

Rock-Eval pyrolysis and vitrinite reflectance trends in the Cleveland Shale Member of the Ohio Shale, eastern Kentucky

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Abstract—Within eastern Kentucky, organic petrographic and geochemical data indicate a southeastwards increase in maturation of the Cleveland Shale Member of the Ohio Shale (Devonian–Mississippian). Reflectance levels of dispersed organic material in the Cleveland Shale increase from 0.5% in the outcrop belt in central Kentucky, to slightly over 1.0% in Pike County, eastern Kentucky. A decrease in fluorescence intensity of liptinitic components, such as *Tasmanites*, accompanies this reflectance increase, as does a shift in fluorescence color of the alginite towards the red. In the highest rank areas, fluorescence is almost absent. Groundmass fluorescence is observed also, and follows trends similar to those shown by the alginite.

Kerogen in the Cleveland Shale is primarily Type II, as indicated by petrographic observations and Rock-Eval data. Total organic carbon contents of this shale decrease from over 12% in the outcrop belt, to less than 2% in the eastern-most part of the study area. Source rock potential ranges from good to very good, with the highest potentials occurring in the outcrop belt. T_{\max} values for this unit increase from under 430°C in the outcrop belt to over 450°C in the southeast, confirming the increase in maturation trends indicated by vitrinite reflectance data.

Both petrographic and geochemical maturation parameters place the Cleveland Shale of eastern Kentucky within the oil window. Comparison with maturation data for Pennsylvanian-age coals upsection suggests that maturation indices are retarded, or suppressed, in the Devonian shales. The level of maturation indicated for the Cleveland may be problematical considering that the Ohio Shale is a major gas-producer in this area.

Key words—maturation, kerogen, Devonian Shale, vitrinite suppression, organic petrology

INTRODUCTION

This paper presents total organic carbon (TOC) and Rock-Eval pyrolysis data for the Cleveland Member of the Ohio Shale (eastern Kentucky), and compares these data to vitrinite reflectance values. This is part of an ongoing study of the Devonian–Mississippian shales of Kentucky, the objectives of which are to evaluate depositional and maturation controls on the petrographic and geochemical characteristics of these sediments, and to relate maturation levels and source rock type to oil and gas potential.

Previous work in this laboratory has suggested that suppression of vitrinite reflectance may occur in the Cleveland Shale, and that levels of organic maturation determined from reflectance data may be lower than anticipated (Rimmer and Cantrell, 1989). In the present study, Rock-Eval pyrolysis was performed on the Cleveland Shale in order to confirm the maturation level and to evaluate the source rock potential and type of organic matter present in this shale.

Geologic setting

The organic-rich Devonian–Mississippian shales of the Appalachian Basin have been studied extensively in terms of stratigraphy, paleoenvironments, and tectonics (Ettensohn, 1979; Ettensohn *et al.*, 1981; Ettensohn, 1985a, b). The shales have been inter-

preted as deep basinal facies of the Catskill Delta (Woodrow, 1985). Within the basin, black organic-rich shales accumulated under anaerobic conditions; intervals of bioturbated greenish-gray shales reflect dysaerobic to marginally aerobic conditions (Barron, 1982). Within this basin sedimentation and accumulation of organics were controlled by paleogeography, paleoclimate, and tectonic activity as they influenced sediment input and development of a stratified water column (Ettensohn, 1985).

The Devonian shales crop out in the Knobs region of central Kentucky, surrounding Ordovician sediments of the Bluegrass area, and along the Cincinnati Arch of southern Kentucky. From the outcrop belt, the Devonian shales dip into the subsurface towards the east (into the Appalachian Basin) and also to the west (into the Illinois Basin). Within eastern Kentucky, the shale dips from the outcrop belt towards the southeast where maximum present-day burial depths reach 730 m (Dillman, 1980). Thicknesses of the shale sequence range from 35 to 60 m in the outcrop belt to approx. 460 m in eastern Pike County (Dillman, 1980).

Total organic content (TOC) of the black shales can be as high as 15–20 wt %, with gray shale units having lower organic contents (Conant, 1961; Potter *et al.*, 1980; Schmoker, 1980). Within eastern Kentucky, TOCs for the black, organic-rich shale units

decrease towards the east; for example, the Lower Huron decreases from 10 to 3% (Potter *et al.*, 1980). With respect to type and source, organic matter in the Ohio Shale is varied, and includes a predominantly marine assemblage with minor amounts of terrestrial input. Ettensohn (1985) suggested that the black shales accumulated during times of transgression, which were associated with high organic and nutrient input, resulting in an abundance of marine planktonic organisms. Large quantities of organics accumulated and were preserved under anoxic conditions produced by a stratified water column, and in the absence of either benthonic fauna or substantial clastic influx (Ettensohn, 1985). Maynard (1981) showed that the black units contained more organic matter of marine origin than the lighter shales which have lower organic contents and a higher proportion of humic material. He also indicated an increase in terrestrial carbon towards the northeast. These shales can be described as marinite shales, indicating that they contain a predominance of marine-derived kerogen, although land-derived components (vitrinite, fusinite, and sporinite) can be observed also (Hutton, 1987; Robl *et al.*, 1987). Terrestrial material would have been derived from the diverse floras of the Catskill Delta, including some of the arborescent

forms such as *Archaeopteris*, *Lepidosigillaria*, and *Eospermatopteris* (Banks *et al.*, 1985).

METHODS

Sampling and petrographic analysis

Samples were collected from cores and cuttings from eastern Kentucky in an area that extends from the outcrop belt towards the east and southeast where the shales are buried at increasingly greater depths (Fig. 1). Members of the Ohio Shale were identified using gamma-ray and formation density logs, published lithologic descriptions and visual inspection (Ettensohn *et al.*, 1979). The current paper is restricted to data collected on samples obtained from the Cleveland Shale Member.

