

Effects of smectite on the oil-expulsion efficiency of the Kreyenhagen Shale, San Joaquin Basin, California, based on hydrous-pyrolysis experiments

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ABSTRACT

The amount of oil that maturing source rocks expel is expressed as their expulsion efficiency, which is usually stated in milligrams of expelled oil per gram of original total organic carbon (TOC_o). Oil-expulsion efficiency can be determined by heating thermally immature source rocks in the presence of liquid water (i.e., hydrous pyrolysis) at temperatures between 350°C and 365°C for 72 hr. This pyrolysis method generates oil that is compositionally similar to natural crude oil and expels it by processes operative in the subsurface. Consequently, hydrous pyrolysis provides a means to determine oil-expulsion efficiencies and the rock properties that influence them. Smectite in source rocks has previously been considered to promote oil generation and expulsion and is the focus of this hydrous-pyrolysis study involving a representative sample of smectite-rich source rock from the Eocene Kreyenhagen Shale in the San Joaquin Basin of California. Smectite is the major clay mineral (31 wt. %) in this thermally immature sample, which contains 9.4 wt. % total organic carbon (TOC) comprised of type II kerogen. Compared to other immature source rocks that lack smectite as their major clay mineral, the expulsion efficiency of the Kreyenhagen Shale was significantly lower. The expulsion efficiency of the Kreyenhagen whole rock was reduced 88% compared to that of its isolated kerogen. This significant reduction is attributed to bitumen impregnating the smectite interlayers in addition to the rock matrix. Within the

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interlayers, much of the bitumen is converted to pyrobitumen through crosslinking instead of oil through thermal cracking. As a result, smectite does not promote oil generation but inhibits it. Bitumen impregnation of the rock matrix and smectite interlayers results in the rock pore system changing from water wet to bitumen wet. This change prevents potassium ion (K^+) transfer and dissolution and precipitation reactions needed for the conversion of smectite to illite. As a result, illitization only reaches 35% to 40% at 310°C for 72 hr and remains unchanged to 365°C for 72 hr. Bitumen generation before or during early illitization in these experiments emphasizes the importance of knowing when and to what degree illitization occurs in natural maturation of a smectite-rich source rock to determine its expulsion efficiency. Complete illitization prior to bitumen generation is common for Paleozoic source rocks (e.g., Woodford Shale and Retort Phosphatic Shale Member of the Phosphoria Formation), and expulsion efficiencies can be determined on immature samples by hydrous pyrolysis. Conversely, smectite is more common in Cenozoic source rocks like the Kreyenhagen Shale, and expulsion efficiencies determined by hydrous pyrolysis need to be made on samples that reflect the level of illitization at or near bitumen generation in the subsurface.

INTRODUCTION

The interaction of minerals and organic matter in source rocks during petroleum formation has long been of interest (Grim, 1947; Brooks, 1948). Clay minerals, in particular, were considered to have catalytic effects that enhance the thermal decomposition of organic matter (Johns, 1979; Goldstein, 1983). Although clay minerals, especially smectite, have catalytic properties that can influence petroleum products (Clementz, 1976; Czarnecka and Gillott, 1980; Pinnavaia, 1983), experimental pyrolysis studies have shown smectite to reduce pyrolyzate yields or alter pyrolyzate compositions (Espitalié et al., 1980, 1984; Horsfield and Douglas, 1980; Orr, 1983; Tannenbaum et al., 1986; Hetényi, 1995). These reductions in pyrolysis yields are especially critical when determining oil-expulsion efficiency, which is typically expressed in milligrams of expelled oil per gram of original total organic carbon (TOC_o) in a source rock. The expulsion efficiency of a source rock is paramount to determine oil charge, which is an important attribute in ranking or risking undiscovered oil potential within or among petroleum systems (Demaison and Huizinga, 1994; Lewan et al., 2002; Peters et al., 2006).

Expulsion efficiency is commonly determined from yields derived by laboratory pyrolysis of thermally immature source

rock. As shown in a material balance study of the Illinois Basin (Lewan et al., 2002), various algebraic schemes using yields from open-system pyrolysis (e.g., Rock-Eval) give unrealistically high oil-charge values, which in part trivializes their utility. However, closed-system pyrolysis of source rocks in the presence of liquid water (i.e., hydrous pyrolysis) provides lower and more realistic expulsion efficiencies by generating expelled oil that is compositionally similar to natural crude oil and expelling the oil by processes operative in petroleum systems (Lewan, 1993, 1997). This is in stark contrast to the processes of volatilization and solvent extraction respectively employed by open-system and anhydrous closed-system pyrolysis to obtain products that are not similar to natural crude oil (Lafargue et al., 1989; Behar et al., 1997; Lewan, 1997). In addition, volatilization and solvent-extraction processes used to obtain these pyrolyzates are not operative in petroleum systems. Consequently, hydrous pyrolysis provides the best pyrolysis method to determine expulsion efficiencies and the effects of source rock properties.

This study uses hydrous pyrolysis to examine the effects of smectite on the expulsion efficiency of a thermally immature sample (K-7) of Eocene Kreyenhagen Shale and builds upon earlier findings reported by Lewan and Whitney (1993) and Dolan (1998). The Kreyenhagen Shale is an effective source rock for oil accumulations in the San Joaquin Basin of California (Lillis and Magoon, 2007; Peters et al., 2007a, b) and has recently been the focus for exploration as a tight-oil shale play (OilVoice, 2013). The Kreyenhagen source rock sample (K-7) used in this study is representative of the upper 27 m (89 ft) of the shale section exposed in a slump scarp on the western side of the San Joaquin Basin approximately 17 km (11 mi) north of Coalinga, California. It has a smectite content of 31% and total organic carbon content (TOC) of 9.4 wt. %, which consists predominantly of type II kerogen. Unlike the previously cited studies on artificial unconsolidated mixtures of kerogen and mineral powders, the indurated gravel-size (0.5–2 cm [0.2–0.8 in.]) rock used in this study is more representative of natural associations among minerals, organic matter, and pores. Experimental studies on aliquots of this well-characterized sample eliminate the problem of stratigraphic and regional

variations in source rock textures, mineralogy, and organic-matter amounts and types that encumber the study of rock units at different subsurface maturities over the extent of a petroleum system. The objective of this study is to determine the effect of smectite on the expulsion efficiency of smectite-rich source rock.

MATERIALS AND METHODS

Sample Description

The starting (unheated) K-7 sample used in the hydrous-pyrolysis experiments is from the Skunk Hollow outcrop located north of Coalinga, California, on the west side of the San Joaquin Basin (36.2872 N, 120.34174 W, Fresno County). The outcrop occurs in the scarp of a slump that exposes the upper 27 m (88 ft) of the Kreyenhagen Shale. The sample was collected from an 11-cm (4.3-in.)-thick interval in the unweathered part of the outcrop below the overlying discolored saprolite horizon. Based on unpublished data, K-7 is considered to be representative of the shale lithology that dominates this exposure, which is part of the 40-m (131-ft)-thick “E” lithologic unit described in the neighboring Garza Creek exposure by Cushman and Seigfus (1942). The unweathered character of the sample is verified petrographically by the presence of well-developed pyrite as described by Lewan (1980). The rock has a TOC of 9.4 wt. % with a Rock-Eval hydrogen index (HI) of 258 mg/g TOC and maximum-yield temperature (T_{\max}) of 407°C. The atomic H/C ratio of 1.13 and atomic O/C ratio of 0.22 of the isolated kerogen indicate that it is a thermally immature type II kerogen. This sample was crushed to gravel size (0.5–2 cm [0.2–0.8 in.]) and thoroughly mixed to ensure a homogeneous sample from which aliquots were taken for each hydrous-pyrolysis experiment.

Hydrous Pyrolysis

The hydrous-pyrolysis experiments were conducted in accordance with Lewan (1985, 1993) in which aliquots of crushed gravel-size (0.5–2 cm [0.2–0.8 in.]) K-7 whole rock were heated in the presence of liquid water. Each experiment involved loading a 377-g

aliquot of the K-7 rock into a 1-L stainless-steel (SS-316) reactor with 297 g of distilled water. These proportions of reactor volume, water, and rock ensured that the rock was in contact with liquid water before, during, and after the experiments as prescribed by Lewan (1993). After evacuating the loaded reactor, the head space of the reactor was filled with 7 MPa (1015 psi) of helium and checked for leaks. This pressure was then reduced to a final helium pressure of 241 kPa (35 psi). The reactor was isothermally heated after an average initial heat-up time of 105 min to 270°C, 290°C, 310°C, 330°C, 343°C, 349°C, 355°C, 360°C, or 365°C for 72 hr. In accordance with other hydrous-pyrolysis experiments (Lewan and Ruble, 2002), these conditions represent the full range of petroleum formation, including kerogen decomposition to bitumen and bitumen decomposition to immiscible expelled oil. After the reactor cooled to room temperature, the generated gas, expelled immiscible oil, reacted water, and spent rock were collected as described by Lewan (1985).

