12-16-2017

# Changes in Vitrinite Reflectance and Liptinite Fluorescence with Increasing Rank in Dispersed Organics in the Illinois Basin and its Environmental, Economic, and Political Impacts

Kailey Zalucha-Seaman
kmzalucha@siu.edu

Recommended Citation

Zalucha-Seaman, Kailey, "Changes in Vitrinite Reflectance and Liptinite Fluorescence with Increasing Rank in Dispersed Organics in the Illinois Basin and its Environmental, Economic, and Political Impacts" (2017). *Honors Theses*. 437.
http://opensiuc.lib.siu.edu/uhp_theses/437

# Changes in Vitrinite Reflectance and Liptinite Fluorescence with Increasing Rank in Dispersed Organics in the Illinois Basin and its Environmental, Economic, and Political Impacts

Kailey Marie Zalucha-Seaman

Department of Geology, Southern Illinois University Carbondale

## *Abstract*

Vitrinite reflectance and spectral fluorescence are commonly used together to determine the rank and thermal maturity of shale samples. Although vitrinite is not commonly found in the New Albany Shale, solid bitumen is found in significant amounts; reflectance of solid bitumen provides another method to determine maturity of these samples. The purpose of this study was to compare the vitrinite reflectance and spectral fluorescence of liptinites to determine the thermal maturity of the New Albany Shale, which can benefit those tasked in the industry who determine the oil and gas potential of these source rocks. Establishment of a relationship between vitrinite reflectance and fluorescence can help create another rank parameter (alginite fluorescence) to determine the thermal maturity in the basin. This methodology for determining the hydrocarbon potential can also impact other areas of the country where black shales are exploited, including Eastern Kentucky (Ohio Shale) and North Dakota and Montana (Bakken Shale). This could potentially improve assessments of source rocks in terms of oil or gas, saving companies from potential costly mistakes. The other purpose of this study was to look at the potential political, economic, and environmental impacts that result from the extraction of oil and gas by the process of hydraulic fracturing. Evaluating the impacts of hydraulic fracturing in the State of Illinois allows for a better understanding of how lawmakers, resource companies, and scientists can contribute to a broader view of the regional effects of this activity.

## *Introduction*

The purpose of this study was to compare changes in vitrinite reflectance and spectral fluorescence of liptinites in the New Albany Shale of Illinois with increasing rank. A relationship has been observed between an increase in vitrinite reflectance and a decrease in spectral fluorescence with increasing rank in previous studies (e.g., Rimmer et al., 1993). By establishing this relationship for the New Albany Shale, fluorescence could be used as a rank parameter to determine the oil and gas potential of this unit. This is significant because it has been suggested that vitrinite reflectance can be suppressed in very organic-rich sources such as the New Albany Shale (Price and Barker, 1985; Nuccio and Hatch, 1996). This study will assess whether spectral fluorescence can be used as a thermal maturity parameter if vitrinite suppression is present in the New Albany Shale.

The specific objectives were:

(1) To measure solid bitumen reflectance (BRo) and use this to calculate vitrinite reflectance (VRo);

(2) to compare reflectance (both BRo and VRo) to vitrinite reflectance values reported by the Illinois State Geological Survey (ISGS) (e.g., Barrows et al., 1981);

(3) to measure fluorescence of the maceral, telalginite; and

(4) to compare spectral fluorescence with VRo to determine thermal maturity of the New Albany Shale.

In determining the thermal maturity of the New Albany Shale, it cannot be ignored that there are also environmental, economic, and political impacts when extracting oil or gas through methods such as hydraulic fracturing, which will be further discussed.

## *Geologic Background*

The Devonian New Albany Shale (NAS), located in Illinois and parts of Indiana and Kentucky, is organic rich, and is known to produce oil and gas (Cluff and Dickerson, 1982;

Werner-Zwanziger et al., 2005; Strapoc et al., 2010). The NAS is thought to have sourced as much as 95% of the oil in the Illinois Basin, and may have produced gas in the far southeastern region of Illinois (Cluff and Dickerson, 1982). In shales, there are four groups of kerogen: Type I kerogen is formed primarily from lacustrine environments and generates oil; Type II kerogen is associated with marine environments, and typically produces both oil and gas; Type III kerogen is mostly derived from terrestrial environments and produces mostly gas; and Type IV is considered "dead" carbon, and has little to no hydrocarbon potential (Taylor et al., 1998). The NAS samples used in this study are primarily made up of marine Type II kerogen with abundant telalginite and only traces of vitrinite, the latter indicating terrestrial input (Price and Barker, 1989; Nuccio and Hatch, 1996). Vitrinite represents preserved woody tissues, whereas liptinite represents preserved remains of spores, pollen, algae, and resins (Taylor et al., 1998). Solid bitumen (often seen in source rocks) represents solidified oil that at one time was generated within or migrated through the shale (Cardott et al., 2015). It is also known that solid bitumen reflectance is lower than vitrinite reflectance up to a certain reflectance, and there are several equations that can be used to convert it into vitrinite reflectance (Bertrand, 1993; Landis and Castaño, 1995; Schoenherr et al. 2007; Cardott et al., 2015). Overall, the thermal maturity of the New Albany Shale increases towards the southeast, with vitrinite reflectance increasing and fluorescence intensity decreasing as thermal maturity increases (Cluff and Dickerson, 1982). The thermal maturity of the New Albany Shale increases due to increased temperature and pressure over long periods of time; this alters the rock, causing vitrinite reflectance to increase and spectral fluorescence to decrease (Nuccio and Hatch, 1996; Werner-Zwanziger et al., 2005). At the time of deposition for the New Albany Shale, mostly organic marine material was deposited, with some terrestrial inputs including vitrinite coming from the Catskill Delta to the east

(Woodrow, 1985). At this time in geologic history, most of North America was a topical environment with varying amounts of rainfall from the Appalachian Mountains (Woodrow, 1985).

### *Methods*

The samples were originally collected from cores in select locations throughout Illinois, as indicated by the circled sample names on Fig. 1. These samples were initially prepared by the Illinois State Geologic Survey (e.g., Barrows et al., 1981), and very thin (<2-3mm) 1” square mounts were prepared. As preliminary hand polishing of these mounts was unsuccessful, samples were cut into thirds on a diamond saw blade, then oriented on their side and re-embedded in epoxy in a 1 ¼” round mold. This process produced a sample with strips of kerogen that were considerably thicker (~1/3 inch), which would allow multiple polishes without grinding away the sample. The samples were polished using a Buehler AutoMet 250 polisher, using 320, 400, and 600 grits followed by 1 and 0.06 micron polishes. The samples were examined using a Leica DM2500P reflected-light microscope with both blue- and white-light illumination, using a 50x objective under oil immersion. Photomicrographs were taken with a Retiga 2000R camera and QCapture Pro 6.0 program. J&M Analytic MSP200 Coal Reflectance Program was used for solid bitumen reflectance; 30 measurements per sample were taken according to ASTM standards, then averaged. The J&M Analytic TIDAS system was used for spectral analysis in oil immersion with 10 scans per sample of the maceral, telalginite. Spectral scans included intensity at 550 and 650 nm, Q* (relative intensity at 650 nm/relative intensity at 550 nm), wavelength of maximum intensity (in nm), and maximum intensity, then averaged. Spectral scans were different from standard fluorescence methods; since intensity at 500 nm cannot be taken under oil immersion, intensity at 550 nm was taken instead and used in the Q* equation as the relative intensity at 650 nm/relative intensity at 550 nm.