Splits of each sample were crushed to less than 2 mm. One portion of each crushed sample was mixed with epoxy resin to make two whole-rock petrographic pellets, which were ground and polished according to standard coal-polishing techniques (Stach *et al.*, 1982). Organic petrographic constituents were identified using both white- and blue-light reflectance microscopy, using the classification scheme presented by Hutton (1987). Mean random

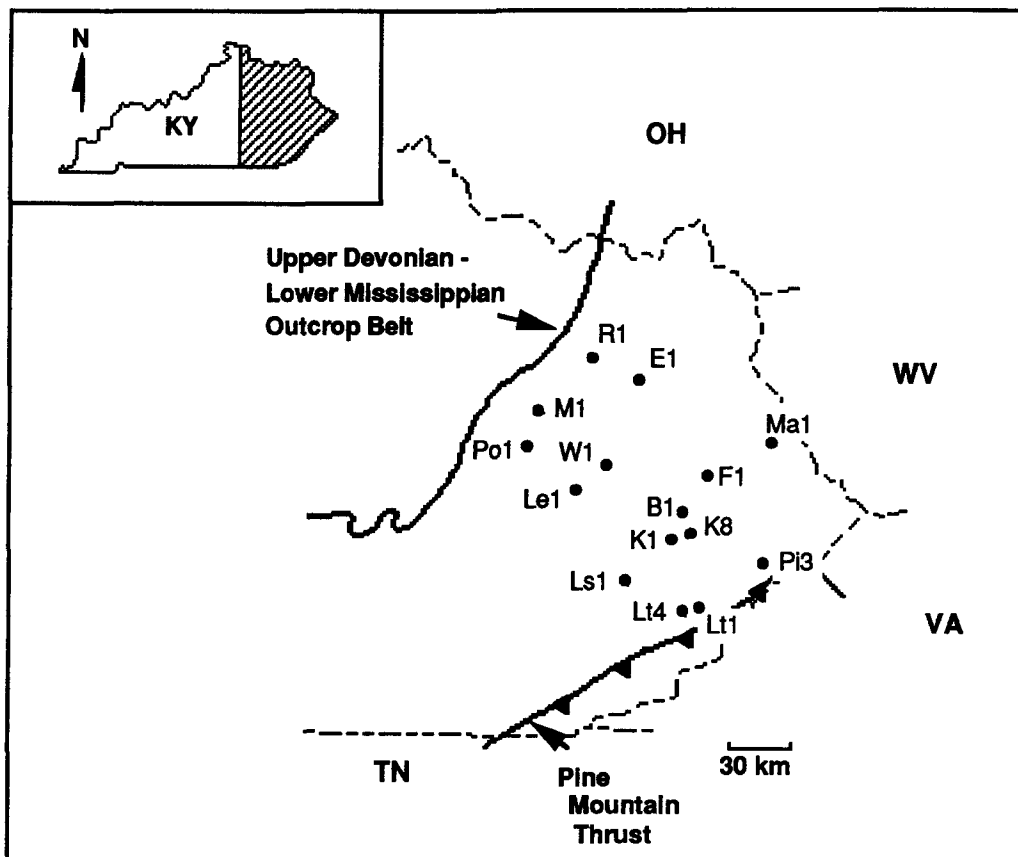


Fig. 1. Well locations for Cleveland Shale samples.

reflectance of vitrinite was determined according to established techniques, measuring 50 particles per sample (Dow and O'Connor, 1982). Obviously reworked material was avoided during the analysis and reflectance histograms were examined carefully to determine the primary vitrinite population. Means and standard deviations were determined after elimination of any obviously reworked material (Dow and O'Connor, 1982).

Rock-Eval pyrolysis

Rock-Eval pyrolysis provides information on the quantity and type of organic matter in a sedimentary rock, in addition to the level of organic maturation (Espitalié *et al.*, 1977). Pyrolysis techniques, such as Rock-Eval, mimic in the laboratory the natural hydrocarbon-generating processes that would occur within the earth at lower temperatures over longer time spans (Waples, 1985). Analyses were performed using a Rock-Eval II (Delsi, Inc.). Each sample was pulverized, and 80 mg was pyrolyzed in an inert atmosphere. Description of the pyrolysis method and use of Rock-Eval parameters are presented by Peters (1986) and Espitalié *et al.* (1977). Parameters used to determine quantity, type, and maturity of organics are shown in Table 1.

RESULTS

Petrography

Petrographically, the Cleveland Shale samples are dominated by alginite (both telaginite, including *Tasmanites*, and lamalginite) and bituminite, with minor amounts of vitrinite and inertinite. In addition, a considerable amount of fluorescing amorphous material appears to be associated with the inorganic groundmass. This agrees with previous petrographic obser-

vations on the Cleveland Member in the outcrop belt by Robl *et al.* (1987) who indicate a predominance of liptinitic material over inertinite and vitrinite. This composition implies, from a petrographic standpoint, that these samples contain Type II kerogen, according to criteria described by Tissot and Welte (1984).

Some vitrinite particles appeared degraded, others are somewhat oxidized. Reflectance measurements were restricted to particles that appeared to be well-preserved, well-polished, and did not exhibit any detectable fluorescence under blue-light illumination. Vitrinite reflectance increases from approx. 0.5% R_o in the outcrop belt to slightly over 1.0% R_o in eastern-most Kentucky (Fig. 2, Table 2). These values are in general agreement with reflectance levels and trends reported for the Lower Huron Member of the Ohio Shale by Curtis (1988).

