Estimation of hydrous-pyrolysis kinetic parameters for oil generation from Baltic Cambrian and Tremadocian source rocks with Type-II kerogen

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Determining kinetic parameters for oil generation from a source rock by hydrous pyrolysis requires a considerable amount of sample (kilograms) and laboratory time (several weeks). In an effort to circumvent these requirements, hydrous-pyrolysis (HP) kinetic parameters for oil generation from Upper Cambrian and Tremadocian source rocks of the Baltic region are estimated by two methods: (1) organic sulfur content in kerogen and (2) HP experiments conducted at 330 and 355°C for 72 h. Estimates for the Upper Cambrian source rocks based on organic sulfur contents gave activation energies from 47 to 56 kcal/mole and frequency factors from 1.156×10^{25} to 1.078×10^{28} m.y.$^{-1}$. Tremadocian source rocks based on organic sulfur content gave estimated activation energies from 60 to 62 kcal/mole and frequency factors from 1.790×10^{29} to 1.104×10^{30} m.y.$^{-1}$. The estimates for the Tremadocian source rocks were less affected by thermal maturation because their low kerogen $S/(S + C)$ mole fractions (<0.018) remained essentially constant. Conversely, the higher kerogen $S/(S + C)$ mole fractions (>0.018) of the Upper Cambrian source rocks decreased with thermal maturation and resulted in overestimation of the kinetic parameters. The second method was designed to estimate kinetic parameters based on two HP experiments. The assumption that the maximum yield in calculating the rate constant at 330°C ($k_{330°C}$) could be determined by a second hydrous pyrolysis experiment at 355°C for 72 h proved not to be valid. Instead, a previously established relationship between Rock-Eval hydrogen index and maximum HP yield for Type-II kerogen was used to calculate $k_{330°C}$ from oil yields generated by the HP experiment at 330°C for 72 h assuming a first-order reaction. HP kinetic parameters were determined from relationships between $k_{330°C}$ and the HP kinetic parameters previously reported. These estimated HP kinetic parameters were in agreement with those obtained by the first method for immature samples, but underestimated the kinetic parameters for samples at higher thermal maturities. Applying these estimated HP kinetic parameters to geological heating rates of 1 and 10°C/m.y. indicated that the Upper Cambrian source rocks would generate oil notably earlier than the overlying Tremadocian source rocks. This was confirmed in part by available data from two neighboring boreholes in the Polish sector of the Baltic.

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INTRODUCTION

The kinetic parameters for oil generation from petroleum source rocks are one of the most important issues in petroleum geochemistry and geology, especially in modelling of petroleum processes (Kosakowski *et al*., 2010; Wróbel and Kosakowski, 2010) and defining petroleum systems (Kotarba *et al*., 2010). The kinetics of the organic matter transformations, and the related processes of petroleum generation, reflect organic matter structure and composition and syn-sedimentary and post-diagenetic processes. Transformation of the organic matter during the burial of petroleum source rocks in the development of a sedimentary basin over geological time relies on chemical kinetics. Therefore, determination of kinetic parameters is critical to determining the timing, extent, and location of petroleum generation (e.g., Lewan and Ruble, 2002; Kotarba *et al*., 2010).

The rate constant (k) for petroleum generation from sedimentary organic matter is described by the Arrhenius equation: $k = A_0 \exp(-E_a / RT)$. The frequency factor (A_0) and activation energy (E_a) are the critical kinetic parameters that equate temperature (T) to rates of petroleum generation with the ideal-gas law constant (R). Two fundamentally different methods for determining these kinetic parameters are (i) isothermal closed-system hydrous pyrolysis (HP; Lewan, 1985) and (ii) non-isothermal open-system anhydrous pyrolysis (Rock-Eval, *SR Analyzer*; Burnham and Braun, 1999). These methods differ not only in experimental conditions, but in reaction products

Fig. 1. Sketch map of the Baltic region showing the location of sampled boreholes and outcrops

and kinetic parameter derivations (Lewan and Ruble, 2002; Behar *et al*., 2003). The credibility of these parameters is subject to discussion (e.g., Burnham, 1998; Lewan, 1998*a*). However, HP kinetics have been shown to provide results more concurrent with constraints of geological and geochemical data than Rock-Eval (RE) kinetics for source rocks containing high-sulfur or low-sulfur oil-prone kerogen (Ruble *et al*., 2001; Lewan and Ruble, 2002; Lewan *et al*., 2006).