For comparison, hydrous-pyrolysis expelled-oil yields from thermally immature chert (WD-4) and shale (WD-5) representative of the Devonian-Mississippian Woodford Shale and shale (P-64) representative of the Permian Retort Phosphatic Shale Member of the Phosphoria Formation are presented. As described by Lewan (1985 and 1987), the Woodford Shale samples contain type II kerogen with TOC contents of 12.7 wt. % for the 7-cm thick shale and 4.3 wt. % for the 6-cm-thick chert. The shale and chert beds are in contact with one another ~13 m (43 ft) below the top of the Woodford Shale at the Oklahoma I-35 road-cut exposure described by Lewan (1985). The sample of Retort Shale Member contains type IIS kerogen with a TOC content of 26.3 wt. % and is from Retort Mountain, Montana (Lewan, 1985). Similar to the Kreyenhagen (K-7) sample, hydrous pyrolysis was conducted on gravel-size (0.5–2 cm [0.2–0.8 in.]) aliquots of these three source rocks at temperatures between 260°C and 365°C for 72 hr using the same product-collection procedures (Lewan, 1985).

Hydrous pyrolysis was also conducted on kerogen isolated from the K-7 sample to evaluate oil-expulsion efficiency without the smectite-rich rock matrix. The kerogen was isolated from the rock

through a series of treatments involving acid digestion (i.e., 18% HCl, 52% HF, and concentrated HCl at 100°C), heavy-liquid separation with ZnBr (2.1 g/cm³), and Soxhlet extraction with benzene:methanol azeotrope. Details for this isolation procedure are given by Lewan (1986). This experiment was conducted in a 0.5-L stainless-steel (316) reactor with 28 g of the isolated kerogen and 195 g of distilled water. The experiment was run at 349.0 ± 0.5°C for 72 hr. This condition is near maximum expelled-oil yields reported for source rocks with type II and IIS kerogen (350°C to 360°C for 72 hr; Lewan and Ruble, 2002). The same loading and product-recovery procedures previously described for the whole-rock experiments were used for the kerogen experiment (Lewan, 1985).

X-ray Diffraction

Unheated and pyrolyzed samples were hand crushed with mortar and pestle until the sample passed through a no. 18 sieve (1 mm). These samples were then dispersed ultrasonically in approximately 200 mL of distilled water for 5–10 min. Samples were then soaked for 48–72 hr and lightly crushed again using mortar and pestle. This slurry was then passed through a no. 200 sieve (75 µm), leaving the silt and clay fractions in the dispersion. This fraction was ion-rinsed by centrifuge at 5000 rpm for 30 min. The clear supernatant was decanted making certain that sample was not lost. The silt and clay were then redispersed in distilled water, and the ion washing was repeated two more times. After ion washing, the less-than-2-µm fraction was obtained by standard centrifuge techniques (Starkey et al., 1984). The clay dispersion was mounted on a glass slide by the technique described by Drever (1973) and Moore and Reynolds (1989). This method provides oriented-clay mounts that are ready for the x-ray diffraction (XRD) and standard clay identification procedures as described by Moore and Reynolds (1989).

The clay-mounting preparations were attempted with as few chemical treatments as possible. However, the pyrolyzed samples contained excessive organic matter that made the clay-mounting method difficult. As an alternative, the pyrolyzed samples underwent an additional treatment that removed

excess organic matter in the whole rock sample. After passing the sample through a no. 18 sieve (1 mm), the sample was soaked in a 10% solution of H₂O₂ for 48 hr in a 50°C water bath. This removed enough organic matter for the collected less-than-2- μ m fraction to adhere to the glass slide when the oriented mount was made. Moore and Reynolds (1989) caution that the use of oxidizing agents, such as H₂O₂, may cause changes to the clay minerals. However, preliminary tests on the unheated K-7 sample using the methods described above with and without H₂O₂ treatment showed no significant differences in the diffraction patterns (Dolan, 1998).

The less-than-2- μ m-fraction mounts were analyzed using a Siemens D500 diffractometer with a Cu target and graphite monochromator. The diffractometer was operated at 30 mA and 49 kV. Samples were scanned from 2° to 35° 2 θ (i.e., angle of diffracted rays). The oriented mounts were analyzed air dried (AD), ethylene-glycol solvated (EG; 24 hr at 60°C), and after heating at 300°C and 550°C. Glycolated (gly) XRD scans of the less-than-2- μ m-size fraction exhibit a strong low-angle reflection that migrated from about 5.2° to 6.2° 2 θ as experimental temperatures increased. At higher experimental temperatures, the scans exhibit a decrease of the mixed-layer 001/002 illite and smectite (I/S)-gly (\approx 10° 2 θ) and 002/003 I/S-gly (\approx 15° 2 θ) peaks. This makes the application of convenient peak-migration methods (Środoń, 1980; Środoń and Eberl, 1984; Moore and Reynolds, 1989) for determining illite and smectite content in the mixed layer difficult. However, under glycolated conditions, the maximum of the first-order I/S peak can be used to determine percent illite (%I) in the mixed-layer clay (Velde and Vasseur, 1992). The method used for the determination of illite and smectite content in the mixed-layer clay is modified from that proposed by Velde and Vasseur (1992).

Using NEWMOD[®] (Reynolds, 1980), calculations can be made to establish the change in peak position and peak width as a function of I/S expandability and the number of coherently diffracting layers (N) in the crystallites. According to these models, the width and position of the first-order I/S peak are a function of composition and the number (N) of coherently scattering layers in the grain (Moore and

Reynolds, 1989, p. 89). The number of coherently scattering layers in this theoretical model changes as a range of values (i.e., $N = 2-4, 3-5$, etc.). To construct this model, some assumptions must be made. We assume that the mixed-layer component of this system contains only smectite and illite, and that the Reichweite (R) equals zero (literally “reach back” and denoted R0). This means that the interstratification is random, or the influence that a specific layer (illite or smectite) has on its nearest neighbor is zero (Reynolds, 1980). We assume that, under ethylene glycol solvation, the smectite (001) peak appears at 16.9 Å, and for all conditions, the illite (001) appears at 10 Å. The exchange cation is assumed to be Ca⁺² in the smectite interlayer, which can be used as the default ion in the NEWMOD[®] program (Moore and Reynolds, 1989). It is reasonable to assume that the interlayer spacing remains constant in the experimental system, and that sample K-7 is well mixed with regard to clay composition and does not change significantly from sample to sample. With the exception of the thermally induced changes, the composition is not changing significantly. Therefore, it is reasonable that the interlayer distances of smectite or illite will not differ significantly from sample to sample. With these assumptions in place, it is possible to construct a plot of mixed-layer (001) peak position (glycol solvated) against peak breadth (full width at half maximum, FWHM) to model percent smectite in the mixed-layer illite and smectite. Velde and Vasseur (1992) show this method to have a reproducibility of \pm 5% smectite. Percent-smectite values determined by this method compare well with those determined by the Δ 2 θ method of Moore and Reynolds (1989) for the unheated and low-temperature (\leq 310°C) samples in which the 001/002 I/S-gly (\approx 10° 2 θ) and 002/003 I/S-gly (\approx 15° 2 θ) peaks could be measured.

Semiquantitative XRD analysis of unheated K-7, P-64, WD-5, and WD-4 whole-rock samples was conducted by K/T GeoServices, Inc., Gunnison, Colorado, using Jade Software (Materials Data, Inc.) with the whole pattern fitting and Rietveld refinement option. A diffraction model is fitted to the measured XRD pattern by nonlinear least-square optimization using background, profile parameters, and lattice constants. Mixed-layer clay ordering and expandability are determined by comparing diffraction data of the

glycolated-clay mounts with one-dimensional diffraction profiles generated with the NEWMOD[®] program (Reynolds, 1980). The analysis is on an organic-matter-free basis. This study normalizes the analysis to the measured TOC of the rock.