Fluorescence of *Tasmanites* was observed during blue-light analysis. Fluorescence color of these algae changes from bright yellow in the outcrop belt to orange in the southeast. As the color shifts towards orange, fluorescence intensity decreases. This trend is to be expected considering the measured increase in vitrinite reflectance. Quantitative measurements of this fluorescence shift are part of this ongoing project and will be reported in a future paper.

In many samples, a weakly fluorescing groundmass was observed suggesting the presence of hydrogen-rich organic matter, possibly in association with inorganics such as clay minerals. The fluorescence of this groundmass decreased with increasing vitrinite reflectance. This type of fluorescing matrix has been described as "organo-mineral associations" or "fluorescent groundmass" (Robert, 1981). Robert (1988) noted that groundmass fluorescence disappears either before or towards the end of the oil window, between reflectances of 0.8 and 1.2%.

Table 1. Application of Rock-Eval Pyrolysis,* TOC, and vitrinite reflectance parameters in the assessment of the amount, type, and thermal maturity of organic matter (modified from Peters, 1986; additional data from Tissot and Welte, 1984; Tissot *et al.*, 1987)

Application	Parameters			
	Quantity	TOC (wt.%)	S1	S2
Source rock generative potential	Poor	0.0-0.5	0.0-0.5	0.0-2.5
	Fair	0.5-1.0	0.5-1.0	2.5-5.0
	Good	1.0-2.0	1.0-2.0	5.0-10.0
	Very good	> 2.0	> 2.0	> 10.0
	Type†	HI	S2/S3	
Type of hydrocarbon generated	Gas	0-150	0-3	
	Gas + oil	150-300	3-5	
	Oil	> 300	> 5	
	Maturation ±	PI	T_{max} (°C)	R_o (%)
Level of thermal maturation	Top of oil window	0.1	430-445 (430-435)	0.5
	Bottom of oil window	0.4	470 (450-455)	1.35 (1.1)

*Nomenclature: S1 = mg HC/g rock; S2 = mg HC/g rock; S3 = mg HC/g rock; HI = mg HC/g Corg; PI = S1/(S1 + S2).

†Assumes level of thermal maturation equivalent to $R_o = 0.6\%$.

± Values are approximate. Many parameters (particularly T_{max}) are dependent on the type of organic matter. Values in parentheses are for Type II kerogen.

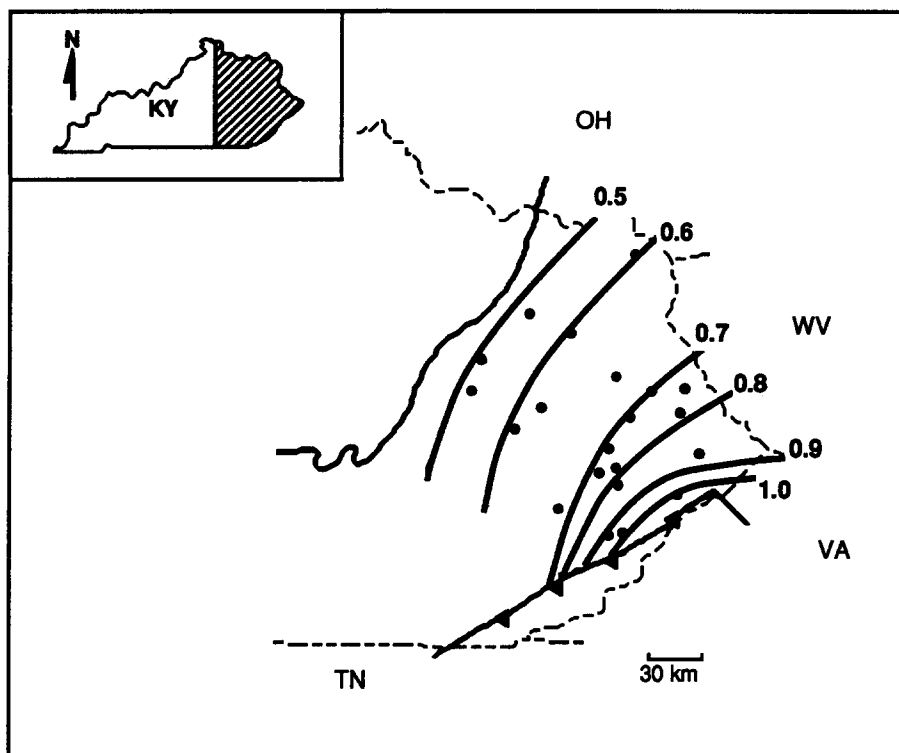


Fig. 2. Mean random vitrinite reflectance (% R_o , in oil) for the Cleveland Shale (from Rimmer and Cantrell, 1989).

Geochemical analyses

Geochemical data will be discussed in terms of source rock generative potential, type of organic matter, and level of organic maturation following criteria indicated in Table 1.

Source rock generative potential. Total organic carbon contents for these Cleveland Shale samples vary from 11 to 14% in the outcrop belt to less than 2% in easternmost Kentucky (Table 2, Fig. 3). Although these samples represent small intervals (3–9 m) within the Cleveland Shale, these values and

trends agree with those reported previously for the black shales in this region (Potter *et al.*, 1980). Relative to source rock generative potential (Peters, 1986) (see Table 1), these TOC levels put the Cleveland Shale in a good category in eastern Kentucky, to the very good category towards the outcrop belt.