The procedure for determining HP kinetic parameters is time-consuming and requires several kilograms of immature sample. In some studies, published HP kinetic parameters for oil generation from source rocks with Type-I, -II, and -IIS kerogen have been successfully applied to source rocks with similar kerogen types (Lewan, 2002; Pitman *et al*., 2004; Roberts *et al*., 2004). However, relationships between activation energies (E_a), frequency factors (A_0) and kerogen organic-sulfur content provide an indirect method of determining HP kinetic parameters (Lewan, 1998*b*; Lewan and Ruble, 2002; Lewan *et al*., 2006) that are more specific to a given source rock (e.g., Higley *et al*., 2009). The objective of the current study is to use this indirect method to estimate HP kinetic parameters for early Paleozoic source rocks with Type-II kerogen in the Baltic region. In addition, these estimated kinetic parameters were tested on samples on which hydrous pyrolysis experiments at 330 and 355°C for 72 h have been conducted.

SAMPLES AND METHODS

SAMPLES

Samples for this study are from onshore Estonia and Sweden, and on- and off-shore Poland (Fig. 1). The depths at which these samples were collected and geochemical data characterizing their kerogen types and thermal maturity are given in Table 1. The samples are arranged in order of increasing thermal maturity based on the reflectance of vitrinite-like macerals. Four samples (denoted in bold print in Table 1) had sufficient quantities and organic richness to conduct hydrous pyrolysis experiments at 330 and 355°C for 72 h. The four samples represent one Upper Cambrian shale and three Tremadocian shales. Three of them were collected from cores of boreholes localized in the Polish Exclusive Economic Zone of the Baltic Sea operated by LOTOS Petrobaltic S.A. Company, and one from a cliff exposure in the village of Pakri (Estonia; Fig. 1).

ANALYTICAL METHODS

Screening pyrolysis analyses of rock samples were carried out with a Rock-Eval Model II instrument equipped with an organic carbon module. Measurements of mean random

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Location and geochemical description of rock samples and kinetic parameters estimated from S/(S + C) of isolated kerogen

Borehole/sample designation[#]	Depth [m]	Strat.	Sample location	TOC [wt.%]	R_o [%]	T_{max} [°C]	HI	Kerogen Atomic Ratios			E_a	$logA_0$ (log[1/h])
								H/C	O/C	S/(S + C)		
Pakri 1	**outcrop**	**O–Tr**	**Estonia**	**16.5**	**0.33**	**421**	**448**	**0.92**	**0.05**	**0.011**	**60.0**	**19.31**
AS-39	outcrop	Cm$_3$	Sweden	15.5	0.48	426	292	0.94	0.06	0.021	54.7	17.57
AS-38	outcrop	Cm$_3$	Sweden	16.4	0.51	425	325	0.96	0.05	0.025	52.6	16.87
AS-33*	outcrop	Cm$_3$	Sweden	13.2	0.52	424	350	1.12	0.07	0.035	47.3	15.12
B4-N1 comp.	**1192–1197**	**Cm$_3$**	**PL-off.**	**13.0**	**0.56**	**436**	**364**	**0.94**	**0.02**	**0.018**	**56.3**	**18.09**
AS-36	outcrop	O–Tr	Sweden	8.1	0.57	440	345	0.96	0.03	0.007	62.2	20.01
B6-3 comp.	1426–1438	Cm$_3$	PL-off.	13.2	0.62	441	331	0.91	0.03	0.010	60.6	19.49
B3-9	1413.85	Cm$_3$	PL-off.	14.0	0.63	430	424	1.10	0.04	0.010	60.6	19.49
B4-1	1103.70	O–Tr	PL-off.	10.8	0.73	441	353	1.01	0.03	0.004	63.7	20.54
B7-1 comp.	**2320–2323**	**O–Tr**	**PL-off.**	**9.6**	**0.74**	**434**	**289**	**0.93**	**0.04**	**0.012**	**59.5**	**19.14**
B21-1	1731.70	Cm$_3$	PL-off.	14.6	0.84	440	245	0.87	0.03	0.008	61.6	19.84
B6-2 comp.	**1432–1438**	**O–Tr**	**PL-off.**	**10.6**	**0.86**	**441**	**302**	**0.95**	**0.02**	**0.008**	**61.6**	**19.84**
D bki 3 (Db 3)	2680.90	Cm$_3$	PL-on.	7.2	0.99	438	101	0.81	0.06	0.012	59.5	19.14
B16-1	1847.50	Cm$_3$	PL-off.	9.5	1.00	439	131	0.74	0.05	0.010	60.6	19.49
Białogóra 4K (Bg 4K)	2775.20	Cm$_2$	PL-on.	4.9	1.01	447	117	0.81	0.04	0.016	57.4	18.44
B16-1	1857.60	Cm$_3$	PL-off.	8.8	1.03	441	154	0.75	0.04	0.011	60.0	19.31
Białogóra 3 (Bg 3)	2681.10	Cm$_3$	PL-on.	10.8	1.03	436	134	0.77	0.03	0.012	59.5	19.14
arnowiec 6K (Zn 6K)	2828.50	Cm$_3$	PL-on.	8.8	1.05	443	104	0.75	0.04	0.007	62.2	20.01