Inorganic Chemical Analysis

Nine major elements (Si, Al, Fe, K, Mg, Na, Ti, Ca, and P) were determined on the unheated and pyrolyzed rocks by SGS Mineral Services (2013), Ontario, Canada, using inductively coupled plasma-atomic emission spectrometry (ICP-AES; method ICP16). Samples are fused with lithium metaborate in a graphite crucible, and digested samples are aspirated into the ICP-AES instrument. The elemental emission signal is measured simultaneously for the nine elements and calibrated with rock-reference materials (David L. Fey, U.S. Geological Survey, 2013, personal communication; SGS Minerals, 2013).

Rock-Eval Analyses

Rock-Eval II analyses were conducted on a sample split of 100 mg or less. Powdered samples were heated under a helium atmosphere at 300°C for 3 min, and then the temperature was increased to 600°C at a rate of 25°C/min. Pyrolysis products are generated and swept through a splitter to a flame ionization detector (FID) and cold trap. Free volatile products vaporized at the initial 3-min hold time at 300°C. This vaporization is recorded as the S_1 peak (mg/g of rock). As the temperature begins to ramp between 300°C and 600°C, generated products are vaporized and recorded as the S_2 peak (mg/g of rock). The decomposition of organic oxygen-containing compounds occurs between 300°C and 390°C and the resulting CO₂ is measured by a thermal conductivity detector (TCD). This product is reported in mg CO₂/g rock and referred to as the S_3 peak. A fourth peak called S_4 measures the residual carbon by oxidation under an air atmosphere at 600°C (mg CO₂/g rock). Total organic carbon (TOC) is computed from the S_1 , S_2 , and S_4 peaks and is reported in weight percent. Several parameters determined from these measurements are hydrogen index ($HI = S_2/TOC \times 100$),

oxygen index ($OI = S_3/TOC \times 100$), temperature at maximum S_2 (T_{max}), and production index ($PI = S_1/[S_1 + S_2]$). The whole-rock analyses were run at the U.S. Geological Survey by Ted Daws and the less-than-2- μ m-fraction analyses were conducted at Humble Geochemical Services, Humble, Texas. The notation TOC_o refers to total organic carbon of the original K-7 sample, and TOC_R refers to total organic carbon of the recovered pyrolyzed rock.

Organic Chemical Analyses

Bitumen was extracted from the unheated and pyrolyzed rocks by Soxhlet extraction of 10 to 100 g of powdered sample in glass-fiber thimbles. Boiling chips, a copper strip for sulfur scavenging, and 350 mL of an azeotropic mixture of benzene and methanol (60/40 wt. %) were placed in 500-mL round-bottom boiling flasks. Extraction proceeded for 24 hr or until the extraction was complete as indicated by clear solvent in the siphon tube. The extract and solvent were filtered using a glass microfiber GF/A filter on a funnel-fritted glass assembly. The extract was vacuum evaporated to about 5 to 10 mL and transferred to a volumetric flask. An aliquot (1–5 mL) was taken from the volumetric flask and placed in a tared vial. The solvent was evaporated from the aliquot with the residual weight being bitumen content.

RESULTS AND DISCUSSION

Source Rock Chemistry and Maturity

The hydrous-pyrolysis conditions of 270°C to 365°C for 72 hr used in this study have been shown to simulate the entire oil window (Lewan, 1985). Kerogen partial decomposition to polar-rich bitumen occurs in the lower temperature range and peaks between 300°C and 330°C after 72 hr. Generation of expelled hydrocarbon-rich oil from the decomposition of bitumen overlaps with the later stages of bitumen generation. Expelled-oil generation continues at higher temperatures and reaches a maximum between 350°C and 365°C after 72 hr. Hydrous-pyrolysis temperatures greater than 365°C for times greater than 72 hr represent conditions for oil cracking to gas and

Table 1. Rock-Eval Analyses of Unheated Whole Rock (K-7) and Its Pyrolyzed Recovered Rock*

Conditions (°C for 72 hr)	TOC (wt. %)	S ₁	S ₂ (mg/g rock)	S ₃	T _{max} (°C)	HI (mg/g TOC)	OI	PI S ₁ /[S ₁ + S ₂]
Unheated	9.4	0.23	24.29	7.91	407	258	84	0.01
270	8.0	0.61	20.40	2.30	428	257	29	0.03
290	7.5	0.48	12.90	3.02	434	172	40	0.04
310	6.8	0.61	4.52	2.05	442	67	30	0.12
330	6.7	0.72	3.34	2.01	446	50	30	0.18
343	6.4	0.61	2.75	2.18	437	43	34	0.18
349	6.4	1.0	1.74	1.22	516	27	19	0.36
355	6.4	0.63	1.49	1.26	508	23	20	0.30
360	6.4	0.85	2.07	1.87	530	32	29	0.29
365	6.3	0.78	2.01	1.90	ND**	32	30	0.28

*Rock-Eval pyrolysis data for unheated whole rock (K-7) and its pyrolyzed aliquots of recovered rock from hydrous pyrolysis at various temperatures for 72-hr durations.

**ND = not determined because of poor peak resolution.

pyrobitumen (Willette, 2011), which were avoided in this study.

Rock-Eval pyrolysis data for the rocks recovered from the experiments are in Table 1 with selected parameters plotted in Figure 1. Initially, a significant decrease exists in TOC from the unheated value of 9.4 wt. % to 6.8 wt. % at 310°C and followed by a slight decrease to 6.7 wt. % at 330°C (Figure 1A). Another slight decrease to 6.4 wt. % occurs at 343°C, and thereafter, TOC remains essentially constant to 360°C. At 365°C, the TOC decreases slightly to 6.3 wt. %. This only represents a 33% decrease in TOC through the oil window, which is low compared with the usual 50% decrease for source rocks with type II kerogen (Baskin, 1997). Similar to TOC, the hydrogen index (HI) has its largest decrease at lower experimental temperatures from 258 mg/g TOC in the unheated sample to 67 mg/g TOC at 310°C (Figure 1B). This is followed by a small decrease to 43 mg/g TOC at 343°C and nearly constant values fluctuating between 23 and 32 mg/g TOC to 365°C. With the exception of a slight drop in the 343°C experiment, T_{max} increases gradually from 407°C in the unheated sample to 446°C (Figure 1C). The T_{max} increases abruptly to 516°C at the 349°C experiment, followed by fluctuations between 508°C and 530°C at the higher experimental temperatures of 355°C and 360°C, respectively. Note that the interpretive HI-T_{max} plots by Bordenave et al. (1993, their figure 2–25) classify the unheated kerogen as type II

with a strong mineral-matrix effect or mixture with type III kerogen.

Chemical analyses of nine major elements are given in Table 2. Relative to the unheated sample, a small gradual increase in their concentration occurs with increasing experimental temperature that can be explained in part by the loss of TOC (Table 1) as a result of oil and gas expulsion from the rock. This indicates that these elements are not lost to the water surrounding the rock chips during the experiments. Availability of K in the rock is particularly important when considering smectite-to-illite conversion. The presence of K does not necessarily indicate availability for this conversion, but its concentrations (1.23 to 1.48 wt. %) and near-constant Al/K (4.5–4.8) and K/Ti (4.2–4.6) ratios indicate that the rocks are not depleted in K by water leaching during the experiments (Table 2).