S1 values indicate the amount of hydrocarbons (mg HC/g rock) that are present in the rock in a free or adsorbed state; S2 values represent the potential to generate hydrocarbons (mg HC/g rock) through thermal decomposition of the kerogen (Waples, 1985; Peters, 1986). S1 values for the Cleveland (Table 2)

Table 2. Mean Random Vitrinite Reflectance (R_o , %, in oil), Total Organic Carbon (weight %), and Rock-Eval Pyrolysis Data* for Cleveland Shale Samples from Eastern Kentucky

Sample No.	Well No.	County	Depth (m)	R_o (%)	TOC (wt%)	T_{max} (°C)	S1	S2	S3	PI	S2/S3	HI	OI
DS-1	B1	Breathitt	-304	0.66	6.18	439	2.53	30.22	0.69	0.08	43.79	488	11
DS-2	E1	Elliot	-18	0.55	3.80	431	1.12	18.84	0.61	0.06	30.88	495	16
DS-3	F1	Floyd	-188	0.56	5.00	440	1.95	26.78	0.57	0.07	46.98	535	11
DS-4	K1	Knott	-403	0.70	7.35	443	3.25	27.96	0.46	0.10	60.78	380	6
DS-5	K8	Knott	-370	0.69	3.95	441	1.88	16.38	0.39	0.10	42.00	414	9
DS-6	Lel	Lee	-55	0.62	9.63	433	2.71	49.55	0.75	0.05	66.06	514	7
DS-7	Ls1	Leslie	-444	0.57	6.39	442	2.55	23.12	0.61	0.10	37.90	361	9
DS-8	Lt1	Letcher	-644	1.00	1.89	445	0.97	3.03	0.40	0.24	7.57	160	21
DS-9	Lt4	Letcher	-614	0.87	4.86	443	2.33	9.15	0.62	0.20	14.75	188	12
DS-10	Ma1	Martin	-463	0.65	4.72	443	1.90	20.56	0.59	0.08	34.84	435	12
DS-11	M1	Montgomery	247	0.50	11.35	428	2.78	57.37	1.49	0.05	38.50	505	13
DS-12	Pol	Powell	209	0.53	14.19	427	3.37	70.75	2.01	0.05	35.19	498	14
DS-13	R1	Rowan	253	0.49	12.00	431	2.80	67.45	1.66	0.04	40.63	562	13
DS-14	W1	Wolfe	-64	0.65	8.21	434	2.66	42.33	0.87	0.06	48.65	515	10
DS-16	Pi3	Pike	-659	1.00	1.20	456	0.52	1.25	0.66	0.30	1.89	104	55

*Nomenclature: S1 = mg HC/g rock; S2 = mg HC/g rock; S3 = mg CO_2 /g rock; PI = S1/(S1 + S2); HI = mg HC/g C_{org} ; OI = mg CO_2 /g C_{org} .

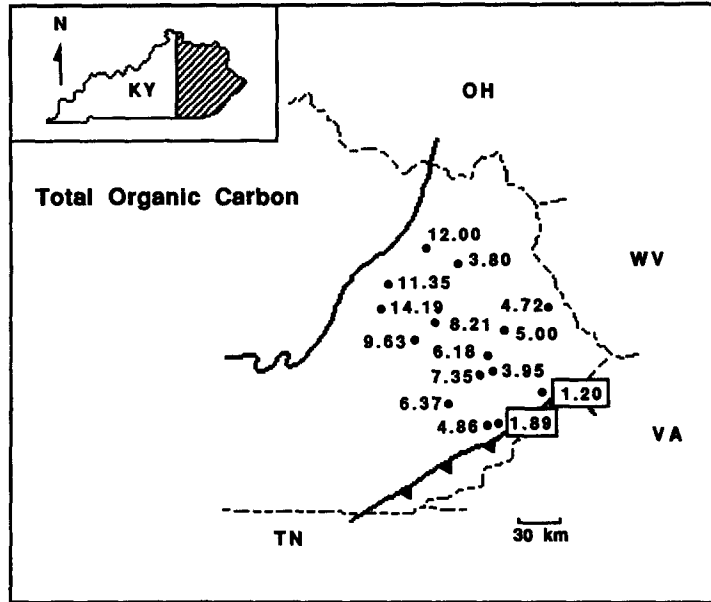


Fig. 3. Total organic carbon contents (TOC, wt %) for Cleveland Shale samples, eastern Kentucky.

indicate a fair to good source rock potential in easternmost Kentucky. In the outcrop belt (R1, M1, and Po1), S1 values are over 2.0; the lowest S1 values (< 1.0) are seen in samples that are closest to the Pine Mountain Thrust (Pi3 and Lt1). An eastwards decrease is also seen in S2: samples in the outcrop belt have values between 50 and 70, whereas Pi3 and Lt1 (along Pine Mountain) have values of 1.25 and 3.03, respectively (Table 2). Samples which have the lowest S2 values are also the highest rank samples (Fig. 4).

Type of organic matter. The type of organic matter can be determined from a plot of the hydrogen index (HI) versus the oxygen index (OI), where HI is $(S2/TOC)100$, OI is $(S3/TOC)100$, and S3 is mg

CO_2/g rock (Espitalié *et al.*, 1977). As calculated, these indices are independent of the total amount of hydrocarbons present, and are closely related to the elemental composition of the kerogen. The strong correlation between the hydrogen index and the H/C ratio, and between the oxygen index and the O/C ratio, makes it possible to plot HI versus OI as a modified van Krevelen diagram (Espitalié *et al.*, 1977).