– samples used in hydrous pyrolysis experiments denoted in bold print; Strat. – stratigraphy; R_o – reflectance of the vitrinite-like macerals; T_{max} – maximal temperature of the S_2 peak (Rock-Eval); HI – hydrogen index [mg HC/g TOC]; E_a – activation energy [kcal/mol]; A_0 – frequency factor; Cm$_2$ – Middle Cambrian, Cm$_3$ – Upper Cambrian, O–Tr – Ordovician–Tremadocian; PL – Poland, off. – offshore, on. – onshore; * – geochemical data after Lewan and Buchardt (1989)

vitrinite-like reflectance (R_o) were carried out with a *Zeiss-Opton* microphotometer at a wave-length of 546 nm, in oil. Sample preparation and point counts were carried out in accordance with the ICCP procedure (Taylor *et al.*, 1998). Isolation of kerogen for elemental analysis was achieved by *Soxhlet* extraction of pulverized samples with dichloromethane:methanol (93:7 vol.), decalcification of the solid residue with hydrochloric acid at room temperature, removal of silicates with concentrated hydrofluoric acid, removal of neoformed fluoride phases with hot concentrated HCl, heavy liquid separation (aqueous ZnBr$_2$ solution, density 2.1 g/ml), and *Soxhlet* extraction with the above-mentioned solvent mixture. The elemental composition of isolated kerogen (C, H, N and S) was determined with a *Carlo Erba EA 1108* elemental analyser. The quantity of pyrite remaining in the kerogen concentrate was analysed as iron, on a *Perkin-Elmer Plasma 40 ICP-AES* instrument after digesting the ash from burned kerogen (815°C, 30 min.) with hydrochloric acid. The organic sulfur content in kerogen was calculated as the difference of total and pyritic sulfur. The oxygen content was calculated as the difference of 100 percent taking into account C, H, N, S, moisture and ash content. The calculated atomic ratios and the S/(S + C) mole fractions are given in Table 1 for all the samples.

The hydrous pyrolysis experiments involved isothermally heating 400 g of crushed gravel-sized (0.5 to 2.0 cm) Upper Cambrian and Tremadocian shales in 1-litre Parr reactors composed of stainless-steel 316 or Hastelloy-C276 in the presence of 375 g of distilled water for the shale experiments. These pro-

portions of rock and water were calculated according to Lewan (1993a) to ensure that the rocks were in contact with liquid H$_2$O (i.e., water) before, during, and after the experiments. After loading and sealing the reactor, the remaining headspace was evacuated and filled with 170 to 175 kPa of helium. The reactor was then placed in an electric heater and brought to the desired experimental temperature. Isothermal heating was conducted at temperatures of 330 and 355°C ($\pm$0.5°C). Cool-down times ranged from 18 to 24 h. At the end of the experiments and following gas collection, the immiscible expelled oil was quantitatively removed from the water surface in the reactor with a Pasteur pipette and a benzene rinse (Lewan, 1993a). Immiscible oil quantity was calculated as the sum of the expelled oil recovered by the pipette and evaporated benzene rinse.

