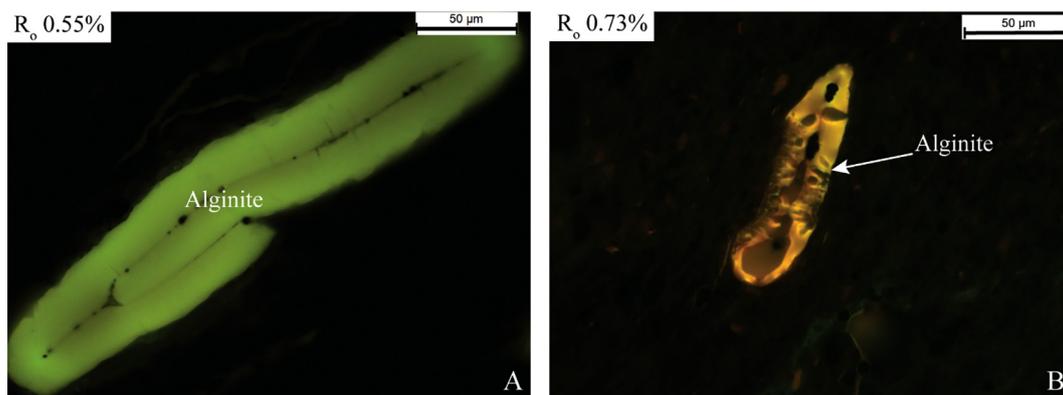


Fig. 7. Photomicrographs of alginite derived from *Tasmanites* cysts in the New Albany Shale (A) and the Rhinestreet Shale (B) in fluorescence mode.

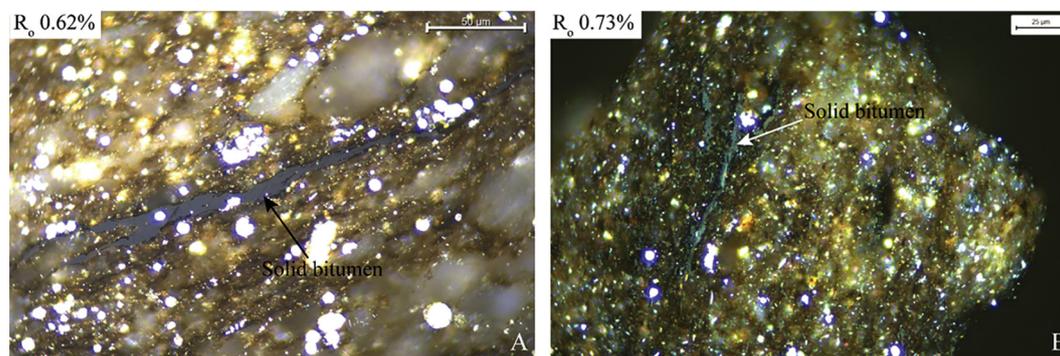


Fig. 8. Photomicrographs of solid bitumen in the Ohio Shale from Columbus (A) and the Rhinestreet Shale (B) in reflected white light and oil immersion.

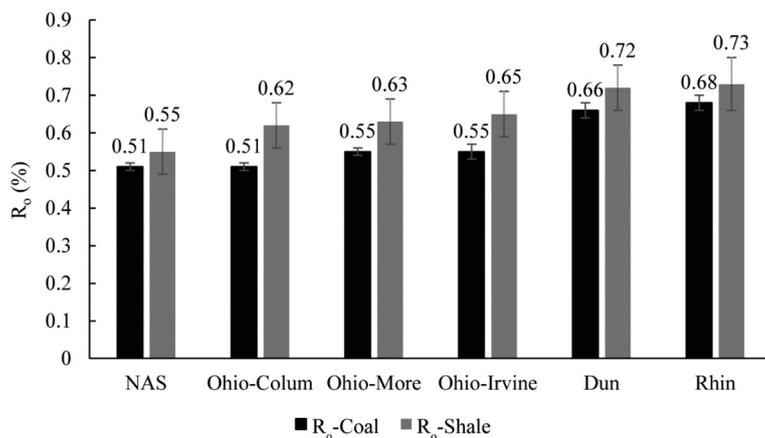


Fig. 9. Histogram of the mean random R_o of shales and enclosed coals. NAS = New Albany Shale from Shepherdsville, KY; Ohio-Colum = Ohio Shale from Columbus, OH; Ohio-More = Ohio Shale from Morehead, KY; Ohio-Irvine = Ohio Shale from Irvine, KY; Dun = Dunkirk Shale from Dunkirk, NY; Rhin = Rhinestreet Shale from Derby, NY (Table 1). Error bars show standard deviation.