For most of our samples, Type II (and some Type I) kerogen is suggested by such a plot (Fig. 5). Trends in HI and OI for kerogen types with increasing

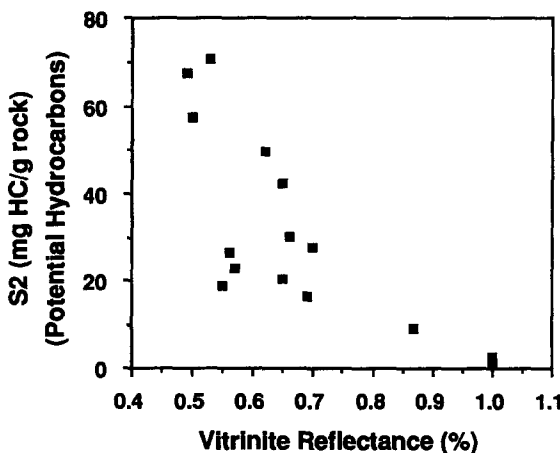


Fig. 4. Plot of S2 (potential hydrocarbons, mg HC/g rock) versus vitrinite reflectance (% R_o , in oil), Cleveland Shale.

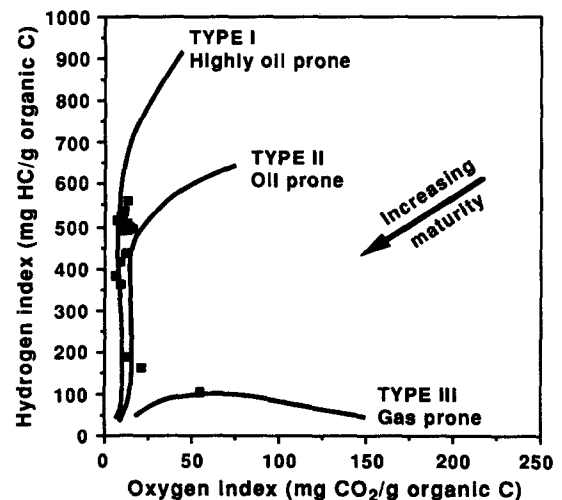


Fig. 5. Crossplot of oxygen index (OI) vs hydrogen index (HI) showing hydrocarbon generative types for the Cleveland Shale.

thermal maturity are indicated by the heavy lines in Fig. 5, with the most mature samples plotting towards the lower left hand corner (Peters *et al.*, 1986). Most of the samples have hydrogen indices above 300 (Table 2), which would suggest a kerogen that is oil prone. Pi3 appears to be gas prone (Type III). Two other samples (Lt1 and Lt4) have low hydrogen indices and plot close to the Type III area. Wells Pi3, Lt1, and Lt4 are in areas that have a higher level of maturation (Fig. 2, Table 2), and the HI values may reflect rank rather than original composition. These three samples plot in the bottom right corner of Fig. 6. Type II kerogen is also indicated by a plot of HI versus T_{\max} (Fig. 7).

These geochemical data are in agreement with our petrographic observations, and with previous work which suggested a range in composition between Type II and Type I for maceral concentrates of the Cleveland Shale within the outcrop belt (Robl *et al.*, 1987). These authors indicated that samples which plotted in the Type I field were alginite-rich maceral fractions; much of the remaining material was bituminite which plotted in the Type II field. Minor amounts of vitrinite present in their samples plotted between the Type II and Type III fields.

Level of organic maturation. The level of organic maturation can be estimated using T_{\max} (°C) and the production index (PI) (Table 1). The oil and gas thresholds tend to be dependent upon kerogen type (Dow, 1977; Tissot and Welte, 1984; Peters, 1986). The use of T_{\max} as a maturation parameter is reviewed by Tissot *et al.* (1987). T_{\max} , while not recommended for use with Type I kerogens, is considered to be a good maturation index in Type II and III kerogens. For Types II and III, T_{\max} values for the oil threshold are 430–435°C, while the gas threshold occurs at approx. 450–455°C for Type II and 465–470°C for Type III.

T_{\max} ranges from less than 430°C in the outcrop belt to over 450°C close to Pine Mountain Thrust

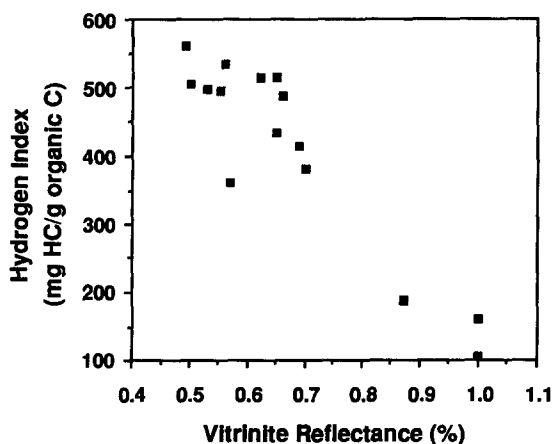


Fig. 6. Plot of hydrogen index (HI) vs vitrinite reflectance (% R_o , in oil), Cleveland Shale.

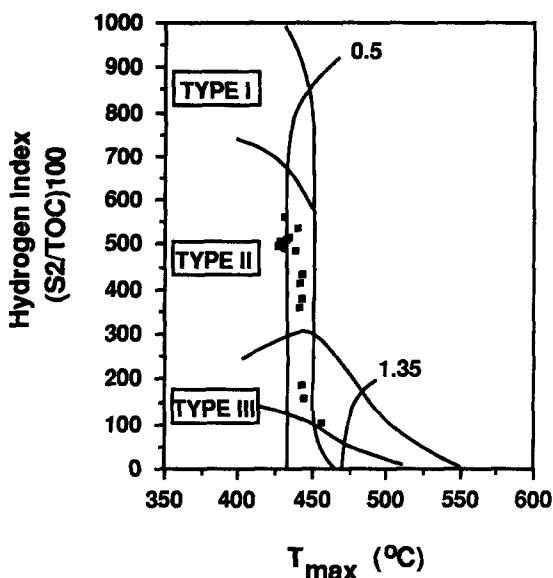


Fig. 7. Crossplot of T_{\max} (°C) vs hydrogen index (HI), Cleveland Shale.