ESTIMATION OF KINETIC PARAMETERS BASED ON ORGANIC SULFUR CONTENT IN KEROGEN

Lewan (1985) reported that time-temperature relations of oil generation can differ significantly from one another depending on their organic sulfur content. This diversity is explained in part by the fact that S-S and S-C bonds are weaker than C-C bonds in organic matter. As a result, these sulfur bonds break at lower thermal maturities and the free radicals they generate initiate cleavage of C-C bonds at correspondingly lower thermal maturities (Lewan, 1998b). Therefore, kerogens with high or-
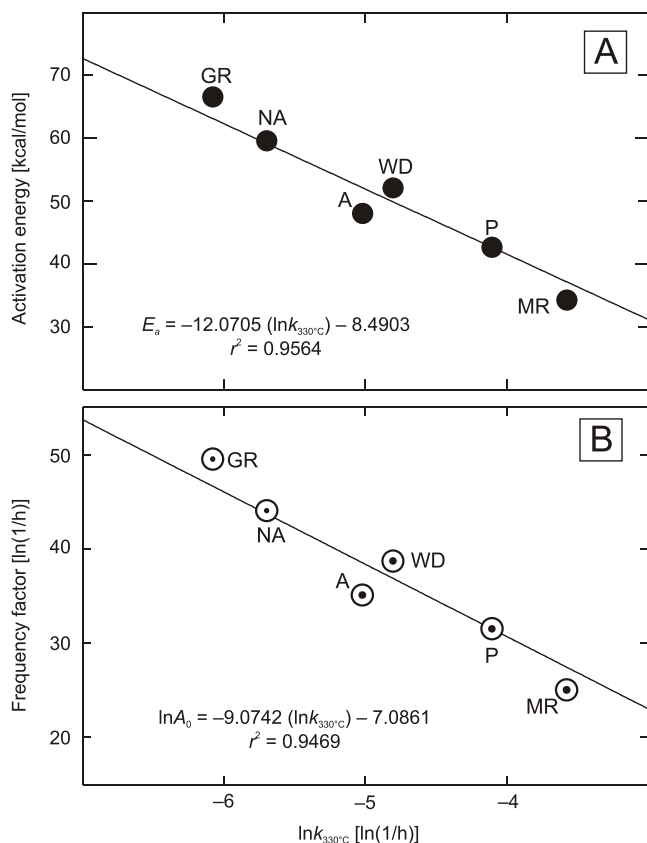
Fig. 2A – activation energy; B – logarithm of frequency factor *versus* the rate constant for 330°C from previously published HP kinetic parameters (Lewan and Ruble, 2002)

GR – Green River Fm., NA – New Albany Shale, WD – Woodford Shale, A – Alum Shale, P – Phosphoria Fm., MR – Monterey Fm.

ganic sulfur contents have lower activation energies than low-sulfur kerogens. This is in agreement with observations by Orr (1986) that petroleum generation from source rocks with high organic sulfur kerogen (i.e., Type-IIS) starts at lower stages of catagenesis. Lewan and Ruble (2002) reported an excellent correlation ($r^2 = 0.995$) between HP kinetic parameters and organic sulfur content in the immature kerogen denoted as a mole fraction with carbon [i.e., S/(S + C)], as expressed in Equation 1.

$$E_a = -530.73[S / (S + C)] + 65.87 \qquad [1]$$

Lewan and Ruble (2002) also reported an excellent correlation ($r^2 = 0.999$) between activation energies (E_a, kcal/mole) and frequency factors (A_0, [1/h]) determined by hydrous pyrolysis. This compensation relation is expressed in Equation 2.

$$\log A_0 = (E_a - 1.335) / 3.039 \qquad [2]$$

These two equations may be used to estimate HP kinetic parameters of a source rock by determining the organic sulfur and carbon content of its immature Type-II kerogen.

ESTIMATION OF KINETIC PARAMETERS BASED ON RESULTS OF TWO HYDROUS PYROLYSIS EXPERIMENTS

This method for estimating HP kinetic parameters involved conducting two hydrous pyrolysis experiments on aliquots of the four source rock samples. One experiment is intended to estimate a maximum oil yield, which for Type-II kerogen typically occurs at or near 355 ±5°C for 72 h (Lewan and Ruble, 2002). The other experiment conducted at a lower thermal stress condition is intended to determine a rate constant at a given temperature. This study uses the expelled oil yields from experiments conducted at 330°C for 72 h to determine rate constants (i.e., $k_{330°C}$) because this condition typically yields 30 to 60 percent of the maximum expelled oil generation for Type-II kerogen (e.g., Lewan and Ruble, 2002; Lewan *et al.*, 2006).

Relationships between $k_{330°C}$ and activation energies and frequency factors of previously reported HP kinetic parameters (Lewan and Ruble, 2002) provide expressions that can be used to estimate E_a and A_0 based on one rate constant. These relationships for rate constants calculated with Equation 1 for 330°C (i.e., $k_{330°C}$) are plotted against their activation energies and frequency factors in Figure 2A and B. A good correlation ($r^2 = 0.9564$) for ln $k_{330°C}$ with activation energies is expressed by:

$$E_a = -12.07(\ln k_{330°C}) - 8.49 \qquad [3]$$

and a good correlation ($r^2 = 0.9469$) for ln $k_{330°C}$ with the frequency factors is expressed by:

$$\ln A_0 = -9.074(\ln k_{330°C}) - 7.086 \qquad [4]$$

Estimating $k_{330°C}$ with expelled oil yields from one experiment assumes a first order reaction rate expressed as:

$$k_T = \left\{ \ln\left[1 / \left(1 - X_T \right) \right] \right\} / t \qquad [5]$$

where: T is 330°C, X is the fraction of expelled oil and t is 72 h.

The fraction X is expressed as the expelled oil yield at 330°C after 72 h divided by the maximum expelled oil yield of the source rock in hydrous pyrolysis experiments.