## *Results*

The New Albany Shale samples are primarily Type II kerogens, containing large amounts of the maceral, telalginite. There are significant amounts of solid bitumen, inertinite, various inorganics, but very few pieces of vitrinite. This is seen with Fig. 2, where the white light photomicrographs show the solid bitumen, inorganics, and inertinite (photomicrograph 2E). Pieces of alginite are seen in Fig. 2 (photomicrographs B, D, F, H), with no telalginite fluorescing in samples NAS 120 and 126, seen in photomicrographs J and L.

Table 1 shows the vitrinite reflectance reported by the Illinois State Geologic Survey (ISGS Vit. Ro (%)), the measured solid bitumen reflectance (Solid Bitumen Ro (%)), and the measured vitrinite reflectance collected on samples where vitrinite was identified, and the calculated vitrinite reflectance (Vit. Ro (%)). BRo was recalculated to Vit. Ro using the equation, Ro = (BRo+0.2443)/1.0495 (Schoenherr et al., 2007), and is reported in Table 1 as Calc. VRo (%). Solid bitumen differs from vitrinite, it typically has a lower reflectance until higher maturities are reached where solid bitumen can have a higher reflectance compared to vitrinite. Previous studies have determined equations to calculate vitrinite reflectance from solid bitumen reflectance (Bertrand, 1993; Landis and Castano, 1995; Schoenherr et al., 2007).

In samples NAS 376, NAS 184, and NAS 126, vitrinite was also observed during the solid bitumen reflectance analysis, allowing a few vitrinite reflectance measurements to be taken. The samples demonstrated a difference of ~0.3% Ro between vitrinite reflectance and solid bitumen reflectance.

Table 2 shows the fluorescence data collected on telalginite under blue-light illumination (oil immersion). The data demonstrates the increase in Q* and $\lambda_{max}$ wavelength with thermal maturity and with an increase in vitrinite reflectance. The data for the $\lambda_{max}$ intensity appears less reliable, with the exception of the decrease in intensity in sample NAS 184, which is closer to the edge of the oil/gas window of thermal maturity. Note that samples NAS 120 and 128 has no fluorescence, and has a vitrinite reflectance that indicates they are past oil generation.

Q* values increase relatively regularly with increases in vitrinite reflectance, with samples NAS 120 and 128 having a Q* value of 0 (Fig. 3). Figure 4 shows that the first three samples increase steadily in $\lambda_{max}$ intensity as vitrinite reflectance increases, then with the fourth sample, NAS 184, the $\lambda_{max}$ intensity decreases before going to 0 for samples NAS 120 and 128. Figure 5 has little increase in $\lambda_{max}$ wavelength with increased vitrinite reflectance for the first three samples; in the fourth sample, NAS 184, $\lambda_{max}$ wavelength is 600.6 nm compared to the range of 574.8 nm-576.2 nm for the first three samples. The $\lambda_{max}$ wavelength then drops to 0 in samples NAS 120 and 128.

## *Discussion*

There is a clear difference in the fluorescence color of the telalginite as solid bitumen reflectance increases. In sample NAS 233 (Fig. 2B) the telalginite is an intense bright green/yellow, which then becomes dull in sample NAS 376 (Fig. 2D) and NAS 128 (Fig. 2F). Telalginite in sample NAS 184 (Fig. 2H) is a very dull orange/brown at a vitrinite reflectance at 0.81%. In samples NAS 120 and 126 (vitrinite reflectance's of 1.19% and 1.58%, respectively) the photomicrographs show that there is no fluorescence in the samples (Fig. 2J, L). Ultimately, the color of the telalginite shifts from bright yellow to a dull yellow to orange/brown with increase in vitrinite reflectance. Telalginite fluoresces a bright yellow color in samples NAS 233, 376, and 128, the Q* value is between 0.64 and 0.87, and the $\lambda_{max}$ wavelengths are clustered closely together with values ranging from 574.8 nm to 576.2 nm. Sample NAS 184 fluoresces a very dull orange/brown, the Q* value is 1.08, and the $\lambda_{max}$ wavelength is 600.6 nm. An increase in vitrinite reflectance coincides with the increase in Q* and $\lambda_{max}$ wavelength. Previous studies in other basins such as the Cleveland Shale Member of the Ohio Shale in Kentucky have determined that the fluorescence color shifts with increase in vitrinite reflectance (Rimmer et al., 1993).

NAS 233 (Fig. 6), illustrates the difference in reflectance between the solid bitumen (Fig. 6A) and a degraded piece of vitrinite (Fig. 6B), revealing that the vitrinite has a much higher reflectance than the solid bitumen. To select an equation to convert the measured solid bitumen reflectance to the vitrinite reflectance, measurements taken on vitrinite were considered. A comparison of re-calculated vitrinite reflectance with actual measured vitrinite reflectance led to the selection of the equation of $Ro = (BRo+0.2443)/1.0495$ (Schoenherr et al., 2007) for the NAS. Note that for three of the samples (NAS 233, NAS 128, and NAS 120), there was no reliable vitrinite found or measured during analysis. Comparison of the original ISGS vitrinite reflectance with the vitrinite reflectance recalculated from solid bitumen reflectance, it is clear that the ISGS measured vitrinite reflectance is much lower than the vitrinite reflectance calculated in this study as shown in Fig. 7. After converting the vitrinite reflectance taken by the ISGS with the same $Ro = (BRo+0.2443)/1.0495$ equation (Schoenherr et al., 2007), the original ISGS reflectance more closely match those acquired during this study (Fig. 8).

The differences between the vitrinite reflectance and solid bitumen reflectance is clear, and it leads to the possibility that the initial ISGS vitrinite reflectance may have collected at least some data on solid bitumen rather than vitrinite. This is illustrated in Fig. 7 where the vitrinite reflectance determined in this study are considerably higher than the original ISGS vitrinite reflectance. If the ISGS vitrinite reflectance measurements are re-calculated with equation, Ro = (BRo+0.2443)/1.0495 (Schoenherr et al. 2007) (making the assumption that they were solid bitumen reflectance measurements), the data more closely matches the new vitrinite reflectance data. Further analyses will be required to confirm this possibility. Other studies have suggested that incorrect measurements on solid bitumen as opposed to vitrinite can have a large impact (~0.2-0.4% Ro difference) on thermal maturity assessments, and can be common even with experienced petrographers (Landis and Castano, 1995; Wei et al., 2016).