Table 1

Measured vitrinite reflectance (R_o), number of measurements, standard deviation, and alginite fluorescence of the studied coal and shale samples.

| Sample | Location | Formation | Lithology | R_o | N | SD | Alginite fluorescence |
|--------|--------------------|-------------------|-----------|-------|-----|------|-------------------------|
| NAS-1 | Shepherdsville, KY | New Albany Shale | Coal | 0.51 | 203 | 0.01 | |
| NAS-2 | | | Shale | 0.55 | 94 | 0.06 | Greenish yellow |
| Ohio-1 | Columbus, OH | Ohio Shale | Coal | 0.51 | 122 | 0.01 | |
| Ohio-2 | | | Shale | 0.62 | 64 | 0.06 | Greenish yellow |
| Ohio-3 | Morehead, KY | Ohio Shale | Coal | 0.55 | 131 | 0.01 | |
| Ohio-4 | | | Shale | 0.63 | 96 | 0.06 | Greenish yellow |
| Ohio-5 | Irvine, KY | Ohio Shale | Coal | 0.55 | 123 | 0.02 | |
| Ohio-6 | | | Shale | 0.65 | 114 | 0.06 | Greenish yellow |
| Dun-1 | Dunkirk, NY | Dunkirk Shale | Coal | 0.66 | 143 | 0.02 | |
| Dun-2 | | | Shale | 0.72 | 34 | 0.06 | Yellow to orange yellow |
| Rhin-1 | Derby, NY | Rhinestreet Shale | Coal | 0.68 | 154 | 0.02 | |
| Rhin-2 | | | Shale | 0.73 | 91 | 0.07 | Yellow to orange yellow |

N = number of measurements; SD = standard deviation.

et al., 2012a; Teng et al., 2017; Liu et al., 2018). Therefore, the impregnation of vitrinite by bitumen could potentially affect the R_o measurements of black shales, however, its influence should be negligible.

Peters et al. (2018) studied R_o suppression through hydrous pyrolysis experiments on artificial rocks composed of vitrinite-rich coal and varying contents of liptinite-rich kerogen and concluded that R_o suppression occurs in vitrinite mixed with liptinite macerals because free radicals generated from bitumen and associated volatile products contribute to termination reactions that dampen the aromatization process of co-occurring vitrinite. In this study, the coal lenses are about 1–2 mm thick and are in direct contact with enclosing black shales. Any chemical reaction that influences the maturation of vitrinite should therefore have the same effect on vitrinite in coals and shales alike. The free radical reaction mechanism is therefore unlikely to have caused the difference in R_o of shales and enclosed coals observed in this study.

Misidentification of solid bitumen for vitrinite can influence the R_o measurements of shales as well (Wei et al., 2016; Hackley and Lewan, 2018) because solid bitumen transformed from oil-prone macerals has a lower reflectance than co-occurring vitrinite below R_o 1.0% in black shales (Hackley and Lewan, 2018; Liu et al., 2019a). Hackley and Lewan (2018) conducted artificial maturation of coals and shales and found that the reflectance of solid bitumen is always lower than that of vitrinite subjected to the same temperature below R_o 1.6%. Based on a suppressed R_o trend (Lewan, 1993) and solid bitumen reflectance trend, they suggested that mistaking solid bitumen for vitrinite could explain the commonly reported R_o suppression in upper Paleozoic marine shales of early to mid-oil window maturity. Dispersed vitrinite particles in shales examined in this study are similar to vitrinite fragments in associated coals (Fig. 6), and are unlikely to be solid bitumen that fills the void spaces between mineral grains and fractures (Mastalerz et al., 2018). In addition, solid bitumen is very rare in the studied New Albany