Assuming that the yields of expelled oil at 355°C after 72 h represent maximum yields, a relationship between HP maximum yields for immature source rocks with Type-II kerogen (HP$_{max\ oil}$) and Rock-Eval hydrogen indices (HI) has been established by Lewan *et al.* (2006). This relationship shows a good correlation ($r^2 = 0.9428$) between the two parameters based on eight different source rocks and is expressed as:

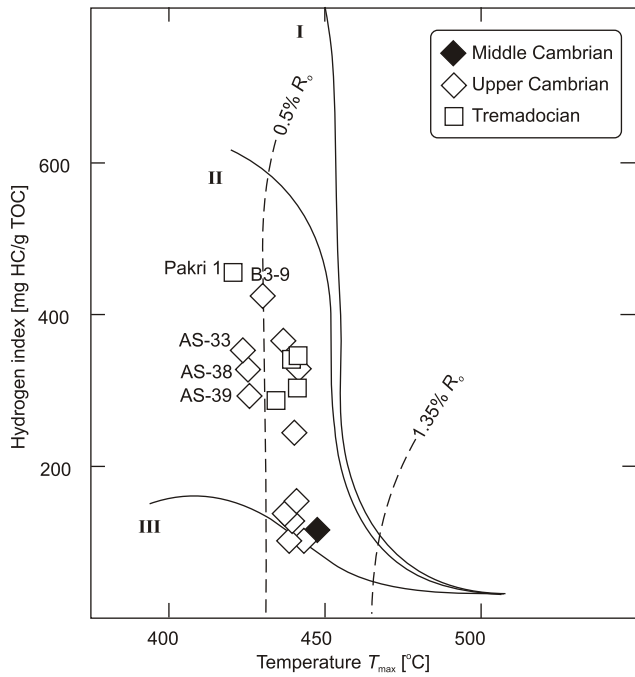$$HP_{max\ oil} = HI / 2.028 \qquad [6]$$

Fig. 3. Rock-Eval hydrogen index *versus* T_{max} temperature for recognition of kerogen type and determining the thermal maturity of organic matter in Cambrian and Tremadocian source rocks of the Baltic region

Trend lines of individual kerogen types (I, II and III) and maturity ranges after Espitalié *et al*. (1985); R_o – vitrinite reflectance scale
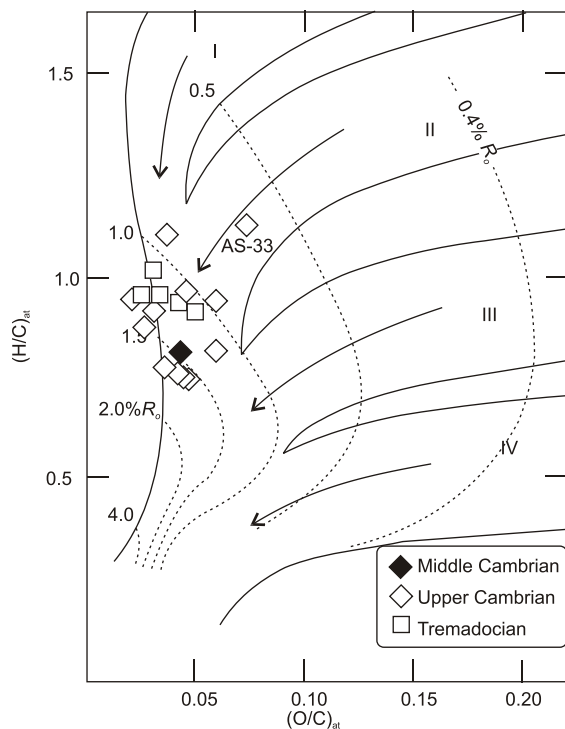

Fig. 4. Atomic H/C *versus* atomic O/C ratios of isolated kerogen from Cambrian and Tremadocian source rocks of the Baltic region