Hydrous-Pyrolysis Yields

The hydrous-pyrolysis yields of bitumen extract, expelled oil, and generated hydrocarbon (HC) gas are given in Table 3 and plotted against experimental temperatures in Figure 2. Bitumen from the recovered rock is the initial product at 270°C, and it decomposes at higher temperatures to expelled oil. This overlapping two-step reaction sequence of kerogen partially decomposing to polar-rich bitumen, followed by bitumen decomposing to hydrocarbon-rich

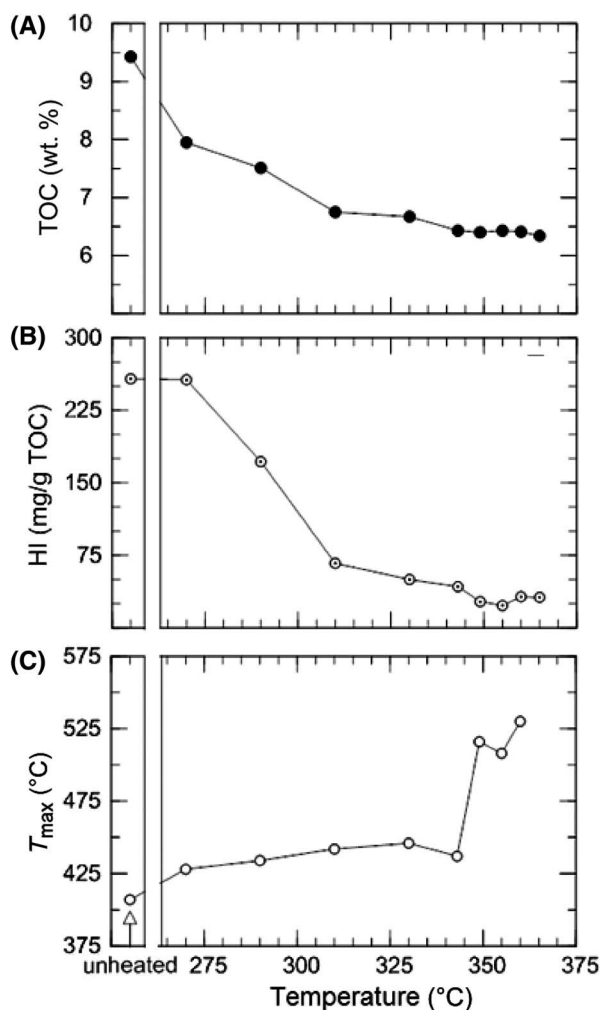


Figure 1. Rock-Eval data for the unheated rock (K-7) and its pyrolyzed aliquots plotted against experimental temperatures for 72-hr durations: (A) total organic carbon (TOC); (B) hydrogen index (HI); (C) temperature (°C) at which S₂ reaches a maximum (T_{max}).

Table 2. Elemental Analyses (Wt. %) by ICP-AES of Major Elements in Unheated and Pyrolyzed Aliquots of Kreyenhagen Shale Sample K-7

Conditions	Si	Al	Fe	K	Mg	Na	Ti	Ca	P	Al/K	K/Ti
Unheated	25.40	5.69	2.40	1.23	0.96	0.70	0.28	0.26	0.10	4.6	4.4
270°C/72 hr	28.00	6.44	2.27	1.34	0.85	0.60	0.31	0.31	0.14	4.8	4.3
290°C/72 hr	29.30	6.16	2.27	1.36	0.85	0.60	0.30	0.20	0.08	4.5	4.5
310°C/72 hr	28.80	6.28	2.23	1.38	1.01	0.60	0.30	0.21	0.18	4.6	4.6
330°C/72 hr	28.70	6.63	2.56	1.40	1.08	0.70	0.33	0.43	0.17	4.7	4.2
343°C/72 hr	29.60	6.60	2.39	1.40	1.10	0.60	0.32	0.27	0.11	4.7	4.4
349°C/72 hr	29.30	6.60	2.36	1.40	1.08	0.60	0.32	0.26	0.10	4.7	4.4
355°C/72 hr	27.90	6.48	2.56	1.43	1.00	0.70	0.32	0.25	0.07	4.5	4.5
360°C/72 hr	29.60	6.89	2.46	1.48	1.13	0.70	0.33	0.27	0.10	4.7	4.5
365°C/72 hr	29.20	6.78	2.51	1.45	1.09	0.70	0.32	0.36	0.16	4.7	4.5

oil, has been recognized in other hydrous-pyrolysis studies (Lewan, 1985; Ruble et al., 2001), oil-shale retorting (Hubbard and Robinson, 1950; Allred, 1966), and natural petroleum formation (Louis and Tissot, 1967). However, several notable peculiarities in the yields are shown in Figure 2 compared with other hydrous-pyrolysis studies on source rocks containing type II and IIS kerogen (Lewan, 1985). Typically, maximum bitumen generation is observed between 300°C and 330°C for 72-hr experiments. Maximum bitumen for the Kreyenhagen Shale occurs at the lowest experimental temperature of 270°C for 72 hr (Figure 2). The amount of decrease in bitumen is typically equal to the amount of expelled oil generated (Lewan, 1985). This does not occur for sample K-7 from the Kreyenhagen Shale (Figure 2).

Another peculiar aspect of the hydrous-pyrolysis yields is the small amount of expelled oil. This becomes most obvious by comparing the yields of generated expelled oil from the Kreyenhagen Shale with those of the Woodford Shale and Retort Shale Member, which also contain immature type II kerogen (Lewan, 1985). As shown in Figure 3, the maximum expelled oil yield of 40 mg/g TOC for the Kreyenhagen Shale is more than six times less than that from chert or shale from the Woodford Shale (380 and 247 mg/g TOC, respectively) and Retort Shale Member (276 mg/g TOC). This reduced yield for the smectite-rich Kreyenhagen Shale becomes more apparent by comparing expelled-oil yield from its isolated kerogen generated at 349.0 ± 0.5°C for 72 hr (Figure 3). This difference is an 88% reduction

Table 3. Hydrous-Pyrolysis Yields for Kreyenhagen Shale (K-7)

Temperature (°C for 72 hr)	Bitumen (mg/g TOC _R)	Expelled Oil (mg/g TOC ₀)	Hydrocarbon Gas (μg/g TOC ₀)
Unheated	118.3	0.0	0.0
270	191.5	11.5	ND*
290	171.5	21.8	11.0
310	111.9	22.9	22.0
330	84.9	23.6	29.8
343	85.7	30.1	35.7
349	49.4	36.5	39.6
355	71.3	40.1	41.6
360	75.7	40.5	42.0
365	73.0	39.7	43.6

*ND = Not determined.

from the isolated kerogen to the whole rock. The main difference in the matrices of these source rocks is the amount of smectite. Smectite is the major clay mineral (31 wt. %) in the Kreyenhagen Shale, whereas illite is the major clay mineral in the samples of Woodford Shale and Retort Shale Member (Table 4).

Major reduction in pyrolyzate yields because of smectite has also been observed in anhydrous

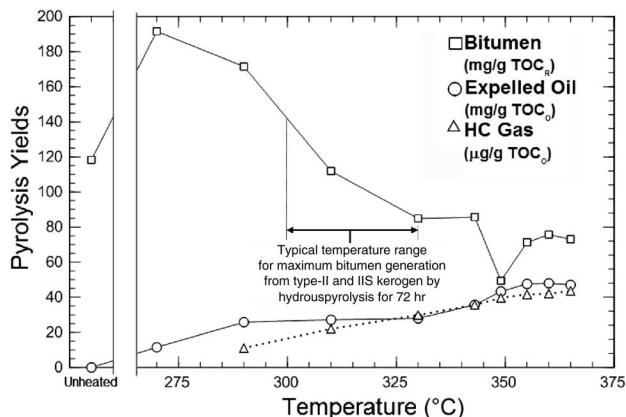


Figure 2. Hydrous-pyrolysis yields plotted against experimental temperatures for 72-hr durations. Bitumen yields are based on milligrams of extract and grams of TOC_R of recovered rock. Expelled oil yields are based on milligrams of oil floating on the water surface after the experiment and grams of TOC₀ of unheated rock (K-7). Generated μg of hydrocarbon (HC) gas collected in headspace of reactor after the experiment and grams of TOC₀ of unheated rock (K-7). Temperature range for typical bitumen generation is from Lewan (1985).

open- and closed-system pyrolysis but not to this extent. Orr (1983) showed a 74%–77% reduction in the HI for an isolated type I kerogen mixed with smectite to give a 0.5 wt. % TOC. Espitalié et al. (1980) also found a reduction in expulsion efficiencies when oil shale with 9.6 wt. % TOC of type II kerogen was mixed with clay minerals in open-system pyrolysis. For mixtures resulting in TOC values of 0.9 wt. %, HI values were reduced by 56% for smectite and 81% for illite. These reductions are less than the 88% observed for the Kreyenhagen Shale (Figure 3), but open-system pyrolysis yields are volatilized products swept from the sample by He carrier gas, which is not an operative process in the