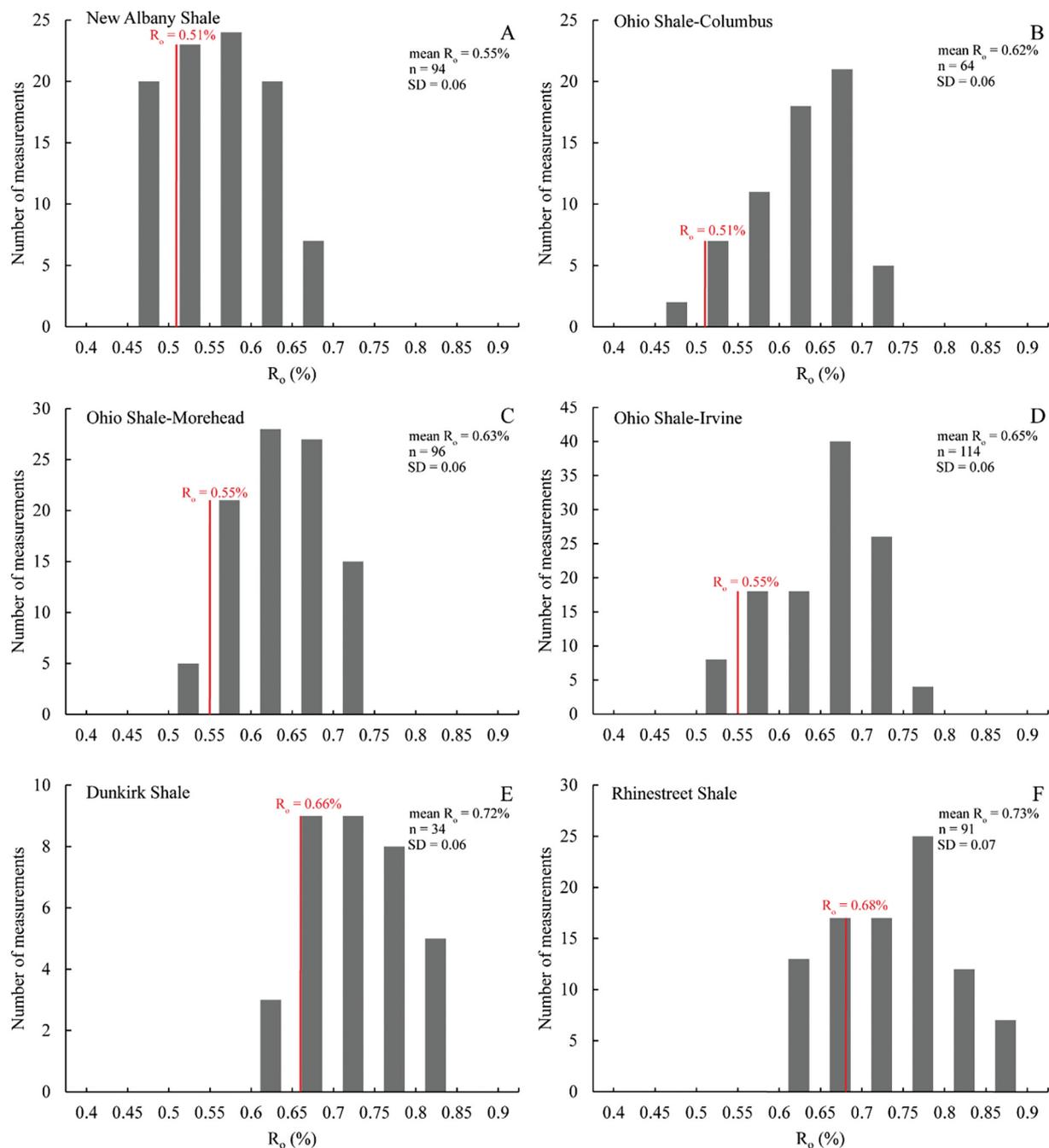


Fig. 10. Histograms of measured R_o of dispersed vitrinite particles in shales that enclose coal lenses. (A) New Albany Shale from Shepherdsville, KY; (B) Ohio Shale from Columbus, OH; (C) Ohio Shale from Morehead, KY; (D) Ohio Shale from Irvine, KY; (E) Dunkirk Shale from Dunkirk, NY; (F) Rhinestreet Shale from Derby, NY (Table 1). n = number of measurements; SD = standard deviation. Red bar indicates the mean R_o of enclosed coals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Shale and Ohio Shale samples because of their low thermal maturities.

Thermal maturity of black shales as indicated by R_o is an important parameter in reconstructing the thermal history of sedimentary basins and in the exploration for hydrocarbon resources. In this study, the R_o of black shales is 0.04–0.11% (average 0.07%) higher than that of enclosed coals (Fig. 10). Although this R_o difference does not significantly shift the hydrocarbon generation window of the studied black shales, a reevaluation of the applicability of R_o in black shale successions is still recommended, because some vitrinite could become severely oxidized and result in erroneous evaluation of thermal maturity. In addition, oxidized vitrinite can be indistinguishable from “normal” vitrinite (unoxidized) at high maturities. Therefore, R_o should be combined with

other thermal maturation indices such as solid bitumen or zooclast reflectance, Rock-Eval T_{max} , fluorescence of liptinite macerals, or the conodont alteration index to accurately evaluate the thermal history of black shale successions (Teichmüller and Durand, 1983; Bertrand and Héroux, 1987; Tissot et al., 1987; Petersen et al., 2013; Hackley and Cardott, 2016; Mastalerz et al., 2018; Liu et al., 2019a; Schmidt et al., 2019).

5. Conclusions

Coal lenses enclosed in several Upper Devonian black shale formations from the eastern United States provided a unique opportunity to

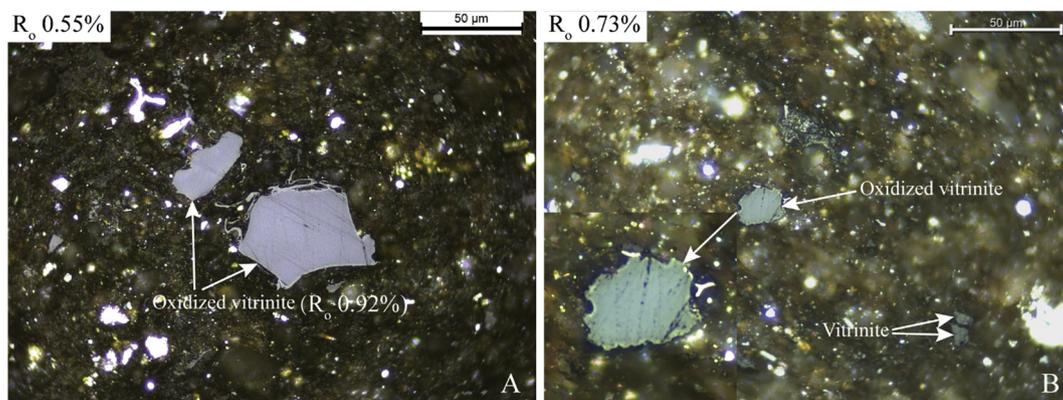


Fig. 11. Photomicrographs of oxidized vitrinite in reflected white light and oil immersion. (A) New Albany Shale from Shepherdsville, KY. Note the sharp edges of the vitrinite particles and the oxidized rim of the larger vitrinite particle. These two particles were excluded for R_o measurements. (B) Rhinestreet Shale from Derby, NY. Insert image is the close-up view of the oxidized vitrinite particle showing an oxidized rim.