Differences in sample preparation and polishing can be a factor in vitrinite reflectance measurements. A poor polish results in lower reflectance values, producing error in the data.; it is possible that the polishes attained in the current study were of higher quality due to modern techniques.

Werner-Zwanziger et al. (2005) concluded that Type II kerogen, such as telalginite, in the New Albany Shale experiences a more gradual chemical change with maturity, measured by vitrinite reflectance, and vitrinite reflectance in the SE region of Illinois ranges from 0.94% to 1.40% (increasing towards the southeast). Thermal maturity of the New Albany Shale increases towards the southeast going from the oil window (0.5-1.35% Ro) to the wet gas window (1.35-2.0%), with the furthest northwest sample (NAS 233) having the lowest thermal maturity, and the furthest southeast sample (NAS 126) having the highest thermal maturity. Fluorescence is lost around ~1.2% Ro, near the end of the oil window. Previous studies have suggested that vitrinite suppression of as much as ~0.3% may be present in the New Albany (Price and Barker, 1985; Nuccio and Hatch, 1996). It has also been shown that vitrinite reflectance of the Herrin

(No. 6) coal seam (Pennsylvanian) in the Illinois Basin ranges from 0.45-0.71% (Thomas and Damberger, 1976). This range in coal vitrinite reflectance values falls within the same range of those for the New Albany Shale, a unit that has been buried much deeper in the basin and therefore should have higher reflectance values. If during these previous studies of the NAS, solid bitumen was measured instead of vitrinite, the true vitrinite reflectance could be lower by ~0.3%. More data will be needed to assess this question by analyzing coal samples from the Illinois Basin to determine their vitrinite reflectance and liptinite fluorescence, as well as by analyzing more New Albany Shale samples to determine their vitrinite reflectance and liptinite fluorescence.

### *Impact*

Extraction of oil and gas using hydraulic fracturing from organic-rich Devonian shale has been a controversial political, environmental, and economic concern throughout the country (Rabe, 2014; North et al., 2014; Loomis and Haefele, 2017). Hydraulic fracturing is a process of extraction that pressurizes rock until it is cracked, causing the oil or gas to be more easily extracted (North et al., 2014). This process has been controversial due to the negative environmental impacts that are often associated with fracking (Loomis and Haefele, 2017). Part of the goal of this project was to evaluate how hydraulic fracturing of the New Albany Shale could affect local and state politics, economics, and the environment in Illinois. It was determined that the thermal maturity of the New Albany Shale increases towards the southeast, with the calculated vitrinite reflectance indicating potential for oil and gas production, making hydraulic fracturing of the New Albany Shale a possibility in the state of Illinois. As of 2014, 31 states have reserves of gas and oil which can be used for extraction (Rabe, 2014), affecting over

50% of American states with how their state and local governments plan to handle these reserves and any possible extraction of them. Illinois is one of these states; with the Illinois Hydraulic Fracturing Regulatory Act 2013 and the Illinois Department of Natural Resources released its first fracking well permit to Woolsey Operating Company in 2017 (Associated Press, 2013).

As part of this project, Illinois State Senator Jason Barickman of the 53rd district (R-IL) was interviewed. When asked, "How do you think hydraulic fracturing will affect the state, its citizens, and economy?", Sen. Barickman replied, "The critical variable that was considered was the employment factor and this industry could bring a significant number of jobs to Illinois." Sen. Barickman further expressed that this is why many states, such as Illinois, have allowed fracking, because it brings a lot of revenue to their economy. Studies have found that oil and gas extraction through hydraulic fracturing has led to greater investment and employment opportunities for states because of the relative low cost that this method provides (Rabe, 2014). An example of this includes North Dakota, which had the lowest unemployment rate in the country of 2.6% in 2013, and this economic growth was seen throughout the state with increases in median household income and population growth (Brown, 2014). Sen. Barickman described how he and other state politicians attended a conference, and the North Dakota politicians attending described how their state has extra revenue from hydraulic fracturing. Sen. Barickman suggested many politicians in the state want to bring something positive to Illinois, and to bring in the extra revenue that fracking could generate.

When asked how fracking could potentially impact renewable energy in the state, Barickman responded, "Dollars that are generated through fracking will be reused in research and development that could go into increasing the renewable energy portfolio at large." Overall, by using hydraulic fracturing as a replacement for coal for production of electricity, this has allowed for opportunities for governments to plan and practice for less environmental affects since coal produces a lot more negative environmental effects than shale (North et al., 2014). Some of these negative environmental effects of coal include air pollution and carbon dioxide, and shale gas from hydraulic fracturing is found to emit half the amount of $CO_2$ compared to coal when generating electricity (North et al., 2014). However, hydraulic fracturing doesn’t come without its own controversy with negative environmental impacts. These negative impacts can include the following: contamination of water sources, air pollution from methane gas, noise from drilling, and increased earthquake activity due to wastewater injection, often associated with hydraulic fracturing (Loomis and Haefele, 2017). One of the most controversial of these is water pollution, where a lot of the water that is used to inject in the ground can interfere with drinking water sources, and even can come back up to the surface, bringing new contaminants with it, possibly contaminating sources of drinking water (Rabe, 2014). Another study has shown that 1-3% of houses within 1 mile of well sites see contaminated drinking water, air pollution, noise from drilling, and truck traffic which can lower property value (Loomis and Haefele, 2017). More specifically, Illinois law states that well sites must be 500 feet away from any residents, places of worship, schools or hospitals. The wells must also be 1500 feet away from any surface water and/or groundwater for public drinking.

States range from banning hydraulic fracturing completely such as New York, while other such as North Dakota encourage it (Rabe, 2014), and this brings up the topic of why the states are put in the position to decide the best way to regulate hydraulic fracturing instead of the federal government. Sen. Brickman said that each state is culturally different, which is why many states want to control regulation of fracking. When asked whether the federal government should have more of a role in regulating fracking he responded with, “[My] initial reaction would be no, let the states make these decisions based on the uniqueness and the traits that the people of these states [have] because if you try and blanket over the entire country you won't recognize the difference between a New Yorker and Illinoisan and Californian and North Dakotan." He also expressed that it would be difficult for the federal government to design a law that would fit every state's needs and wants, making it more reasonable to make laws at the state level instead.