Kerogen type and thermal maturity boundaries after Hunt (1996); R_o – vitrinite reflectance scale
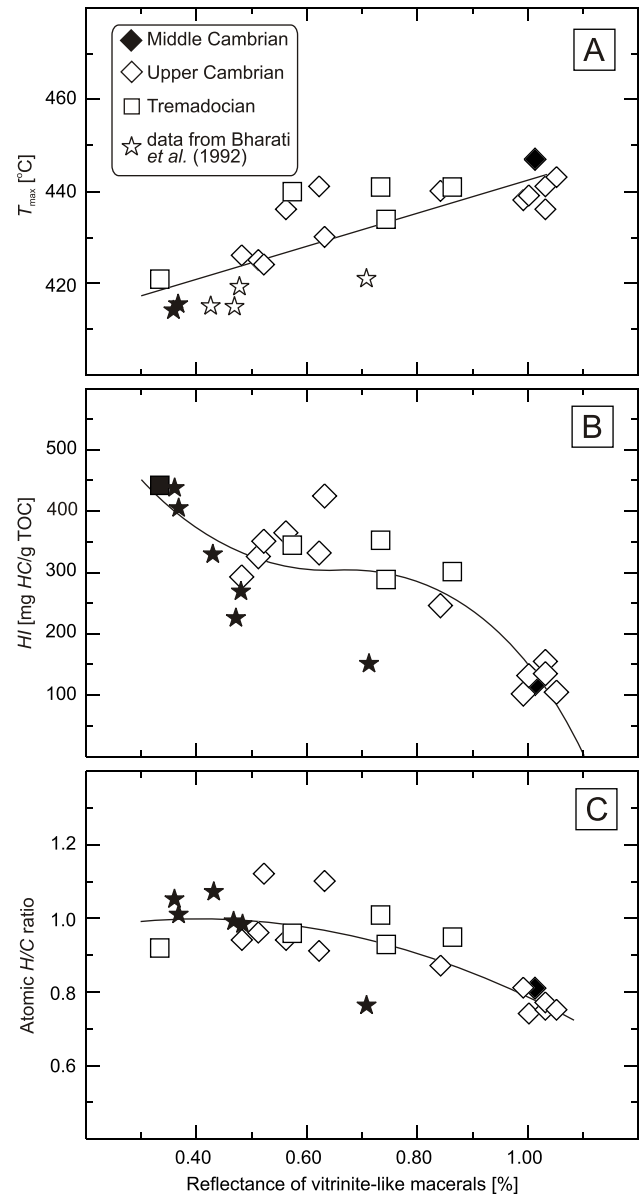
Fig. 5A – Rock-Eval T_{max}; B – Rock-Eval hydrogen index; C – kerogen atomic H/C ratio *versus* reflectance of vitrinite-like macerals

Curves are based on best-fit regressions using all of the data

RESULTS AND DISCUSSION

GENETIC TYPE AND MATURITY OF THE ORGANIC MATTER

　　Rock-Eval hydrogen index *versus* T_{max} temperature (Fig. 3) and atomic H/C *versus* O/C ratios (Fig. 4) indicate that Type-II kerogen is predominant in all of the samples confirming the results of e.g., Bharati *et al*. (1992, 1995), Schleicher *et al*. (1998) and Lewan and Buchardt (1989). The maturity indices of the organic matter (Rock-Eval T_{max} and HI, kerogen H/C atomic ratio and reflectance of the vitrinite-like macerals) are evidence that thermally immature or low maturity samples were re-

stricted to outcrops in Sweden and Estonia as previously reported by Buchardt *et al.* (1986), Lewan and Buchardt (1989), Buchardt and Lewan (1990), Leventhal (1991), Bharati *et al.* (1992, 1995), and Johannes *et al.* (2007). In the Polish part of the Baltic region Cambrian and Ordovician source rocks are early- and mid-mature (Table 1 and Figs. 3–5). Schleicher *et al.* (1998) and Grotek (2006) demonstrated late- and post-mature phase conditions in the deep buried levels close to the Teisseyre-Tornquist Zone. Figure 5 shows that there are general relationships between T_{max}, hydrogen index, atomic H/C ratio and the reflectance of vitrinite-like macerals, but these parameters are dependent on the kinetics of petroleum formation as described by Lewan (1985). For this reason, the vitrinite-like reflectance values are used as a thermal stress indicator. As reported by Buchardt and Lewan (1990), these reflectance values are suppressed relative to true vitrinite derived from vascular plants but do increase with increasing thermal maturity. The scatter around the general trends in Figure 5 may reflect differences in the petroleum-generation kinetic parameters of the samples as well as the influence of radioactive elements, occurring sometimes in large amounts (Lewan and Buchardt, 1989).