(Fig. 8). Assuming a Type II kerogen, this places most of the study area within the oil window. In the outcrop belt, R1, M1, and Po1 show T_{\max} values of 431, 428, and 427°C, respectively, which could be considered to be either slightly immature or on the threshold of oil generation, considering the accuracy of this type of measurement (1–3°C) (Peters, 1986). Values increase towards the southeast reaching a T_{\max} of 456°C in well Pi3. According to gas threshold values suggested by Tissot *et al.* (1987), this easternmost region should have experienced gas generation. Comparison of Figs 2 and 8 indicates reasonable agreement between trends for T_{\max} and R_o , and, in fact, we see a fairly good correlation between these values ($r = 0.81$) (Fig. 9).

A second parameter that can be used to estimate the level of maturation is the production index (PI) which is $S1/(S1 + S2)$, otherwise referred to as the transformation ratio. The threshold for oil production should occur around 0.1 and continue through 0.4, beyond which point gas would be the main hydrocarbon phase produced. Most of the samples show very low production index values, with most values being below or close to 0.1 (Table 2). The highest values are seen in the southeast where Pi3, Lt1, and Lt4 show PI values of 0.30, 0.24, and 0.20, respectively. Production index correlates very well with vitrinite reflectance for the Cleveland samples ($r = 0.95$) (Fig. 10).

DISCUSSION

Vitrinite suppression

Vitrinite reflectance data indicate that the Ohio Shale appears to be within the oil window, with

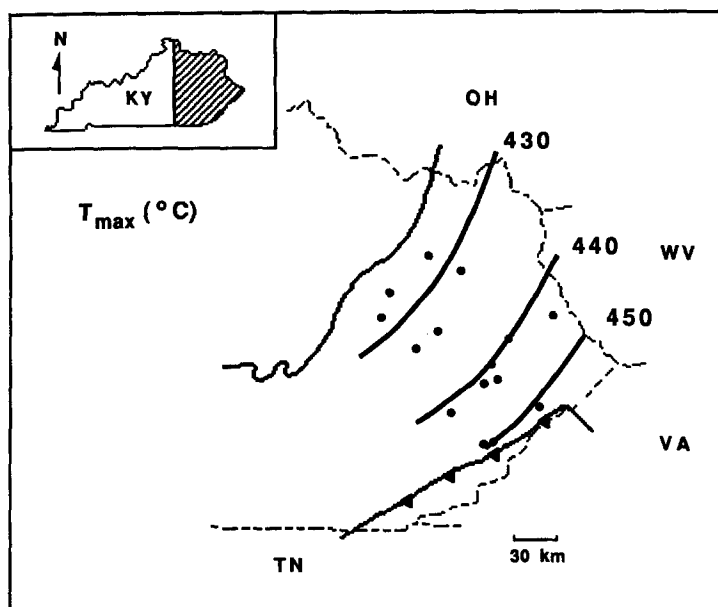


Fig. 8. T_{\max} ($^{\circ}\text{C}$) values for the Cleveland Shale samples, eastern Kentucky.

reflectance values between 0.5 and 1.0% R_o . These values are approximately the same as vitrinite reflectances measured in the Fire Clay coal seam (Pennsylvanian) (Hower and Rimmer, 1991), despite the significant stratigraphic separation of the Devonian shales and the Fire Clay coal (as much as 900–1250 m in the easternmost part of the study area). Based on the 0.3% R_o/km reflectance gradient reported by Hower and Rimmer (1991) for the coal-bearing section in this area, the shales in Pike County should have reflectances of approx. 1.2% R_o , not the 0.9–1.0% R_o values that are seen.

The first question that arises is whether or not it is reasonable to use such a high reflectance gradient in this region. A 0.3% R_o/km gradient corresponds to

an elevated paleogeothermal gradient of approx. 60 $^{\circ}\text{C}/\text{km}$, which is double the “normal” geothermal gradient (30 $^{\circ}\text{C}/\text{km}$ would be indicated by 0.15% R_o/km according to Robert (1988)). O’Hara *et al.* (1990) argued that this gradient is reasonable for this area considering the low conductivity of the shale-rich Pennsylvanian section. Similarly, Pollack and Cercone (1993) suggested that thick sections of coals, carbonaceous mudstones or other organic-rich rocks have very low thermal conductivities, which in turn create very steep geothermal gradients throughout the section, affecting all underlying rocks. Thus, the use of such a gradient may be justifiable. Hower and Rimmer (1991) suggested even higher gradients for the coal-bearing section in other parts of southeastern Kentucky. If a “normal” gradient (0.15%

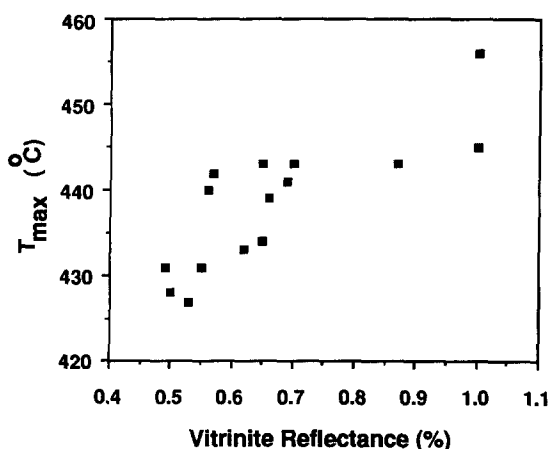


Fig. 9. Plot showing relationship between T_{\max} ($^{\circ}\text{C}$) and vitrinite reflectance (% R_o , in oil).