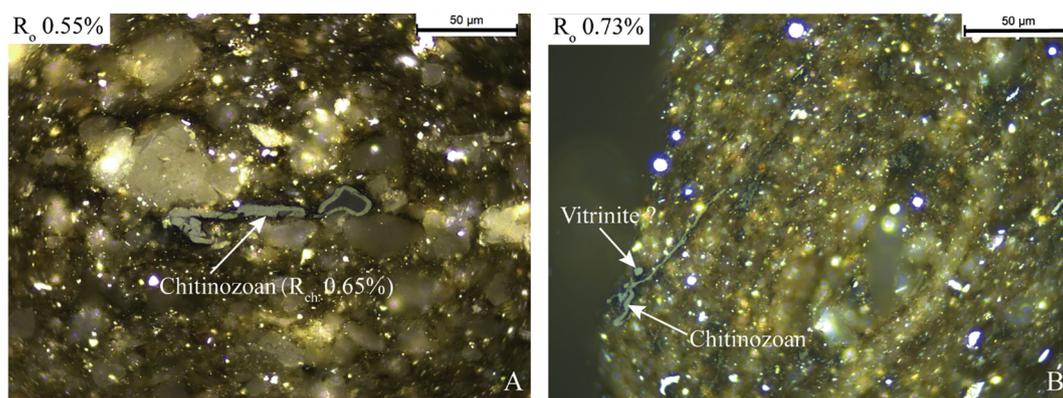


Fig. 12. Photomicrographs of chitinozoan fragments in the New Albany Shale (A) and the Rhinestreet Shale (B) in reflected white light and oil immersion. Note that the vitrinite-like particle next to a chitinozoan fragment in panel B has a comparable reflectance to the chitinozoan fragment, suggesting that it could be a chitinozoan fragment cut perpendicular to the chitinozoan. R_{ch} = chitinozoan reflectance.

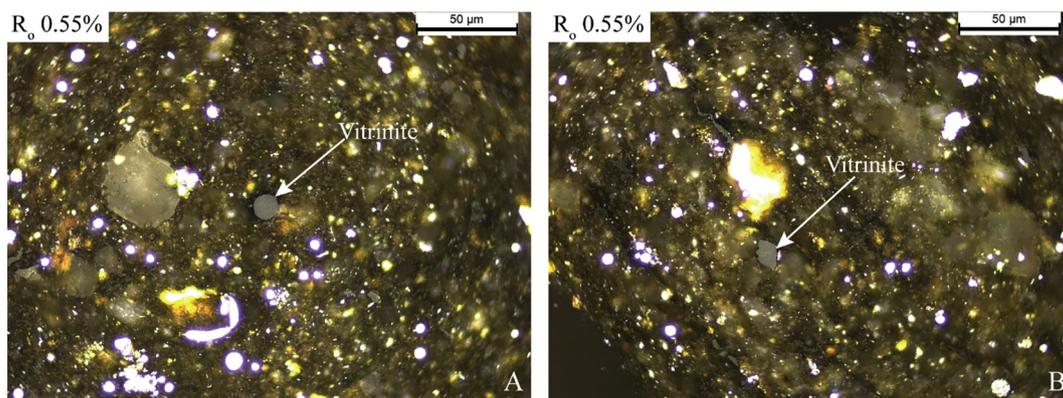


Fig. 13. Photomicrographs of dispersed vitrinite particles in shales in reflected white light and oil immersion. (A) Rounded vitrinite particles that could be cor-pogelinite. (B) Vitrinite particles with sharp edges that could be fragments of collotelinite. New Albany Shale sample from Shepherdsville, KY.

study the applicability of R_o in assessing the thermal maturity of black shale successions. Vitrinite in shales occurs as small dispersed particles ($\sim 5 \mu\text{m}$) in the mineral matrix, whereas coals embedded in shales occur as lenses about 1–2 mm thick and 10–20 cm long in outcrop and contain only vitrinite when examined under the microscope. These coal lenses could be tree trunks or branches transported from nearby land or exposed arches. The measured mean random R_o of dispersed vitrinite particles in black shales is 0.04–0.11% (average 0.07%) higher than that of enclosed coals with R_o ranging from 0.51–0.68%. The higher R_o of dispersed vitrinite particles in shales could be caused by oxidation of

small vitrinite precursor particles because small particles are more frequently suspended during transport to the site of deposition and reworking of bottom sediments after deposition than large driftwood pieces that will turn into enclosed coal lenses during burial diagenesis. Misidentification of fragments of zooclasts such as chitinozoans without recognizable morphological features for dispersed vitrinite particles and variability of phytoclasts in black shales could also contribute to the higher R_o values of shales than those of enclosed coals. When assessing the thermal maturity of black shales via R_o measurements, one should be mindful of the large heterogeneity of vitrinite in black shale

successions.