HP KINETIC PARAMETERS ESTIMATED FROM ORGANIC SULFUR CONTENT IN KEROGEN

Based on the kerogen S/(S + C) mole fractions, the activation energies were estimated with Equation 1 and are given in Table 1 for all the samples irrespective of their thermal maturity levels. These estimated activation energies were in turn used to estimate frequency factors with Equation 2. Sample AS-33 from Upper Cambrian strata in southern Sweden has the lowest E_a value of 47.3 kcal/mol, which is similar but slightly less than the 48.1 kcal/mol determined by Lewan and Buchardt (1989). The highest estimated E_a is 63.7 kcal/mol for sample B4-1 from the Tremadocian strata from a depth of 1.104 m in the Polish sector of the Baltic Sea. The range of these two extreme values are from samples that have low thermal maturities (vitrinite-like reflectance <0.8%). Kerogen S/(S + C) mole fractions are expected to decrease with increasing thermal maturity, but they are not significantly lower in the more mature rocks (vitrinite-like reflectance >0.8%) and as a result the estimated E_a values remain within the range of 47 to 64 kcal/mol (Table 1). Although S/(S + C) mole fractions of Type-IIS kerogen have been shown to decrease significantly with thermal maturation in hydrous py-
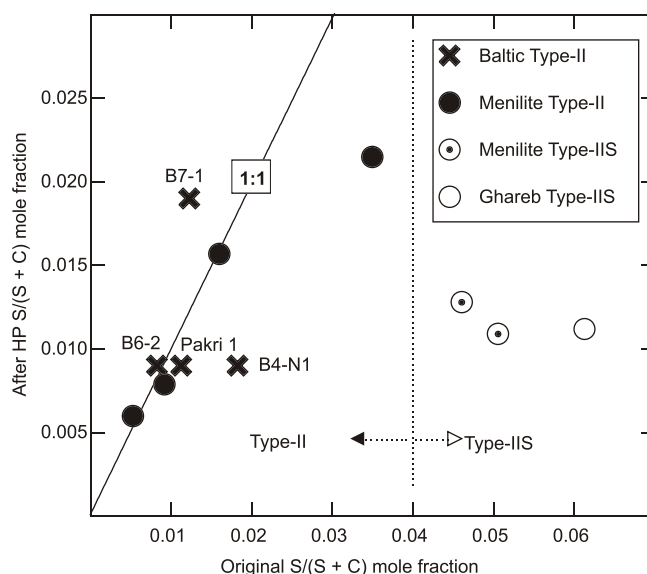

Fig. 6. Plot of kerogen S/(S + C) mole fractions before and after thermal maturation by hydrous pyrolysis of samples used in this study and from Curtis *et al.* (2004) for the Menilite Shales and Amrani *et al.* (2005) for the Ghareb Limestone

The vertical dashed line separating Type-II and -IIS kerogen is based on the conversion of the atomic S/C ratio of 0.04 defined by Orr and Sinninghe Damsté (1990) to a S/(S + C) mole fraction of 0.0385

rolysis experiments (Idiz *et al.*, 1990; Nelson *et al.*, 1995; Amrani *et al.*, 2005), hydrous pyrolysis of source rocks with Type-II kerogen show essentially no change (Curtis *et al.*, 2004). This behaviour is shown correlating S/(S + C) mole fractions of Menilite Shales with Type-II and -IIS kerogen (Curtis *et al.*, 2004), Ghareb Limestone with Type-IIS kerogen (Amrani *et al.*, 2005) and four samples from this study before and after hydrous pyrolysis experiments (Fig. 6). Even though individual rocks were heated in different conditions (Menilite Shales – two-step sequential HP conducted in 330°C/72 h followed by 355°C/72 h; Ghareb Limestone – 365°C/72 h and Baltic samples – 355°C/72 h) they probably reach maturities corresponding to the final stage of the low-temperature thermogenic process (R_o 1.6–1.7%). This statement confirms previous studies: Kotarba *et al.* (2009) showed that the heating at 330°C for 72 h and the subsequent heating of the same sample at 355°C for 72 h gave a final vitrinite reflectance of 1.60% R_o, Lewan (1985)

Table 2

Mean, standard deviation, and range of estimated HP kinetic parameters based on organic sulphur content of kerogens within specified thermal maturity ranges based on reflectance of vitrinite-like macerals

Geologic Age Units	E_a [kcal/mol]			$\log A_0$ (log[1/h])		
Ordovician–Tremadocian	Mean	Minimum	Maximum	Mean	Minimum	Maximum
0.3 to 0.6% R_o ($n = 2$)	61.1 ±1.5	60.0	62.2	19.66 ±0.49	19.31	20.01
0.6 to 0.9% R_o ($n = 3$)	61.6 ±2.1	59.5	63.7	19.84 ±0.70	19.14	20.54
Upper Cambrian						
0.3 to 0.6% R_o ($n = 4$)	52.7 ±3.9	47.3	56.3	16.91 ±1.29	15.12	18.09
0.6 to 1.1% R_o ($n = 8$)	60.6 ±0.6	59.5	62.2	19.49 ±0.31	19.14	20.01

n – number of samples; other explanations as in Table 1

showed that the experiment at 365°C for 72 h results to a vitrinite reflectance greater than 1.67% R_o, and according to Lewan (1993*b*) the maturity of organic matter after experiment at 355°C for 72 h corresponds in a vitrinite reflectance of 1.63% R_o.