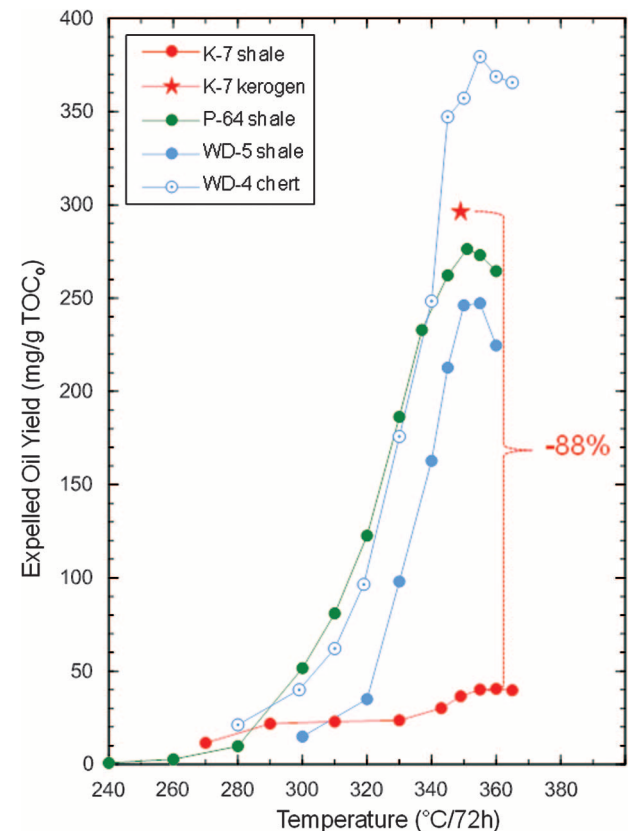


Figure 3. Comparison of expelled-oil yields from Kreyenhagen Shale (K-7 in Figure 2), Woodford Shale (WD-4 chert and WD-5 shale; Lewan, 1985), and Retort Shale Member (P-64; Lewan, 1985) with increasing hydrous-pyrolysis temperatures for 72-hr durations. Expelled-oil yields from hydrous pyrolysis of isolated kerogen from K-7, WD-5, and P-64 source rocks at 350 ± 1°C for 72-hr durations. The posted negative value represents the percent difference between the expelled-oil yields from the Kreyenhagen Shale K-7 sample and its isolated kerogen.

Table 4. Semiquantitative XRD Mineralogy Normalized to Measured TOC (Wt. %)

Mineral	K-7	P-64	WD-5	WD-4
Quartz	14	48	66	91
Opal CT	11	0	0	0
K-feldspar	5	1	2	0
Plagioclase	14	0	0	0
Carbonates*	0	0	0	tr [†]
Pyrite	1	1	2	1
Marcasite	0	0	0	0
Gypsum	1	0	tr	tr
Jarosite	0	2	0	1
R0 M-L I/S (90% S)**	31	0	0	0
R1 M-L I/S (20% S) [†]	0	0	0	0
R3 M-L I/S (10% S) ^{††}	0	0	5	0
Illite and mica	12	11	11	2
Kaolinite	2	12	1	tr
Chlorite	tr	0	0	0
TOC	9.4	23.6	12.7	4.6
Smectite/Illite and mica	2.66	0.00	0.05	0.00
Smectite/TOC	3.30	0.00	0.04	0.00

*Includes calcite, dolomite, siderite, ankerite, and Fe-dolomite.

**Randomly ordered mixed-layer illite and smectite with 90% smectite layers.

[†]R1 ordered mixed-layer illite and smectite with 20% smectite layers.

^{††}R3 ordered mixed-layer illite and smectite with 10% smectite layers.

[†]tr = < 0.5 wt. %.

subsurface during natural oil generation. Tannenbaum et al. (1986) showed that expulsion efficiencies for isolated type I kerogen were significantly reduced for mixtures with smectite under hydrous and anhydrous closed-system pyrolysis. At a mineral/kerogen ratio of 20, anhydrous closed-system pyrolysis at 300°C for 10 hr gave a 49% and 57% reduced pyrolyzate yield relative to that of the isolated kerogen for smectite and illite, respectively. These expulsion efficiencies are less than those reported for open-system pyrolysis (Espitalié et al., 1980; Orr, 1983), which may be a result of the lower temperatures used in the closed-system pyrolysis. These closed-system pyrolyzate yields are based on solvent extraction, which, like volatilization in open-system pyrolysis, is not operative in the subsurface during natural oil generation.

The anhydrous open- and closed-system pyrolysis also showed that expulsion efficiencies were reduced more by illite than smectite, which is contrary to results from hydrous pyrolysis as shown in

Figure 3. Hydrous-pyrolysis experiments conducted by Tannenbaum et al. (1986) at 300°C for 10 hr showed that smectite reduced expulsion efficiencies more than illite (39% and 13%, respectively). These lower reductions relative to those observed for the Kreyenhagen Shale (Figure 3) are attributed in part to the unconsolidated character of the mineral-kerogen mixtures used by Tannenbaum et al. (1986). Unlike the consolidated gravel-size whole rock used in the hydrous-pyrolysis experiments, water layers can occur between the mineral and kerogen surfaces in the unconsolidated mixtures. These water layers may prevent complete contact between the kerogen and minerals. In hydrous pyrolysis of whole rock, the surrounding water in the reactor only maintains water-saturated pores before bitumen generation and dissolved water in the bitumen during petroleum formation (Lewan, 1997). Water dissolved in the bitumen instead of the surrounding liquid water is the source of hydrogen and the cause of immiscibility and expulsion of hydrocarbon-rich oil (Lewan, 1997).

Hydrocarbon gas generated in the experiments parallels expelled-oil generation but is lower by three orders of magnitude (Figure 2, Table 3). These low hydrocarbon-gas yields indicate that the reduced expelled-oil yields cannot be attributed to preferential oil or bitumen cracking to gas in the presence of smectite. High yields of carbon dioxide (93 to 138 mg/g TOC) are observed in accordance with other hydrous-pyrolysis results because of dissolved water in the bitumen reacting with carbonyl groups (Lewan, 1997). The lack of high carbon dioxide concentrations in most natural gases is attributed to its high solubility in formation waters and its reactivity to form carbonate cements (Lewan, 1997).

Clay Mineralogy (<2- μ m fraction)

The less-than-2- μ m-size fraction consists primarily of smectite (>90%) as an interstratified component in an illite and smectite (I/S) mixed-layer clay, quartz, and discrete illite. Opal-CT is also present, with minor amounts of kaolinite. Figure 4 shows the ethylene-glycol-solvated XRD patterns for the less-than-2- μ m fractions. As the experimental temperatures increase, two changes are evident. First, the kaolinite (001) peak shows a marked decrease in

intensity as temperature increases. This is attributed to its transformation to meta-kaolin, which is amorphous (Grim, 1968, p. 301). This transformation has been reported in nature (Spiro, 1979), but as noted by Dunoyer de Segonzac (1970), it is not a good indicator of temperature because of its dependence on the chemistry of associated waters. The second change is in the shape and position of the low-angle reflection of the mixed-layer (I/S) component.

As experimental temperature increases, percent illite in the mixed-layer clay increases until a 35%–40% illite composition is reached at 310°C and remains within this range at the higher temperatures (Figure 5A). Although the amount of illite in the mixed-layer component remains unchanged at higher experimental temperatures (>310°C), the peak position continues to shift toward higher 2θ values, and its breadth increases (Figure 5B). A working hypothesis to explain these observations is that bitumen, generated from the partial decomposition of kerogen, impregnates the smectite interlayers. Bitumen impregnation of a source rock matrix has been observed in natural and experimental maturation studies (Lewan, 1987). This results in the conversion of an originally water-wet pore system to a bitumen-wet pore system, which is interpreted to be the cause of high electric-log resistivity of maturing source rock (Meissner, 1993). A bitumen-wet system is envisaged to prevent aqueous-ion mobility and dissolution and precipitation reactions from occurring within the rock matrix. As a result, the conversion of smectite to illite ceases when a bitumen-wet pore system occurs in the experiments. This would be at experimental temperatures greater than or equal to 310°C for the Kreyenhagen Shale (Figure 5A).

In addition to the bitumen impregnating the rock matrix, we propose that bitumen also impregnates the smectite interlayers. This interlayer bitumen is envisaged to hinder expansion by glycolation and results in a broader and lower-intensity I/S-gly (001) peak (Figure 5B). The high TOC in the less-than-2-μm fractions supports this interpretation with values between 6.3 and 4.2 wt. % (Table 5). Clementz (1976) has shown that resins and asphaltenes, which are major components of bitumen (Lewan, 1993), can irreversibly enter the smectite interlayers, which reduces expandability and increases TOC content.