The application for a company to get a permit for hydraulic fracturing shows the discretion is given to the Illinois Department of Natural Resources (IDNR). If there are any accidents that exceed the $5,000,000 insurance required for a permit, the IDNR and the director are in charge of how that cost will be covered. Sen. Barickman expressed the legislator of the state makes the law, and then the governor implements the law with the state industries (such as IDNR). It comes down to the governor and the state industries to make rules and regulations, and to enforce them. It is possible that a permit for fracking can be rejected by the municipality it is located in. Further regulation requires tests for cement strength, VOCs, heavy metals, NORMs, well strength, water quality, and other environmental and health impacts, according to the Illinois Hydraulic Fracturing Regulatory Act. According to the article, "Illinois' first fracking permit returned by Kansas company, citing 'costly' regulations." by the Associated Press, Woolsey Company announced that they would not use the permit they obtained because of the "state's burdensome and costly regulations." This process was said to be very strict, and it would not change for any potential applicants in the future.

Interviews to be done in the future include interviewing other politicians and those from the IDNR to better understand the differing political views on hydraulic fracturing and the rules and regulations in place for companies with permits.

## *Conclusion*

This study determined that solid bitumen and vitrinite can be easily confused with one another, and can cause the analysis of thermal maturity to be inaccurate. The presumption is that the original vitrinite reflectance measurements taken on these samples by the Illinois State Geological Survey, may have been collected on solid bitumen, causing the original reflectance data to be lower than the analysis done for this study. By measuring the solid bitumen instead of vitrinite, the ISGS measurements were found to be ~0.3% below the vitrinite reflectance taken for this study. Additional analysis on these samples should be performed to confirm this. Thermal maturity increases towards the southeast, with $\lambda_{max}$ wavelength increasing, Q* increasing, $\lambda_{max}$ intensity decreasing, and vitrinite reflectance increasing. The change in the color and intensity of telalginite fluorescence with increased vitrinite reflectance is also observed, with the color changing from a bright green/yellow, to yellow, to orange, and then to a dull brown. Samples NAS 233, 376, 128, and 184 exhibit fluorescence in the range of vitrinite reflectance from 0.68-0.81%, but fluorescence disappears around 1.2% reflectance, close to where the oil window ends and the gas window begins. Fluorescence is a reliable indicator of the thermal maturity of the New Albany Shale; additional analysis should be done to confirm these observations.

Determining the relationship between spectral fluorescence and vitrinite reflectance as a thermal maturity indicator could help those in the industry tasked with determining the oil or gas potential in the New Albany Shale, and other organic-rich shales in the country by using another rank parameter. This can also prevent costly mistakes, causing companies, and potentially state and local governments, economic loss. Calculated vitrinite reflectance measurements of the New Albany Shale indicate potential for oil or gas extraction, through hydraulic fracturing. Hydraulic fracturing in the state of Illinois is motivated by lawmakers for its opportunity to bring jobs and revenue to the state, but can also come with its own challenges with negative environmental impacts. Because of the tight regulations established by the state, the first permit obtained by a company will not be used, apparently due to the state's strict rules and regulations.

# References Cited

Associated Press, 2017. Illinois' first fracking permit returned by Kansas company, citing 'costly' regulations. Chicago Tribune. November 3rd, 2017 publication.

Barrows, M., Cluff, R., Harvey, R.D., 1981. Petrology and maturation of dispersed organic matter in the New Albany Shale Group of the Illinois Basin: Reprint 1979-N, Champaign, Illinois, Illinois State Geological Survey, 25 pp.

Bertrand, R., 1993. Standardization of Solid Bitumen Reflectance to Vitrinite in Some Paleozoic Sequences of Canada. Energy Sources 15, (2), 269-287.

Brown, T.H., 2014. Fracking fuels an economic boom in North Dakota. Forbes. Jan. 29, 2014 publication.

Cardott, B.J., Landis, C.R., Curtis, M.E., 2015. Post-oil solid bitumen network in the Woodford Shale, USA - A potential primary migration pathway. International Journal of Coal Geology 139, 106-113.

Cluff, R.M., Dickerson, D.R., 1982. Natural Gas Production of the New Albany Shale Group (Devonian-Mississippian) in Southeastern Illinois. Society of Petroleum Engineers Journal, 291-300.

Landis, C.R., Castaño, J.R., 1995. Maturation and bulk chemical properties of a suite of solid hydrocarbons. Organic Geochemistry 22, 137-149.

Loomis, J., Haefele, M., 2017. Quantifying Market and Non-market Benefits and Costs of Hydraulic Fracturing in the United States: A Summary of the Literature. Ecological Economics 138 (C), 160-167.

North, D.W., Stern, P.C., Webler, T., Field, P., 2014. Public and Stakeholder Participation for Managing and Reducing the Risks of Shale Gas Development. Environmental Science Technology 48, 8388-8396.

Nuccio, V.F., Hatch, J.R., 1996. Vitrinite reflectance suppression in the New Albany Shale, Illinois Basin. U.S.G.S Open-File Report 96-665, 37 pp.

Price, L.C., Barker, C.E., 1985. Suppression of Vitrinite Reflectance in Amorphous Rich Kerogen-A Major Unrecognized Problem. Journal of Petroleum Geology 8, 59-84.

Rabe, B., 2014. Shale play politics: The intergovernmental odyssey of American shale governance. Environmental Science Technology 48, 8369-8375.

Rimmer, S.M., Cantrell, D.J., Gooding, P.J., 1993. Rock-Eval pyrolysis and vitrinite reflectance trends in the Cleveland Shale Member of the Ohio Shale, eastern Kentucky. Organic Geochemistry 20, 735-745.

Rimmer, S.M., Thompson, J.A., Goodnight, S.A., Robl, T.L., 2004. Multiple controls on the preservation of organic matter in Devonian-Mississippian marine black shales: geochemical and petrographic evidence. Palaeogeography, Palaeoclimatology, Palaeoecology 215, 125-154

Schoenherr, J., Littke, R., Urai, J.L., Kukla, P.A., Rawahi, Z., 2007. Polyphase thermal evolution in the Infra-Cambrian Ara Group (South Oman Salt Basin) as deduced by maturity of solid reservoir bitumen. Organic Geochemistry 38, 1293-1318.

Strapoc, D., Mastalerz, M., Schimmelmann, A., Drobniak, A., Hasenmueller, N.R., 2010. Geochemical constraints on the origin and volume of gas in the New Albany Shale (Devonian-Mississippian), eastern Illinois Basin. AAPG Bulletin 94, 1713-1740.

Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Robert, P., 1998. Organic Petrography. Gebruder Borntraeger.

Thomas, J.Jr., Damberger, H.H., 1976. Internal Surface Area, Moisture Content, and Porosity of Illinois Coals: Variations with Coal Rank. I.S.G.S. Report Circular No. 493.

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. International Journal of Coal Geology, 128, 222-236.

Werner-Zwanziger, U., Lis, G., Mastalerz, M., Schimmelmann, A., 2005. Thermal Maturity of type II kerogen from the New Albany Shale assessed by $^{13}$C CP/MAS NMR. Solid State Nuclear Magnetic Resonance 27, 140-148.