Acknowledgements

This research was supported by the sponsors of the Indiana University Shale Research Consortium (Anadarko, Chevron, ConocoPhillips, ExxonMobil, Shell, Statoil, Marathon, Whiting, Wintershall, and CNPC). A National Science Foundation equipment grant to J. Schieber (EAR-0318769) provided funds for the purchase of the analytical scanning electron microscope that was used to acquire some of the data and images used in this study. Mastalerz's contribution is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division under Award Number DE-SC0006978. Many thanks to Zalmai Yawar and Zhiyang Li for collecting the coal samples in the field. Financial support for Bei Liu from the China Scholarship Council is also gratefully acknowledged. We thank editor C. Özgen Karacan, Paul Hackley (USGS), and an anonymous reviewer for their constructive comments that greatly improved the manuscript.

Declaration of Competing 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.

References

- American Society for Testing and Materials (ASTM), 2014. D7708 standard test method for microscopical determination of the reflectance of vitrinite dispersed in sedimentary rocks. In: Annual book of ASTM Standards: Petroleum Products, Lubricants, and Fossil Fuels; Gaseous Fuels; Coal and Coke sec. 5, v. 05.06. ASTM International, West Conshohocken, PA.
- Barker, C.E., Pawlewicz, M.J., 1993. An empirical determination of the minimum number of measurements needed to estimate the mean random vitrinite reflectance of disseminated organic matter. *Org. Geochem.* 20, 643–651.
- Barker, C.E., Lewan, M.D., Pawlewicz, M.J., 2007. The influence of extractable organic matter on vitrinite reflectance suppression: a survey of kerogen and coal types. *Int. J. Coal Geol.* 70, 67–78.
- Bertrand, R., 1990. Correlations among the reflectances of vitrinite, chitinozoans, graptolites and scolecodonts. *Org. Geochem.* 15, 565–574.
- Bertrand, R., Héroux, Y., 1987. Chitinozoan, graptolite, and scolecodont reflectance as an alternative to vitrinite and pyrobitumen reflectance in Ordovician and Silurian strata, Anticosti Island, Quebec, Canada. *AAPG Bull.* 71, 951–957.
- Buchardt, B., Lewan, M.D., 1990. Reflectance of vitrinite-like macerals as a thermal maturity index for Cambrian-Ordovician Alum Shale, southern Scandinavia. *AAPG Bull.* 74, 394–406.
- Buiskool Toxopeus, J.M.A., 1983. Selection criteria for the use of vitrinite reflectance as a maturity tool. In: Brooks, J. (Ed.), *Petroleum Geochemistry and Exploration of Europe*. Blackwell Scientific Publications, Oxford, pp. 295–307.
- Buschbach, T.C., Kolata, D.R., 1990. Regional setting of Illinois Basin. In: Leighton, M.W., Kolata, D.R., Oltz, D.F., Eidel, J.J. (Eds.), *Interior Cratonic Basins*. AAPG Memoir 51, pp. 29–55.
- Bustin, R.M., Link, C., Goodarzi, F., 1989. Optical properties and chemistry of graptolite periderm following laboratory simulated maturation. *Org. Geochem.* 14, 355–364.
- Cardott, B.J., Curtis, M.E., 2018. Identification and nanoporosity of macerals in coal by scanning electron microscopy. *Int. J. Coal Geol.* 190, 205–217.
- Carr, A.D., 2000a. Suppression and retardation of vitrinite reflectance, Part 1. Formation and significance for hydrocarbon generation. *J. Petroleum Geol.* 23, 313–343.
- Carr, A.D., 2000b. Suppression and retardation of vitrinite reflectance, Part 2. Derivation and testing of a kinetic model for suppression. *Journal of Petroleum Geology* 23, 475–496.
- Castano, J.R., Sparks, D.M., 1974. Interpretation of vitrinite reflectance measurements in sedimentary rocks and determination of burial history using vitrinite reflectance and authigenic minerals. In: Dutcher, R.R., Hacquebard, P.A., Schopf, J.M., Simon, J.A. (Eds.), *Carbonaceous Materials as Indicators of Metamorphism*. 153. Geological Society of America Special Paper, pp. 31–52.
- Curtis, J.B., 2002. Fractured shale-gas systems. *AAPG Bull.* 86, 1921–1938.
- Goodarzi, F., 1985. Reflected light microscopy of chitinozoan fragments. *Mar. Pet. Geol.* 2, 72–78.
- Goodarzi, F., Murchison, D.G., 1973. Oxidized vitrinites—their aromaticity, optical properties and possible detection. *Fuel* 52, 90–92.
- Goodarzi, F., Norford, B.S., 1985. Graptolites as indicators of the temperature histories of rocks. *J. Geol. Soc.* 142, 1089–1099.
- Goodarzi, F., Norford, B.S., 1987. Optical properties of graptolite epiderm—A review. *Bull. Geol. Soc. Den.* 35, 141–147.
- Goodarzi, F., Norford, B.S., 1989. Variation of graptolite reflectance with depth of burial. *Int. J. Coal Geol.* 11, 127–141.
- Goodarzi, F., Gentzis, T., Harrison, C., Thorsteinsson, R., 1992. The significance of graptolite reflectance in regional thermal maturity studies, Queen Elizabeth Islands, Arctic Canada. *Org. Geochem.* 18, 347–357.
- Goodarzi, F., Gentzis, T., Snowdon, L.R., Bustin, R.M., Feinstein, S., Labonte, M., 1993. Effect of mineral matrix and seam thickness on reflectance of vitrinite in high to low volatile bituminous coals: an enigma. *Mar. Pet. Geol.* 10, 162–171.
- Hackley, P.C., Cardott, B.J., 2016. Application of organic petrography in north American shale petroleum systems: a review. *Int. J. Coal Geol.* 163, 8–51.
- Hackley, P.C., Lewan, M., 2018. Understanding and distinguishing reflectance measurements of solid bitumen and vitrinite using hydrous pyrolysis: Implications to petroleum assessment. *AAPG Bull.* 102, 1119–1140.