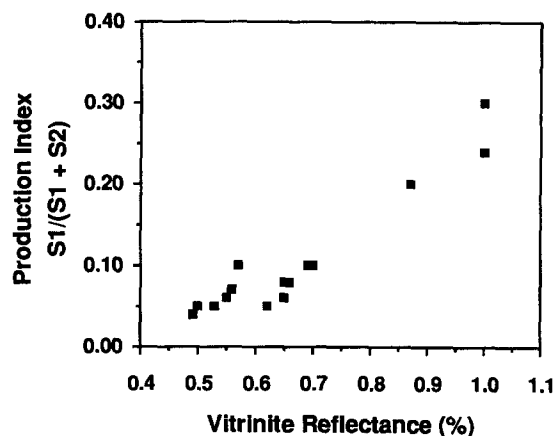


Fig. 10. Plot of production index [$S1/(S1 + S2)$] vs vitrinite reflectance (% R_o , in oil).

R_o /km) is used, one would expect to see reflectance levels of 1.1% in the Devonian shales. It is possible that the reflectance gradient changes with depth (not unlike the "kinky" vitrinite profiles described by Law *et al.*, 1989), but to achieve the reflectance levels observed in the Devonian shales, it would require essentially no increase in maturation over a section as thick as 1250 m. Unfortunately, little is known about vitrinite reflectance values for the section between the Pennsylvanian and the Devonian. Thus, it does appear that the shales exhibit vitrinite suppression, the amount of the suppression being between 0.1 and 0.3%.

There appears to be considerable evidence to support the idea that vitrinite reflectance levels can be suppressed in organic-rich sediments such as the Cleveland Shale. Suppression has been suggested as a potential problem in the New Albany Shale in the Illinois Basin (Barrows and Cluff, 1984); in the organic-rich Miocene Modelo Formation of the Los Angeles Basin (Price and Barker, 1985); in the Mississippian-Devonian Bakken Shale of the Williston Basin (Price *et al.*, 1984); in alginite-rich coals and oil shales (Hutton and Cook, 1980; Kalkreuth and Macauley, 1987); and in Pennsylvanian-age high lipinitic, phosphatic black shales (Wenger and Baker, 1987).

Reflectance suppression may be due to differences in starting materials, different maturation pathways, or to incorporation of hydrogen-rich components during transportation or accumulation, or later during diagenesis and maturation. At the same rank, different vitrinite submacerals, which may indicate different precursor materials or differences in levels of preservation, can have different reflectance levels (as much as 0.1–0.2% R_o) and chemical compositions (Brown *et al.*, 1964; Sitler, 1979; Fujii *et al.*, 1982; Stach *et al.*, 1982; Buiskool Toxopeus, 1983). Durand *et al.* (1986) have suggested that low-reflectance vitrinite, found in marine sequences associated with Type II kerogen, may not be derived from higher plants. Many of these studies relate the lower reflectances to higher hydrogen contents of the vitrinite.

Depositional environment may also influence reflectance: accumulation of peat under anaerobic conditions may result in lower reflectances compared with oxygenated conditions (Newman and Newman, 1982). Robl *et al.* (1987) found that vitrinite and inertinite macerals concentrated from the Devonian shales of the outcrop belt of eastern Kentucky, were enriched in hydrogen relative to their coal counterparts. They suggested that this enrichment occurred during transportation and deposition in the marine environment, or during early diagenesis of the vitrinite (during vitrinite gel formation). Price *et al.* (1984) have also suggested that incorporation of hydrogen-rich compounds into the vitrinite may occur during diagenesis.

Geochemical data presented above supports the level of maturation indicated by vitrinite reflectance.

According to T_{max} data, the Cleveland Shale should indeed be within the oil window between the outcrop belt and southeastern Kentucky, with samples from wells in the extreme southeast approaching the onset of gas generation. This agreement between parameters follows observations made by Price and Barker (1985) who concluded that in Type II kerogen, all maturation indices, including geochemical parameters, will be retarded relative to vitrinite-rich kerogen. They also suggested that hydrogen-rich macerals may mature at reduced rates. Thus, higher burial temperatures are needed to initiate hydrocarbon generation with this type of kerogen. Assuming this argument to be valid, it would be reasonable to expect low levels of maturation in the Devonian shales compared to the Pennsylvanian-age coals up-section.

Maturation levels of the Cleveland Shale in relation to oil and gas generation

For the Ohio Shale, the oil generation zone occurs in much of eastern Kentucky ($R_o > 0.5\%$), the wet gas zone ($R_o > 1.1\%$) in West Virginia, and the dry gas zone ($R_o > 2.0\%$) in eastern-most West Virginia (Fig. 11). In light of these trends, the distribution of oil and gas in eastern Kentucky (Wilson and Sutton, 1976) requires some explanation. Much of the production in this area is from the Ohio Shale and the primary product is gas: the Big Sandy Gas Field is the largest Devonian shale gas-producing field in the Appalachian Basin (Moody *et al.*, 1987). It has been estimated that there are 5000 producing Devonian wells in this area which ultimately will produce 2 trillion cubic feet of gas (Moody *et al.*, 1987). The Devonian shales are considered to be the major source rock for gas in the Appalachian Basin (Avila, 1976). From a geochemical viewpoint, the Devonian shales certainly could serve as source rocks, having high total organic carbon contents, but the type of organics (Type II) and their levels of maturation would suggest oil generation. While it is quite possible that the Ohio Shale has acted as a source rock for oil accumulations in other formations such as the Big Lime, it is appropriate to question why most hydrocarbon production in eastern Kentucky is gas, produced from the Devonian shale itself.