Woodrow, D.L., 1985. Paleogeography, Paleo-climate, and Sedimentary Processes of the Late Devonian Catskill Delta. Geological Society of Amererica Special Paper 201, 51-63.

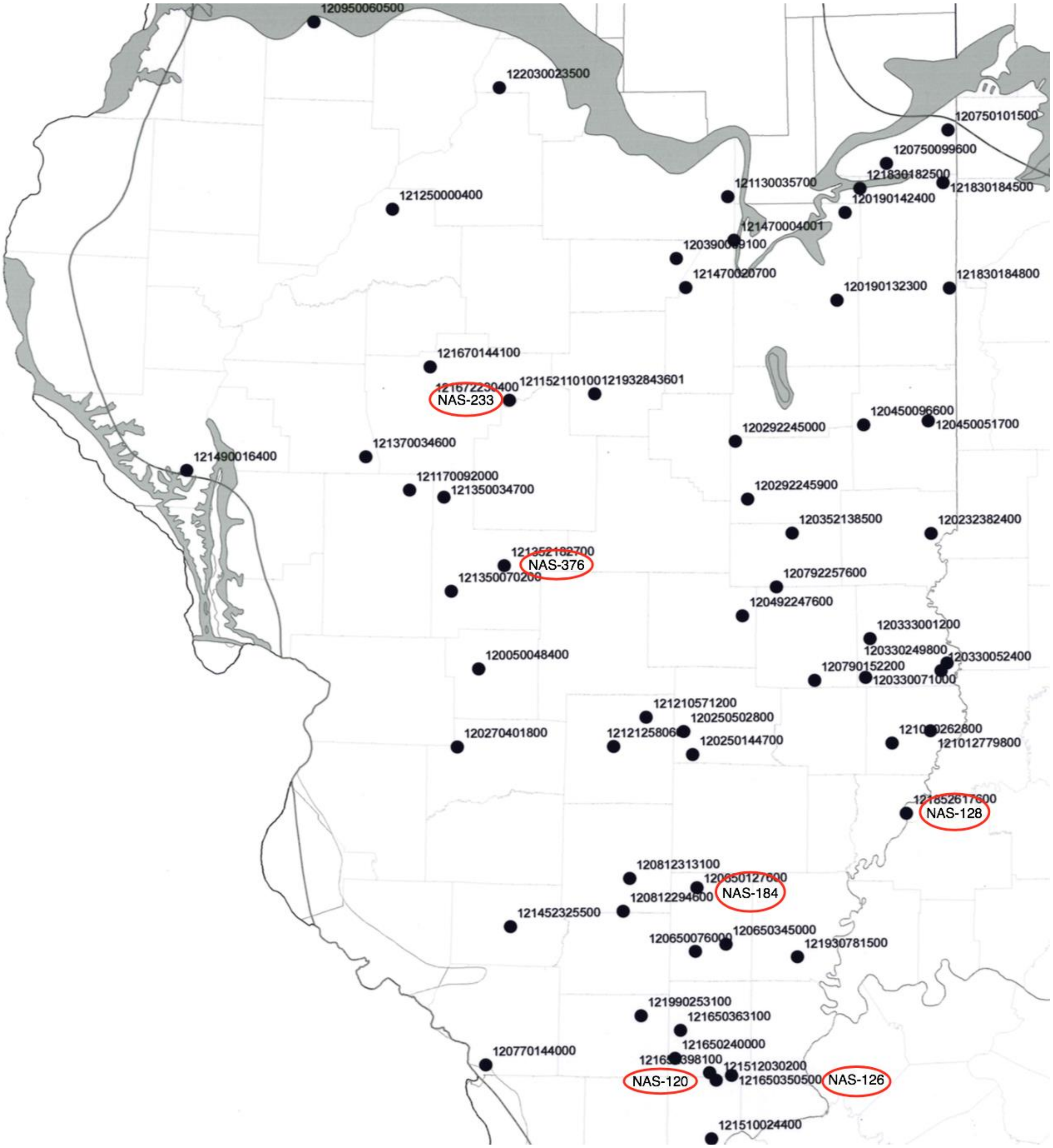
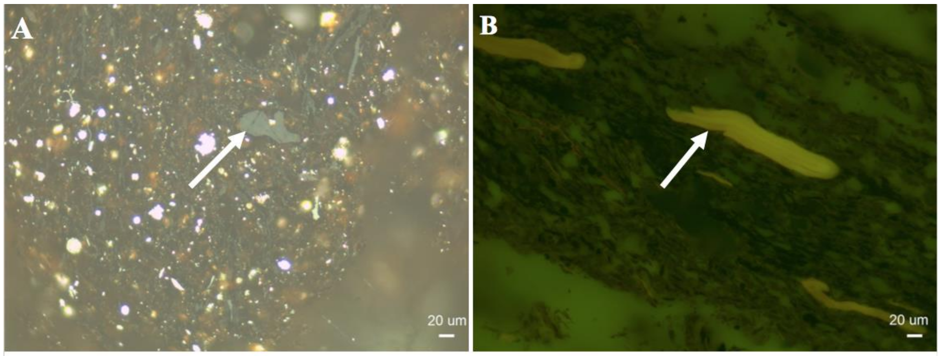


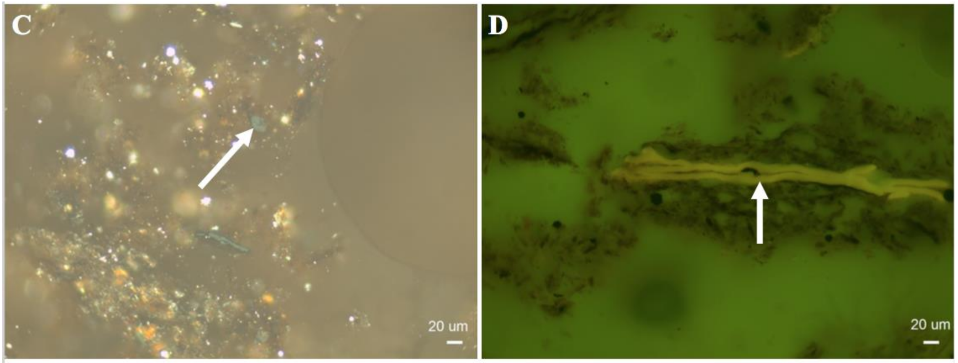
**Figure 1.** Map of the Illinois Basin showing samples used in the study circled in red. The far northwestern sample is NAS 233 and the far southeastern sample is NAS 126. (Base map: courtesy of the Illinois State Geological Survey).