- Hackley, P.C., Araujo, C.V., Borrego, A.G., Bouzinos, A., Cardott, B., Cook, A.C., Eble, C., Flores, D., Gentzis, T., Gonçalves, P.A., Mendonça Filho, J.G., Hámor-Vidó, M., Jelonek, I., Kommeren, K., Knowles, W., Kus, J., Mastalerz, M., Menezes, T.R., Newman, J., Oikonomopoulos, I.K., Pawlewicz, M., Pickel, W., Potter, J., Ranasinghe, P., Read, H., Reyes, J., Rodriguez, G.D.L.R., Fernandes de Souza, I.V.A., Suarez-Ruiz, I., Sýkorová, I., Valentine, B.J., 2015. Standardization of reflectance measurements in dispersed organic matter: results of an exercise to improve interlaboratory agreement. *Mar. Pet. Geol.* 59, 22–34.
- Hackley, P.C., Walters, C.C., Kelemen, S.R., Mastalerz, M., Lowers, H.A., 2017. Organic petrology and micro-spectroscopy of *Tasmanites* microfossils: applications to kerogen transformations in the early oil window. *Org. Geochem.* 114, 23–44.
- Hackley, P.C., Valentine, B.J., Hatcherian, J.J., 2018. On the petrographic distinction of bituminite from solid bitumen in immature to early mature source rocks. *Int. J. Coal Geol.* 196, 232–245.
- Hao, F., Chen, J., 1992. The cause and mechanism of vitrinite reflectance anomalies. *J. Pet. Geol.* 15, 419–434.
- Hao, F., Sun, Y., Li, S., Zhang, Q., 1995. Overpressure retardation of organic-matter maturation and petroleum generation: a case study from the Yinggehai and Qiongdongnan Basins, South China Sea. *AAPG Bull.* 79, 551–562.
- Hao, F., Zou, H., Gong, Z., Yang, S., Zeng, Z., 2007. Hierarchies of overpressure retardation of organic matter maturation: Case studies from petroleum basins in China. *AAPG Bull.* 91, 1467–1498.
- Hood, A., Gutjahr, C.C.M., Heacock, R.L., 1975. Organic metamorphism and the generation of petroleum. *AAPG Bull.* 59, 986–996.
- Hutton, A.C., Cook, A.C., 1980. Influence of alginite on the reflectance of vitrinite from Joadja, NSW, and some other coals and oil shales containing alginite. *Fuel* 59, 711–714.
- International Committee for Coal Petrology (ICCP), 1963. *International Handbook of Coal Petrography*, 2nd ed. Centre National de la Recherche Scientifique, Paris 232 p.
- International Committee for Coal Petrology (ICCP), 1998. The new vitrinite classification (ICCP System 1994). *Fuel* 77, 349–358.
- Jarvie, D.M., 2012a. Shale resource systems for oil and gas: Part 1—Shale-gas resource systems. In: Breyer, J.A. (Ed.), *Shale Reservoirs—Giant Resources for the 21st Century*. AAPG Memoir 97, pp. 69–87.
- Jarvie, D.M., 2012b. Shale resource systems for oil and gas: Part 1—Shale-oil resource systems. In: Breyer, J.A. (Ed.), *Shale Reservoirs—Giant Resources for the 21st Century*. AAPG Memoir 97, pp. 89–119.
- Jones, R.W., Edison, T.A., 1978. Microscopic observations of kerogen related to geochemical parameters with emphasis on thermal maturation. In: Oltz, D.F. (Ed.), *Symposium in Geochemistry: Low Temperature Metamorphism of Kerogen and Clay Minerals*. Pacific Section, Society for Sedimentary Geology, pp. 1–12.
- Kalkreuth, W.D., 1982. Rank and petrographic composition of selected Jurassic-lower cretaceous coals of British Columbia, Canada. *Bull. Can. Petrol. Geol.* 30, 112–139.
- Kenrick, P., Crane, P.R., 1997. The origin and early evolution of plants on land. *Nature* 389, 33–39.
- Lewan, M.D., 1993. Identifying and understanding suppressed vitrinite reflectance through hydrous pyrolysis experiments. In: *Society for Organic Petrology 10th Annual Meeting Abstracts and Program*, pp. 1–3.
- Liu, B., Schieber, J., Mastalerz, M., 2017. Combined SEM and reflected light petrography of organic matter in the New Albany Shale (Devonian-Mississippian) in the Illinois Basin: a perspective on organic pore development with thermal maturation. *Int. J. Coal Geol.* 184, 57–72.
- Liu, B., Schieber, J., Mastalerz, M., 2019a. Petrographic and micro-FTIR study of organic matter in the Upper Devonian New Albany Shale during thermal maturation: Implications for kerogen transformation. In: Camp, W., Milliken, K., Taylor, K., Fishman, N., Hackley, P., Macquaker, J. (Eds.), *Shale Diagenesis: Research Perspectives for Shale Hydrocarbon Reservoirs, Seals, and Source Rocks*. AAPG Memoir 120, pp. 165–188.
- Liu, B., Schieber, J., Mastalerz, M., Teng, J., 2019b. Organic matter content and type variation in the sequence stratigraphic context of the Upper Devonian New Albany Shale, Illinois Basin. *Sediment. Geol.* 383, 101–120.
- Liu, B., Mastalerz, M., Schieber, J., Teng, J., 2020. Association of uranium with macerals in marine black shales: Insights from the Upper Devonian New Albany Shale, Illinois Basin. *Int. J. Coal Geol.* 217, 103351.
- Liu, Y., Zhu, Y., Liu, S., Chen, S., Li, W., Wang, Y., 2018. Molecular structure controls on micropore evolution in coal vitrinite during coalification. *Int. J. Coal Geol.* 199, 19–30.
- Lo, H.B., 1993. Correction criteria for the suppression of vitrinite reflectance in hydrogen-rich kerogens: preliminary guidelines. *Org. Geochem.* 20, 653–657.
- Luo, Q., Hao, J., Skovsted, C.B., Luo, P., Khan, I., Wu, J., Zhong, N., 2017. The organic petrology of graptolites and maturity assessment of the Wufeng-Longmaxi Formations on Chongqing, China: Insights from reflectance cross-plot analysis. *Int. J. Coal Geol.* 183, 161–173.