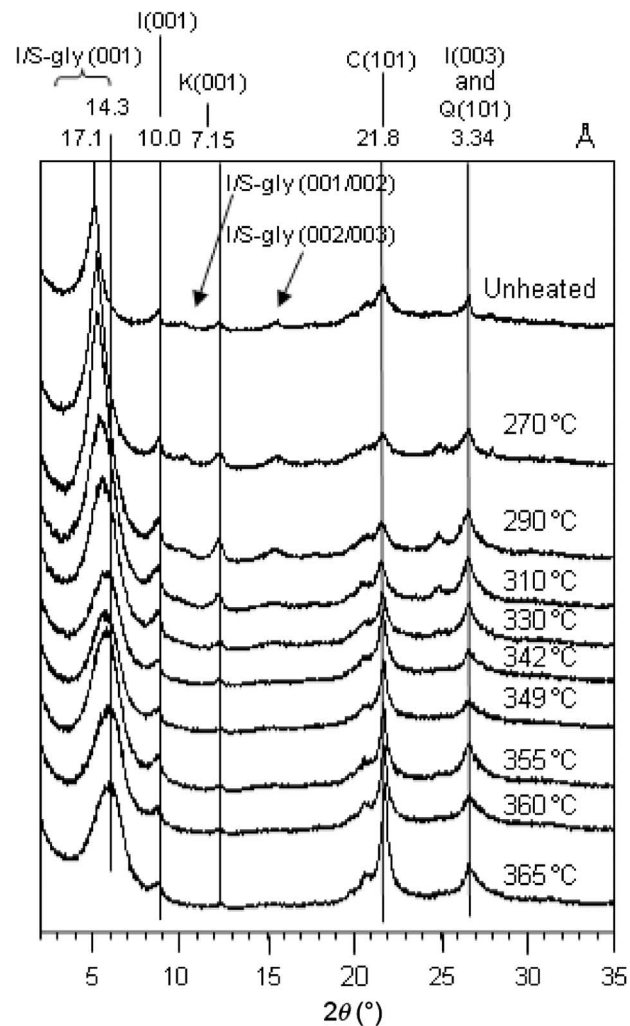
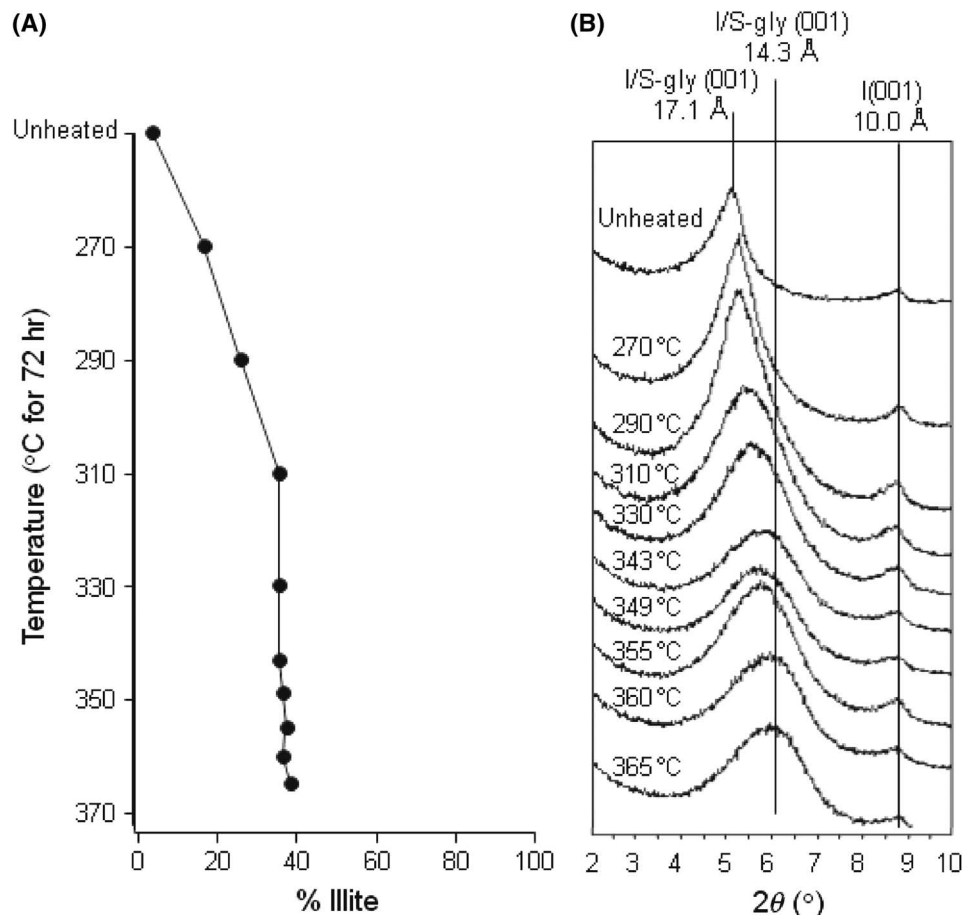


Figure 4. X-ray diffraction scans of the ethylene-glycolated (EG) less-than-2-μm fractions of the unheated rock (K-7) and its pyrolyzed aliquots at different experimental temperatures for 72-hr durations. I/S denotes the (001) peak for the mixed-layer illite and smectite, I denotes the (001) peak for discrete illite, K denotes the (001) peak for kaolinite, C denotes the (101) peak for opal-CT, and Q denotes the (101) peak for quartz with minor (003) peak from discrete illite denoted as I.

Analogous to high-molecular-weight polar-rich bitumen, uncharged oxygen- or nitrogen-bearing organic polymers can also be readily adsorbed into smectite interlayers (Theng, 2012). Theng (1982) reports that uncharged linear polymers like polyethylene glycol readily adsorb into smectite interlayers from aqueous solutions. As the molecular weight of the polyethylene glycol increases from 200 to 20,000 Da, the interlayer adsorption of the polymer increases from 7 to 39 g/100 g of smectite (Parfitt and Greenland, 1970a). Although large quantities of the polymer can be

Figure 5. (A) Plot of modeled weight percent illite in mixed-layer illite and smectite (I/S) (Velde and Vasseur, 1992) in less-than-2- μm fractions of unheated rock (K-7) and its pyrolyzed aliquots against experimental temperatures for 72-hr durations. (B) Enlarged ethylene-glycolated less-than-2- μm fractions XRD scan from Figure 4 between 2° and $10^\circ 2\theta$. Peak width between 5° and $6^\circ 2\theta$ was used to determine modeled percent illite.



adsorbed in the smectite interlayers, polymer desorption is so slow that adsorption is typically considered irreversible (Theng, 1982; Deng et al., 2006).

As shown in Table 5, the high TOC contents of the less-than-2- μm fractions have similar but consistently lower HI values than their equivalent whole rock at temperatures higher than 310°C (Table 1). The lower HI value at 270°C may be attributed to the H_2O_2 treatment of the less-than-2- μm fractions preferentially reacting with the more labile hydrogen-rich parts of the immature organic matter. No significant difference exists in HI at 310°C. The low HI values (≤ 35 mg/g TOC) at higher temperatures ($>310^\circ\text{C}$) indicate that most of the TOC is inert carbon. Within the interlayers, this inert carbon would have originally been solvent-soluble bitumen that has become pyrobitumen. The implication is that unlike the usual conversion of bitumen to hydrocarbon-rich oil by thermal cracking, it has instead converted

to pyrobitumen by crosslinking. This interpretation is supported by the unusually abrupt decrease in bitumen at low temperatures ($<330^\circ\text{C}$) with no compensating increase in expelled oil or hydrocarbon gas (Figure 2). Crosslinking reactions to form pyrobitumen (i.e., inert carbon) occur to different degrees in all pyrolysis experiments (Lewan, et al., 1995; Lewan, 1997) and natural thermal maturation (Muscio and Horsfield, 1996). However, the proportion of crosslinking appears to be enhanced in the presence of smectite. Bitumen impregnation of the smectite interlayers may be responsible for the enhanced pyrobitumen formation, which would result in the observed reduced yields of generated expelled oil (Figure 3). This interpretation is supported in part by the report that organic matter within the interlayers of smectite is highly stable and resists removal by H_2O_2 and chloroform-extraction treatments as reported by Cai et al. (2008). Consequently, this

Table 5. Rock-Eval Pyrolysis Data for <2- μm Fraction of Pyrolyzed Recovered Rock (K-7)

Conditions (°C for 72 hr)	TOC (wt. %)	S_1	S_2 mg/g rock	S_3	T_{max} (°C)	HI mg/g TOC	OI	PI $S_1/[S_1 + S_2]$
270	6.25	0.39	9.75	3.06	426	156	49	0.04
290	IS*	IS	IS	IS	IS	IS	IS	IS
310	6.09	0.23	4.53	1.30	446	74	21	0.05
330	5.92	0.10	2.05	1.70	460	35	29	0.05
343	5.89	0.08	1.00	2.31	515	17	39	0.07
349	4.86	0.10	0.98	1.46	512	20	30	0.09
355	4.21	0.07	0.79	1.52	527	19	36	0.08
360	4.96	0.08	0.78	1.46	545	16	29	0.09
365	4.96	0.13	0.75	1.48	550	15	30	0.15

*IS = insufficient sample.

retained bitumen should not be considered a recoverable resource, but rather inert carbon in the form of pyrobitumen.