**Figure 2.**



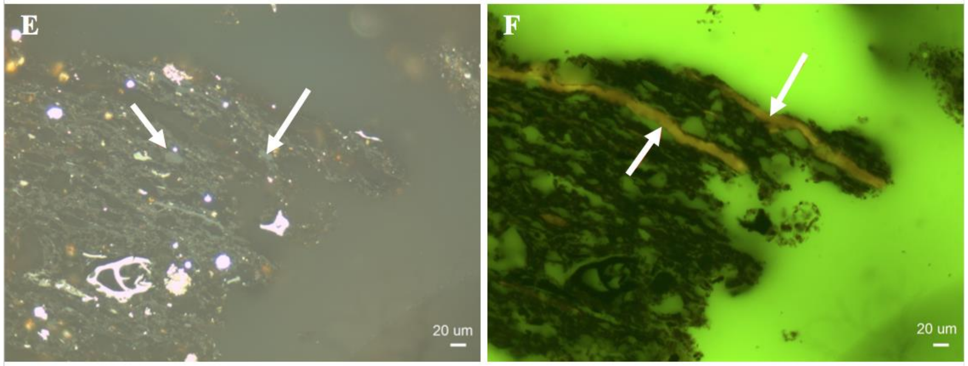
NAS 233, solid bitumen in white light

NAS 233, telalginite in blue light



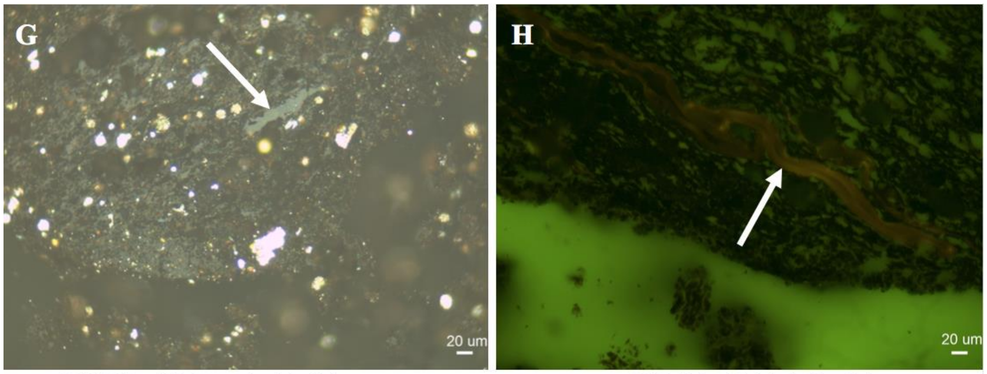
NAS 376, solid bitumen in white light

NAS 376, telalginite in blue light



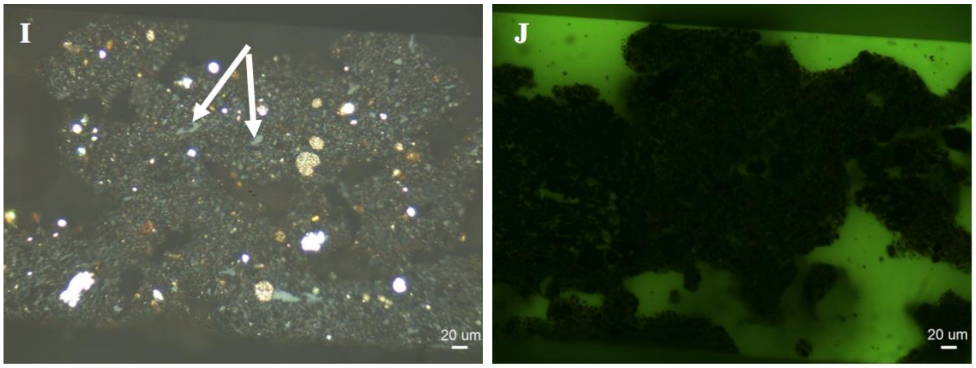
NAS 128, solid bitumen in white light

NAS 128, telalginite in blue light



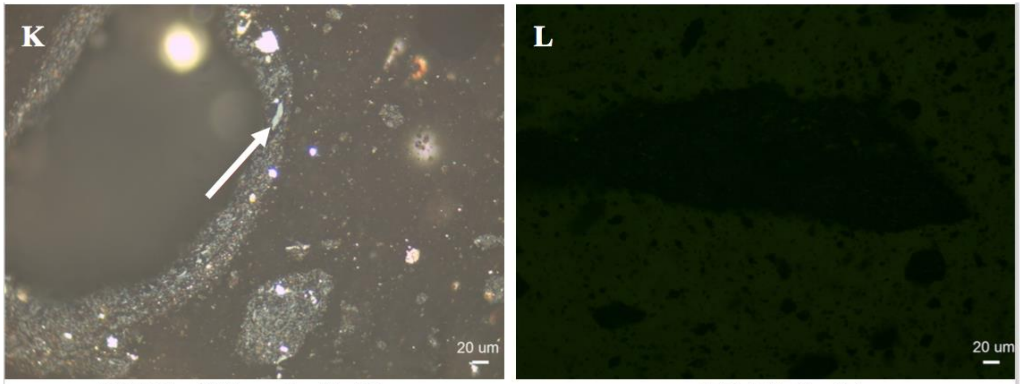
NAS 184, solid bitumen in white light

NAS 184, telalginite in blue light



NAS 120, solid bitumen in white light

NAS 120 in blue light



NAS 126, solid bitumen in white light

NAS 126 in blue light

**Figure 2.** Photomicrographs showing change in NAS macerals with increased maturity. This is expressed with the solid bitumen reflectance increasing (A, C, E, G, I, and K) and the fluorescence changing from a bright green yellow (B), to a duller yellow (D and F), to a very dull orange/brown (H), and to no fluorescence (J and L).

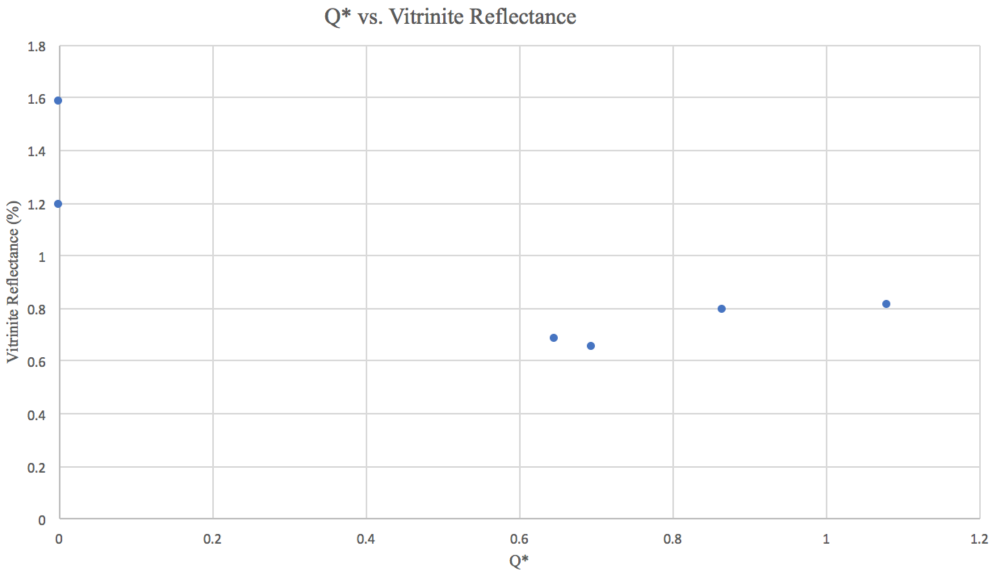


**Figure 3.** Relationship between Q* (relative intensity at 650 nm/relative intensity at 550 nm) and vitrinite reflectance. Q* is shown to increase with the increase of vitrinite reflectance. Q* of samples NAS120 and NAS128 could not be determined since there was no fluorescence.