- Luo, Q., Hao, J., Skovsted, C.B., Xu, Y., Liu, Y., Wu, J., Zhang, S., Wang, W., 2018. Optical characteristics of graptolite-bearing sediments and its implication for thermal maturity assessment. *Int. J. Coal Geol.* 195, 386–401.
- Luo, Q., Fariborz, G., Zhong, N., Wang, Y., Qiu, N., Skovsted, C.B., Suchý, V., Schovsbo, N.H., Morga, R., Xu, Y., Hao, J., Liu, A., Wu, J., Cao, W., Min, X., Wu, J., 2020. Graptolites as fossil geo-thermometers and source material of hydrocarbons: an overview of four decades of progress. *Earth Sci. Rev.* 200, 103000.
- Mählmann, R.F., Le Bayon, R., 2016. Vitrinite and vitrinite like solid bitumen reflectance in thermal maturity studies: correlations from diagenesis to incipient metamorphism in different geodynamic settings. *Int. J. Coal Geol.* 157, 52–73.
- Mastalerz, M., He, L., Melnichenko, Y.B., Rupp, J.A., 2012a. Porosity of coal and shale: Insights from gas adsorption and SANS/USANS techniques. *Energy Fuel* 26, 5109–5120.
- Mastalerz, M., Schimmelmann, A., Lis, G.P., Drobnik, A., Stankiewicz, A., 2012b. Influence of maceral composition on geochemical characteristics of immature shale kerogen: Insight from density fraction analysis. *Int. J. Coal Geol.* 103, 60–69.
- Mastalerz, M., Schimmelmann, A., Drobnik, A., Chen, Y., 2013. Porosity of Devonian and Mississippian New Albany Shale across a maturation gradient: Insights from organic petrology, gas adsorption, and mercury intrusion. *AAPG Bull.* 97, 1621–1643.
- Mastalerz, M., Drobnik, A., Stankiewicz, A.B., 2018. Origin, properties, and implications of solid bitumen in source-rock reservoirs: a review. *Int. J. Coal Geol.* 195, 14–36.
- McCartney, J.T., Teichmüller, M., 1972. Classification of coals according to degree of coalification by reflectance of the vitrinite component. *Fuel* 51, 64–68.
- McFarlan, A.C., 1943. *The Geology of Kentucky*. University of Kentucky, Lexington 531 p.
- McTavish, R.A., 1978. Pressure retardation of vitrinite diagenesis, offshore north-West Europe. *Nature* 271, 648–650.
- McTavish, R.A., 1998. The role of overpressure in the retardation of organic matter maturation. *J. Pet. Geol.* 21, 153–186.
- Mukhopadhyay, P.K., 1994. Vitrinite reflectance as a maturity parameter: Petrographic and molecular characterization and its applications to basin modeling. In: Dow, W.G. (Ed.), *Mukhopadhyay, P.K. Vitrinite Reflectance as A Maturity Parameter, Applications and Limitations*, pp. 1–24.
- Peters, K.E., Hackley, P.C., Thomas, J.J., Pomerantz, A.E., 2018. Suppression of vitrinite reflectance by bitumen generated from liptinite during hydrous pyrolysis of artificial source rock. *Org. Geochem.* 125, 220–228.
- Petersen, H.I., Vosgerau, H., 1999. Composition and organic maturity of Middle Jurassic coals, North-East Greenland: evidence for liptinite-induced suppression of huminite reflectance. *Int. J. Coal Geol.* 41, 257–274.
- Petersen, H.I., Schovsbo, N.H., Nielsen, A.T., 2013. Reflectance measurements of zooclasts and solid bitumen in lower Paleozoic shales, southern Scandinavia: Correlation to vitrinite reflectance. *Int. J. Coal Geol.* 114, 1–18.
- Price, L.C., Baker, C.E., 1985. Suppression of vitrinite reflectance in amorphous rich kerogen—a major unrecognized problem. *J. Pet. Geol.* 8, 59–84.
- Raymond, A.C., Murchison, D.G., 1991. Influence of exinitic macerals on the reflectance of vitrinite in Carboniferous sediments of the Midland Valley of Scotland. *Fuel* 70, 155–161.
- Reyes, J., Jiang, C., Lavoie, D., Armstrong, D.K., Milovic, M., Robinson, R., 2018. Organic petrographic analysis of artificially matured chitinozoan-and graptolite-rich Upper Ordovician shale from Hudson Bay Basin, Canada. *Int. J. Coal Geol.* 199, 138–151.