The gas could have been generated at somewhat greater depths within the Appalachian Basin, possibly within the wet gas zone of West Virginia (Fig. 11), and has since migrated updip into the shales of eastern Kentucky. The shales at the border of Kentucky and West Virginia are very close to the maturation level at which they could generate substantial amounts of gas, therefore migration of only short distances would be required. Westward migration of hydrocarbons in the Appalachian Basin has been suggested by Woodward (1958) who proposed updip migration of hydrocarbons associated with orogenic events. Oliver (1986) proposed a tectonic fluid mechanism to account for the distri-

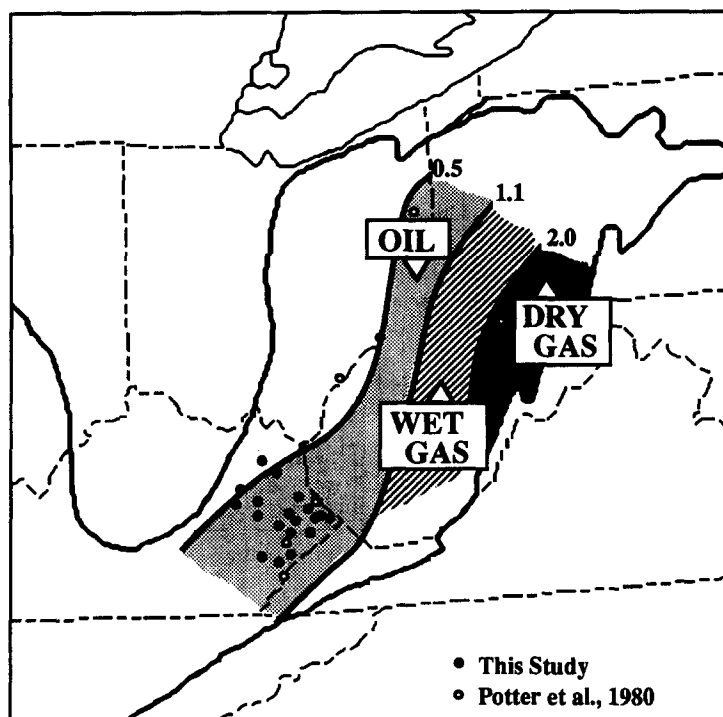


Fig. 11. Organic maturation levels of the Ohio Shale relative to oil and gas generative zones, as indicated by mean vitrinite reflectance (% R_o , in oil) (from Rimmer and Cantrell, 1989).

bution of hydrocarbons in the Appalachian Basin, suggesting that hydrocarbon migration was related to the emplacement of thrust sheets which drove the fluids ahead of them. Is it possible, then, that emplacement of features such as the Pine Mountain Thrust sheet could have influenced the distribution of gas in eastern Kentucky?

Alternatively, this gas may represent accumulations of early thermogenic gas produced within the oil window. As noted by Hunt (1979), gas production begins as early as oil production, but the bulk of the gas generation occurs after the main stage of oil generation. However, the amount of gas formed during liquid oil generation can be significant (Tissot and Welte, 1984). Some oil production is seen, particularly towards the outcrop belt, but relatively little considering the source potential of the Devonian shales.

The key to this problem may lie in the existence of the fluorescent groundmass, which suggests the presence of hydrocarbons, possibly in association with clay minerals. Robert (1988) has suggested that this fluorescent groundmass corresponds to transformation products of the algae. These alteration products may be produced after deposition, as an accumulation product of their metabolism, or they may represent maturation products (Robert, 1988). It is possible, then, that liquid hydrocarbons have been generated but are still held within the shale matrix.

Evidence for some retention of hydrocarbon products within the Ohio Shale comes from porosity and

permeability studies of the Lower Huron in Ohio and West Virginia. For cores collected from the Ohio River area, Soeder *et al.* (1986) reported that a mobile, liquid hydrocarbon phase was present within the pores, resulting in low gas permeabilities. Chromatographic data indicated the presence of a light, paraffinic petroleum. This liquid phase was absent in cores collected from areas deeper in the basin in West Virginia. The high SI values that we noted in the outcrop area which decrease towards the southeast, would support this notion. Soeder *et al.* (1986) indicated that despite the generation of commercial quantities of gas along with the oil, shales which have a high oil-generating potential will not produce gas at the well, due to low permeabilities caused by oil-filled pores. It appears possible, therefore, that at least some of the oil generated by maturation is still held within the shale matrix.

CONCLUSIONS

Several conclusions can be drawn from this study concerning the source rock potential of the Cleveland Shale and its level of thermal maturation.

The level of maturation of the Cleveland Member of the Ohio Shale in eastern Kentucky places it well within the oil window. There is relatively good agreement between petrographic and geochemical maturation parameters for this unit. Compared to Pennsylvanian-age coals upsection, however, the Cleveland Shale may exhibit vitrinite suppression,

and, for that matter, retardation of all maturation parameters. Assuming the 0.3% R_o /km gradient measured in the Pennsylvanian section to be appropriate, the suppression could be as much as 0.2–0.3% R_o . This suppression appears to be related to hydrogen enrichment. Increased hydrogen content could be due to differences in starting materials, which could have different initial compositions or follow different maturation pathways; to incorporation of hydrogen-rich compounds during transportation, deposition, or early diagenesis; or to interaction with hydrogen-rich compounds generated by chemical alteration of alginite during maturation.

In terms of source rock potential, the Cleveland Shale is dominated by Type II kerogen. TOC and Rock-Eval data indicate that, considering the amount, type, and level of maturation of this unit, this shale should have served as a major oil source rock. Within Kentucky, however, much of the hydrocarbon production is gas, much of it being produced from the Devonian shale itself.

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