Earlier studies advocated that the release of interlayer water during the conversion of smectite to illite could assist in the primary migration and expulsion of oil from source rocks (Powers, 1967; Burst, 1969). Although this released water may be a factor in mineral diagenesis in nonsource rocks (i.e., TOC < 0.8 wt. %; Bordenave et al., 1993, p. 260), it does not appear to be significant in primary migration or expulsion of oil from source rocks. As shown in Figure 3, immature source rocks with little or no smectite (Woodford Shale and Retort Shale Member) generate more expelled oil than the smectite-rich Kreyenhagen Shale. This is contrary to the suggestion by Powers (1967) that source rocks with smectite expel more oil than those with illite or kaolinite. The original interlayer water in smectite appears to be displaced by the impregnating bitumen, but this released water does not appear to enhance oil expulsion. Within the smectite interlayers, H_2O can be dissolved in the impregnating bitumen as discussed by Lewan (1997) or a separate phase with bitumen as described in the adsorption of uncharged polymers by Parfitt and Greenland (1970b). Additional studies are needed to determine the water-bitumen phase behavior within the smectite interlayers and the mechanism by which water is lost during the formation of pyrobitumen within the smectite interlayers.

Illitization versus Bitumen Generation

Although smectite can significantly reduce the expulsion efficiency of a source rock, conversion of smectite to illite would lessen or eliminate this reduction depending on when and to what level the conversion occurs relative to bitumen generation. If illitization is complete prior to bitumen generation, no reduction in the expulsion efficiency would occur as observed for the Retort Shale Member and Woodford Shale (Figure 3). However, if bitumen generation occurs during or prior to illitization in a source rock, expulsion efficiencies are expected to decrease proportionally with the degree of illitization and amount of smectite remaining relative to TOC. Previous studies have attempted to relate petroleum formation with increasing illitization of smectite or mixed-layer illite and smectite (Scotchman, 1987; Velde and Espitalié, 1989; Dellisanti et al., 2010). These studies have primarily focused on the relationship between percent illite in mixed-layer illite and smectite and T_{max} derived from Rock-Eval analyses. Although an increase in T_{max} with increasing illitization was observed, the individual relationships for various rocks gave a wide range of relationships that were too broad to provide a common correlation. This breadth of relationships is attributed to differences in the kinetics of petroleum formation and illitization, which may also differ significantly for different kerogen types (Lewan and Ruble, 2002) and pore-water chemistries (Eberl et al., 1993; Huang et al., 1993;

Roaldset et al., 1998), respectively. Bruce (1984) demonstrated this kinetic issue by comparing calculated temperature-time indices (TTI; Waples, 1980) for petroleum formation with measured percent illite in mixed-layer illite and smectite for three wells from Miocene deltaic systems. Onset of oil formation (TTI = 15) ranged from pre- to postillitization among three Gulf Coast wells.

This difference in kinetics is demonstrated in Figure 6 by comparing the times and temperatures required for illitization and bitumen formation. The kinetic parameters for illitization are from Roaldset et al. (1998) for experiments with a 0.01 N KCl solution. Unfortunately, no hydrous-pyrolysis kinetic parameters are currently available for bitumen generation from type II kerogen. However, an approximation can be derived using 1% expelled-oil generation from the kinetic parameters of the Woodford Shale as reported by Lewan (1985). The rationale is that 1% generation of expelled oil requires the development of a continuous bitumen network within the rock matrix (Lewan, 1987). Therefore, a continuous bitumen network should be developed at 1% expelled-oil generation. Figure 6 indicates that bitumen generation occurs before complete illitization at temperatures greater than 258°C in durations of weeks to hours, which are within the range of conditions for laboratory pyrolysis experiments. Conversely, illitization is complete before bitumen formation at lower temperatures and longer durations (one to millions of years), which are more within the range of conditions for natural oil generation. This approximation implies that illitization is complete before bitumen generation at the lower temperatures and longer durations experienced by source rocks during natural maturation. As a result, reductions in the expulsion efficiencies of source rocks like the Kreyenhagen Shale would not be expected. However, variations in the timing of bitumen generation as a result of varying sulfur content in original kerogen or availability of K⁺ for illitization are likely to result in more complex scenarios than the scenario shown in Figure 6.

Determining Oil-Expulsion Efficiencies

Expulsion efficiency of a source rock may be expressed as milligrams of expelled oil per gram of

TOC_o. Hydrous pyrolysis is currently the only laboratory method that generates expelled oil from a source rock that simulates natural oil expulsion (Lewan, 1993), with polar-rich bitumen decomposing to expelled hydrocarbon-rich oil. The expulsion is a consequence of the oil being immiscible in the bitumen and a net volume increase within the rock matrix (Lewan, 1997). Anhydrous-pyrolysis methods yield products by vaporization (open-system pyrolysis; Rock-Eval) or solvent extraction (closed gold-tube pyrolysis), which represent conditions that are not operative in natural petroleum formation. As a result, their products are typically enriched in polars (i.e., resins and asphaltenes) and not representative of hydrocarbon-rich natural crude oils (Lafargue et al., 1989; Blanc and Connan, 1992; Behar et al., 1997; Lewan, 1997). Hydrous pyrolysis of an immature source rock at temperatures between 350°C and 365°C for 72 hr gives maximum expulsion efficiencies that are typically half that of the original Rock-Eval HI (Lewan et al., 2006). Although expulsion efficiencies derived from hydrous pyrolysis have been shown to yield more realistic and lower petroleum-charge values than various algebraic schemes using open-system pyrolysis, it still exaggerates natural expulsion efficiencies by a factor of 1.7 (Lewan et al., 2002; Peters et al., 2006). This correction is caused by the higher temperatures and lower pressures employed in hydrous pyrolysis compared to natural petroleum formation (Lewan et al., 1995).

The significant reduction of expelled oil from the smectite-rich Kreyenhagen Shale relative to its isolated kerogen and the illite-bearing Retort Shale Member and Woodford Shale (Figure 3) indicates that the amount of smectite in a source rock can significantly reduce its expulsion efficiency. In the case of the Kreyenhagen Shale sample used in this study with a smectite/TOC_o ratio of 3.3 (Table 4), the 88% reduction in the expulsion efficiency is expected to decrease as the ratio decreases for other immature source rocks containing type II kerogen. Unfortunately, insufficient data exist in this study to determine the function (e.g., linear, polynomial, power, or logarithmic) that predicts the expulsion-efficiency relationship between an 88% reduction at a 3.3 smectite/TOC_o ratio and 0% reduction when no smectite is present. However, a semilogarithmic