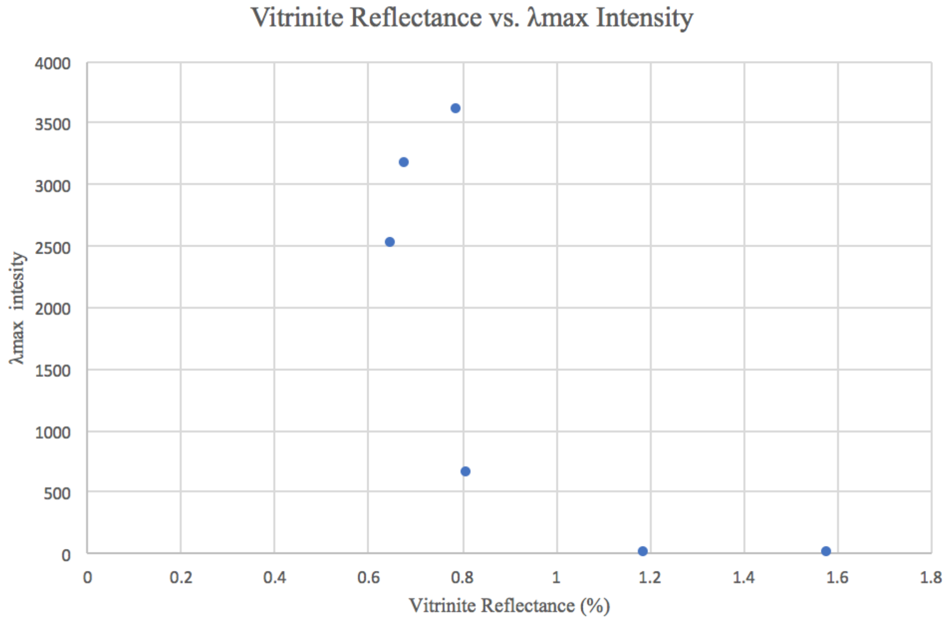


**Figure 4.** Relationship between $\lambda_{max}$ intensity and vitrinite reflectance. $\lambda_{max}$ intensity is shown to increase with samples NAS233, 376, and 128, with a sudden decrease in $\lambda_{max}$ intensity with sample 184 as vitrinite reflectance increases. The $\lambda_{max}$ intensity of NAS120 and NAS128 could not be determined since fluorescence was not visible.

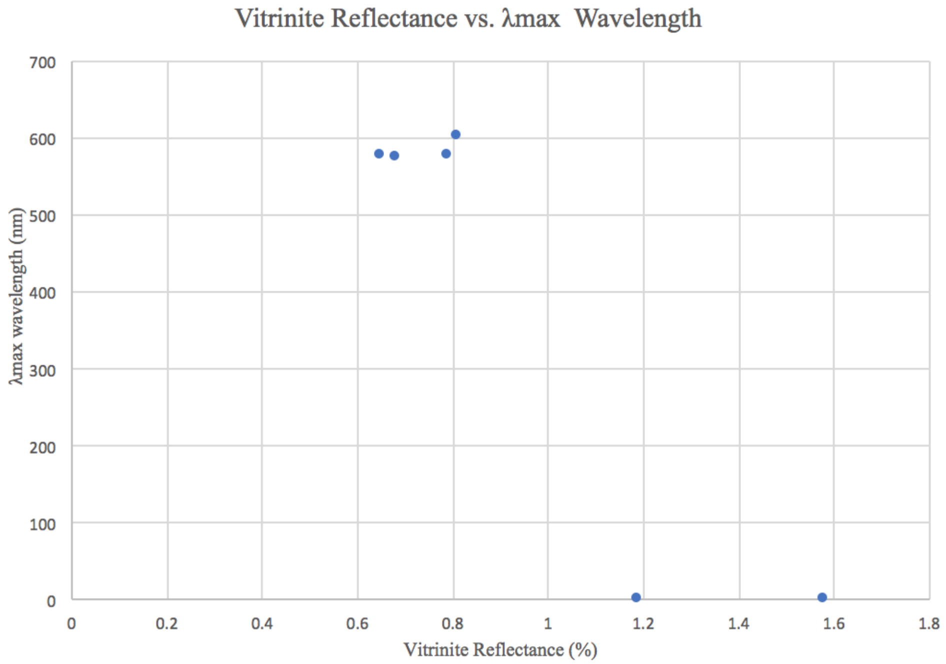
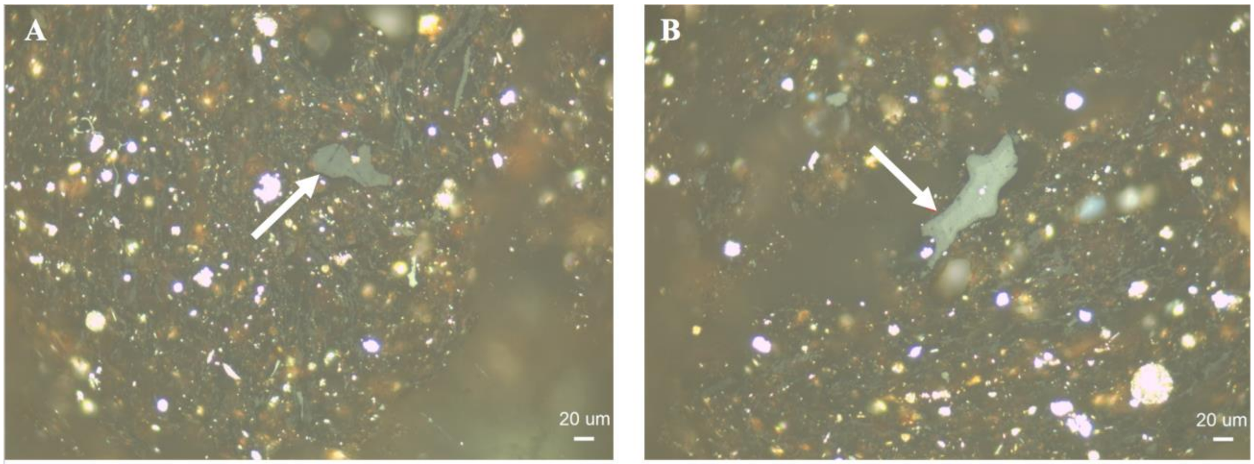


**Figure 5.** Relationship between $\lambda_{max}$ wavelength and vitrinite reflectance. $\lambda_{max}$ wavelength for the samples NAS233, 376, and 128 is shown to be very close together, with NAS 184 having a higher $\lambda_{max}$ wavelength value. Overall, the $\lambda_{max}$ wavelength increases with increased vitrinite reflectance. The $\lambda_{max}$ wavelength of NAS120 and 128 could not be determined since fluorescence was not visible.