- Robl, T.L., Rimmer, S.M., Barron, L.S., 1992. Organic petrography of Mississippian and Devonian shales in east-Central Kentucky. *Fuel* 71, 267–271.
- Rouquerol, J., Avnir, D., Fairbridge, C.W., Everett, D.H., Haynes, J.M., Pernicone, N., Ramsay, J.D.F., Sing, K.S.W., Unger, K.K., 1994. Recommendations for the characterization of porous solids (Technical Report). *Pure Appl. Chem.* 66, 1739–1758.
- Schleicher, M., Koster, J., Kulke, H., Weil, W., 1998. Reservoir and source-rock characterisation of the early Palaeozoic interval in the Peribaltic Syncline, northern Poland. *J. Pet. Geol.* 21, 33–56.
- Schmidt, J.S., Menezes, T.R., Souza, I.V.A.F., Spigolon, A.L.D., Pestilho, A.L.S., Coutinho, L.F.C., 2019. Comments on empirical conversion of solid bitumen reflectance for thermal maturity evaluation. *Int. J. Coal Geol.* 201, 44–50.
- Stach, E., Mackowsky, M.-T.H., Teichmüller, M., Taylor, G.H., Chandra, D., Teichmüller, R., 1982. *Stach's Textbook of Coal Petrology*, third ed. Gebrüder Borntraeger, Berlin-Stuttgart 535 p.
- Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Robert, P., 1998. *Organic Petrology*. Gebrüder Borntraeger, Berlin-Stuttgart 704 p.
- Teichmüller, M., Durand, B., 1983. Fluorescence microscopical rank studies on liptinites and vitrinites in peat and coals, and comparison with results of the Rock-Eval pyrolysis. *Int. J. Coal Geol.* 2, 197–230.
- Teng, J., Mastalerz, M., Hampton, L., 2017. Maceral controls on porosity characteristics of lithotypes of Pennsylvanian high volatile bituminous coal: example from the Illinois Basin. *Int. J. Coal Geol.* 172, 80–94.
- Teng, J., Mastalerz, M., Liu, B., Gognat, T., Hauser, E., McLaughlin, P., 2020. Variations of organic matter transformation in response to hydrothermal fluids: example from the Indiana part of the Illinois Basin. *Int. J. Coal Geol.* 219, 103410.
- Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence*, 2nd ed. Springer-Verlag, Berlin 699 p.
- Tissot, B.P., Pelet, R., Ungerer, P.H., 1987. Thermal history of sedimentary basins, maturation indices, and kinetics of oil and gas generation. *AAPG Bull.* 71, 1445–1466.
- Tricker, P.M., Marshall, J.E., Badman, T.D., 1992. Chitinozoan reflectance: a lower Palaeozoic thermal maturity indicator. *Mar. Pet. Geol.* 9, 302–307.
- Ujiié, Y., Sherwood, N., Faiz, M., Wilkins, R.W., 2004. Thermal maturity and suppressed vitrinite reflectance for Neogene petroleum source rocks of Japan. *AAPG Bull.* 88, 1335–1356.
- Wang, F.P., Gale, J.F., 2009. Screening criteria for shale-gas systems. *The Gulf Coast Association of Geological Societies* 59, 779–793.
- Wang, Y., Qiu, N., Borjigin, T., Shen, B., Xie, X., Ma, Z., Lu, C., Yang, Y., Yang, L., Cheng, L., Fang, G., Cui, Y., 2019. Integrated assessment of thermal maturity of the Upper Ordovician–lower Silurian Wufeng–Longmaxi shale in Sichuan Basin, China. *Mar. Pet. Geol.* 100, 447–465.
- Wei, L., Wang, Y., Mastalerz, M., 2016. Comparative optical properties of macerals and statistical evaluation of mis-identification of vitrinite and solid bitumen from early mature Middle Devonian–lower Mississippian New Albany Shale: Implications for thermal maturity assessment. *Int. J. Coal Geol.* 168, 222–236.
- Wenger, L.M., Baker, D.R., 1987. Variations in vitrinite reflectance with organic facies—examples from Pennsylvanian cyclothem of the Midcontinent, USA. *Org. Geochem.* 11, 411–416.
- Xiao, X., Wilkins, R.W.T., Liu, D., Liu, Z., Fu, J., 2000. Investigation of thermal maturity of lower Palaeozoic hydrocarbon source rocks by means of vitrinite-like maceral reflectance—a Tarim Basin case study. *Org. Geochem.* 31, 1041–1052.