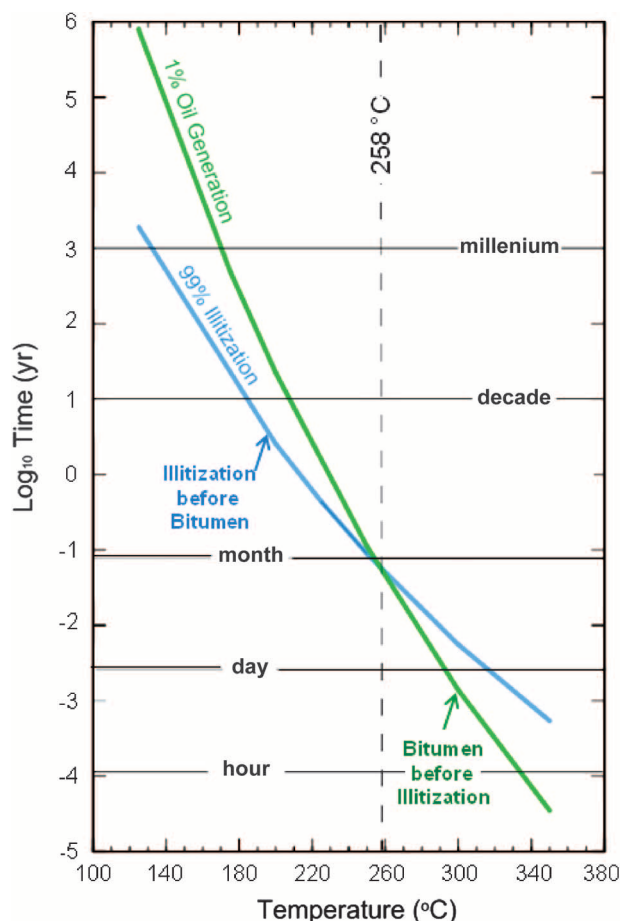


Figure 6. Plot showing the time and temperature required for 99% conversion of smectite to illite based on kinetics derived experimentally by Roaldset et al. (1998; [activation energy $\{E_a\} = 33$ kcal/mol and frequency factor $\{A_0\} = 3.67E + 11/h$]) and for 1% generation of expelled oil based on kinetics experimentally derived on the Woodford Shale (Lewan and Ruble, 2002; $E_a = 52.16$ kcal/mol and $A_0 = 6.51E + 16/h$).

relationship for decreasing expulsion efficiencies for type II kerogen is envisaged to be similar but at lower expulsion efficiencies than that reported by Orr (1983) for various bentonite mixtures with type I kerogen. In addition to the smectite/ TOC_0 ratio, it is critical that the amount of TOC_0 of a rock be considered in evaluating expulsion efficiencies. Petrographic studies have shown that an effective source rock typically requires a TOC_0 greater than 2.4 wt. % to facilitate a continuous bitumen network within the rock matrix for oil expulsion to occur (Lewan, 1987). This TOC limit is in agreement with that proposed by Bordenave et al. (1993, p. 260) for excellent source rocks with type II kerogen based on oil saturation of pores.

Illite is more common than smectite or smectite-dominant mixed-layer illite and smectite in Paleozoic shales (Weaver, 1967). Thermally immature (i.e., prebitumen generation) Paleozoic source rocks like those in the Retort Shale Member and Woodford Shale (Lewan, 1985) have little or no smectite (Table 4). This may be the result of provenance (e.g., Pellenard et al., 1999), illitization during early diagenesis (e.g., Eberl et al., 1993; Somelar et al., 2009), or early brine migration (Grathoff et al., 2001). As these illite-bearing source rocks thermally mature, generated bitumen is available to decompose to expelled oil with no smectite interlayers present to sequester the bitumen and reduce the expulsion efficiency. Hydrous pyrolysis of these types of source rocks at temperatures between 350°C and 365°C for 72 hr is considered to yield representative expulsion efficiencies. Conversely, expulsion efficiencies of smectite-rich source rocks, which are more common in Cenozoic and some Mesozoic shales (Weaver, 1967), require knowing the degree of smectite illitization near the start of bitumen generation. Bitumen generation can be assessed by noting increases in well-log resistivity (e.g., Meissner, 1993) or bitumen/ TOC ratios (e.g., Deng et al., 1996) of a maturing source rock in the subsurface. Conducting hydrous-pyrolysis experiments at 350°C to 365°C for 72-hr durations on samples at or near bitumen generation would give representative expulsion efficiency for smectite-bearing source rocks. Note that all the hydrous-pyrolysis expulsion efficiencies must be corrected (i.e., divide by 1.7) for natural conditions (i.e., lower temperatures and higher pressures) as reported by Lewan et al. (2002).

A more rigorous approach to determining expulsion efficiencies by hydrous pyrolysis of immature smectite-rich source rocks is to pretreat the samples at lower temperatures and longer times in K-rich waters to convert the rock to the degree of illitization observed at or near bitumen generation in the subsurface (Figure 6). Once the level of illitization is attained, the pretreated sample can be subjected to hydrous pyrolysis at temperatures between 350°C and 365°C for 72-hr durations to determine representative expulsion efficiencies. Petrographic observations on cores of the Woodford Shale subjected to hydrous pyrolysis show no signs of bitumen

generation or impregnation of the rock matrix at 250°C after 72 hr (Lewan, 1987). Kinetic parameters reported by Roaldset et al. (1998; [activation energy $\{E_a\}$]) = 33 kcal/mol and frequency factor (A_0) = $3.67E + 11/h$) for a 1.0 N KCl solution indicate that complete illitization of smectite occurs at 250°C after 72 hr. This two-step experimental approach remains to be tested, and a finer grain size for the starting rock may be needed to ensure optimum contact between K-rich water and smectite within the rock. Another consideration is that pretreatments may require temperatures lower than 250°C and times longer than 72 hr for source rocks with type IIS kerogen, which generate bitumen and oil at lower thermal maturities (Lewan, 1985; Lewan and Ruble, 2002).

Regardless of the hydrous pyrolysis approach used, it is imperative that the level of illitization at or near bitumen generation be determined to derive representative expulsion efficiencies for smectite-rich source rocks. If burial rates and thermal gradients vary over the extent of a pod of active source rock, then the degree of illitization may change relative to bitumen generation. The Jeanne d'Arc Basin offshore Newfoundland is a good example, where levels of illitization vary significantly relative to vitrinite reflectance in different wells (Abid and Hesse, 2007). Understanding these variations should help determine areas of a petroleum system that are likely to have a greater petroleum charge. This is particularly important for petroleum systems with Cenozoic, and in some cases, Mesozoic source rocks, which are more likely to contain smectite than Paleozoic source rocks (Weaver, 1967).

CONCLUSIONS

This study shows that smectite reduces source rock oil-expulsion efficiency, contrary to previously proposed hypotheses. Knowing the clay mineralogy of a source rock is critical to determining its oil-expulsion efficiency, particularly if it contains smectite. Hydrous pyrolysis is a laboratory method to simulate natural oil generation and determine the oil-expulsion efficiency of immature source rocks (milligrams of expelled oil per gram of TOC_o). Representative expulsion efficiencies of a source rock

typically occur at experimental temperatures between 350°C and 365°C for 72 hr. As noted by Lewan et al. (2002), hydrous-pyrolysis-derived expulsion efficiencies provide more realistic and lower petroleum-charge values for petroleum systems than various algebraic schemes based on open-system pyrolysis (e.g., Rock-Eval pyrolysis). However, the smectite-bearing Eocene Kreyenhagen Shale with 9.4 wt. % TOC of type II kerogen has an exceptionally low expulsion efficiency of 40 mg/g TOC compared to typical values of 246 to 276 mg/g TOC for illite-bearing source rocks with type II and IIS kerogen (Woodford Shale and Retort Phosphatic Shale Member, respectively). This reduced expulsion efficiency is attributed to bitumen entering smectite interlayers before illitization occurs in the experiments. Interlayered bitumen undergoes crosslinking to form pyrobitumen instead of thermal cracking to form oil. As a result, the expulsion efficiency of the Kreyenhagen Shale sample is reduced by 88% compared to that for type II kerogen isolated from the rock sample. Bitumen impregnation of the rock matrix changes the pore system of a source rock from water wet to bitumen wet, which impedes the mobility of K^+ and the dissolution and precipitation reactions needed for illitization of smectite.

Available kinetic parameters indicate that bitumen formation precedes illitization at typical experimental temperatures and times (270°C to 365°C for 72 hr). Conversely, illitization can precede bitumen formation at lower temperatures and longer times representative of natural maturation depending on the availability of K^+ . These relationships indicate that expulsion efficiencies determined by hydrous pyrolysis on smectite-rich source rocks require knowledge of when and at what level illitization occurs relative to bitumen formation within a maturing source rock. Expulsion efficiencies can then be determined by conducting hydrous pyrolysis on subsurface samples representative of the level of illitization at or near bitumen generation. A possible alternative is to convert the smectite to the representative level of illitization by pretreating the sample with K-rich solutions at low temperature (<258°C) before conducting hydrous pyrolysis between temperatures of 350°C and 365°C for 72 hr to determine expulsion efficiencies.

The need to account for reduced expulsion efficiencies resulting from smectite is more likely in Cenozoic and in some Mesozoic source rocks because of the common occurrence of smectite in shales of these eras (Weaver, 1967). Conversely, Paleozoic source rocks are least likely to have reduced expulsion efficiencies because of early illitization prior to bitumen generation.

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