NAS 233, solid bitumen in white light

NAS 233, vitrinite in white light

**Figure 6.** Photomicrograph A and B demonstrate the difference in reflection, visually between the solid bitumen (on left) and weathered vitrinite (on right) in the same sample, NAS 233. This difference is observed to be ~0.30% based on data collected during this study and by the Illinois State Geological Survey.

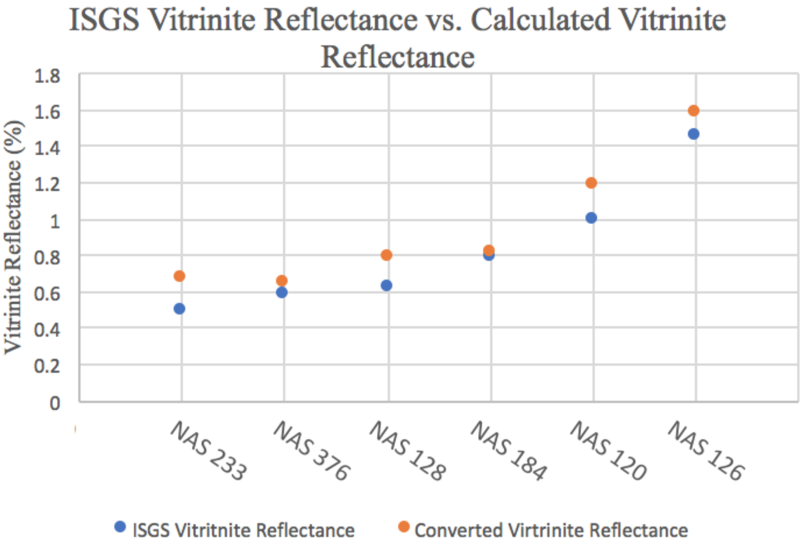


**Figure 7.** ISGS-collected vitrinite reflectance (in blue) versus calculated vitrinite reflectance (in orange) from this study. Vitrinite reflectance was calculated using Schoenherr's equation of Ro=(Bro+0.2443)/1.0495 (Schoenherr et al., 2007). In four of the six samples (NAS 233, 128, 120, and 126) the difference in vitrinite reflection is ~0.3%.

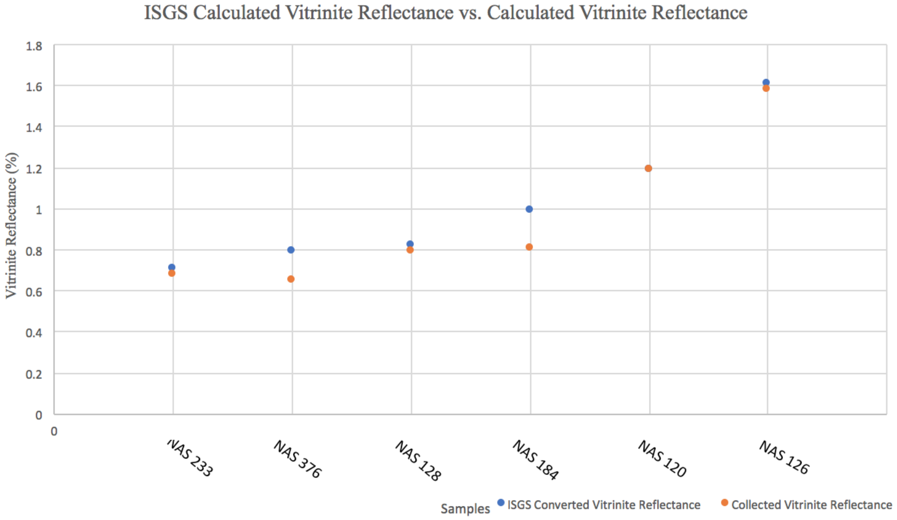


**Figure 8.** ISGS-calculated vitrinite reflectance (in blue) and the calculated vitrinite reflectance from this study (in orange). The ISGS-calculated vitrinite reflectance uses the same equation for the calculated reflectance of the vitrinite reflectance taken during this study (Schoenherr et al., 2007). Four of the six samples (NAS 233, 128, 120, and 126) express little difference in vitrinite reflectance (<0.05%).

| Sample | ISGS Vit. Ro. (%) | Solid Bitumen Ro (%) | Vit. Ro (%) | Calc. VRo (%) |
|---|---|---|---|---|
| NAS 233 | 0.50 | 0.47 | | 0.68 |
| NAS 376 | 0.58 | 0.44 | 0.71 | 0.65 |
| NAS 128 | 0.62 | 0.59 | | 0.79 |
| NAS 184 | 0.79 | 0.61 | 0.82 | 0.81 |
| NAS 120 | 1.00 | 1.00 | | 1.19 |
| NAS 126 | 1.45 | 1.41 | 1.76 | 1.58 |

**Table 1.** Vitrinite and solid bitumen data for NAS samples. ISGS Vit. Ro is the original data supplied by the Illinois State Geological Survey; Solid Bitumen Ro. and Vit. Ro are the solid bitumen and vitrinite reflectance measurements, respectively; Calc. VRo is the calculated vitrinite reflectance using Schoenherr's equation, Ro=(BRo+0.2443)/1.0495 (Schoenherr et al. 2007).

| Sample | 550 nm | 650 nm | Q* | $\lambda_{max}$ wavelength (nm) | $\lambda_{max}$ intensity |
|---|---|---|---|---|---|
| NAS 233 | 2930.70 | 1759.70 | 0.64 | 574.80 | 3158.80 |
| NAS 376 | 2261.60 | 1552.50 | 0.70 | 575.60 | 2525.40 |
| NAS 128 | 3200.80 | 2716.60 | 0.87 | 576.20 | 3596.90 |
| NAS 184 | 547.50 | 585.70 | 1.10 | 600.60 | 653.30 |
| NAS 120 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| NAS 126 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

**Table 2.** Spectral fluorescence data for telalginite in NAS samples. The averaged intensity measurement was acquired at 550 nm and 650 nm; Q* is the averaged relative intensity at 650 nm divided by the relative intensity at 550 nm; $\lambda_{max}$ wavelength is the averaged maximum wavelength taken in nm; $\lambda_{max}$ intensity is the averaged intensity of the maximum wavelength.