The implication is that S/(S + C) mole fractions of immature Type-II kerogen with values less than ~0.018 do not change with thermal maturation within the range of oil generation. As show in Figure 6, S/(S + C) mole fractions of some immature kerogens (e.g., B7-1) with values less than 0.018 can increase with thermal maturation. The S/(S + C) mole fractions of mature kerogens can be used with caution to determine HP kinetic parameters, provided that there is evidence that their immature equivalent was a Type-II kerogen with low organic-sulfur contents (i.e., S/(S + C) <0.018). Table 1 shows that four of the six thermally immature (vitrinite-like reflectance <0.6% R_o) source rocks have S/(S + C) mole fractions equal to or greater than 0.018. As a result, assuming a constant S/(S + C) mole fraction for the thermally mature source rocks this would overstate the estimated HP kinetic parameters. This can be seen in the mean values of the estimated kinetic parameters grouped by geological-age units and thermal maturity ranges in Table 2. Although the number of samples is limited, several general observations can be made. Upper Cambrian source rocks, for which there is the most data, show that the E_a values of the thermally mature samples (R_o >0.6%) are overstated, since immature samples have a mean of 52.7 ±3.9 kcal/mole and the thermally mature samples have a mean of 60.6 ±0.6 kcal/mol (Table 2). This is expected for the Upper Cambrian source rocks because all four immature samples have S/(S + C) mole fractions equal to or greater than 0.018. The Tremadocian source rocks show no significant difference between the mean E_a values of the immature and mature samples (Table 2; 61.1 and 61.6 kcal/mol, respectively). The constancy of the estimated HP kinetic parameters with thermal maturation is explained in part by the Type-II kerogen in the two immature Tremadocian samples having S/(S + C) mole fractions less than 0.02 (Table 1). Estimated kinetic parameters for the Upper Cambrian–Tremadocian source rocks may be influenced by irradiation of organic matter by radiogenic element decay (Lewan and Buchardt, 1989). With only one sample of a Middle Cambrian source rock, which is thermally mature (vitrinite-like reflectance of 1.01% R_o) it is difficult to assess the utility of its estimated HP kinetic parameters. However, its S/(S + C) mole

fraction of 0.016 (Table 1) suggests the estimated HP kinetic parameters are likely overstated.

KINETIC PARAMETERS ESTIMATED FROM HYDROUS PYROLYSIS EXPERIMENTS

The estimation of kinetic parameters from HP experiments requires knowledge of the maximum oil yield of a source rock to calculate the fraction of reaction (X) at 330°C after 72 h. The two approaches used here to determine the maximum yield are (1) the relationship between maximum HP yield and Rock-Eval HI for immature Type-II and -IIS kerogen (Equations 6) and (2) a hydrous pyrolysis experiment at 355°C after 72 h assuming that this gives the maximum oil yield. The two approaches give different maximum yields (Table 3). Equation 6 consistently gives higher maximum yields than those determined by HP. This suggests that assuming maximum yields for hydrous pyrolysis of a source rock at these conditions is too low relative to maximum yields determined by Equation 6. This is a result of the assumption that 355°C for 72 h represents conditions for maximum oil generation for all source rocks. Lewan and Ruble (2002) have reported maximum yields of some source rocks at 360°C for 72 and 96 h and Lewan *et al.* (2006) at 360 and 365°C for 72 h. Therefore, the imprecision of this assumption negates the universal use of 355°C for 72 h to determine maximum oil yields, and only Equation 6 is used to estimate maximum oil yields. This assumption is restricted only to Type-II and -IIS kerogens (Lewan *et al.*, 2006).

Using the maximum yields from Equation 6, the fraction of reaction (X) was determined for the source rocks at 330°C after 72 h. These X values were used in Equation 5 to calculate the rate constants at 330°C ($k_{330°C}$) and are given in Table 3. The $k_{330°C}$ values are used in Equations 3 and 4 to estimate hydrous pyrolysis E_a and A_0 values, respectively. These estimated values in Table 3 are compared with those estimated by S/(S + C) mole fractions (Table 1) in Figure 7. The two immature source rocks (vitrinite-like reflectance <0.6%) show good agreement with differences in E_a values less than 1 kcal/mole and log A_0 values less than 0.6. However, differences become greater with increasing thermal maturity as shown by the mature source rocks (vitrinite-like reflectance >0.6%). In both mature source rocks, the kinetic parameters estimated by the S/(S + C) mole fractions are higher. This can be explained in part by the mature

Table 3

Results of estimating HP kinetic parameters based on two hydrous pyrolysis experiments; one experiment at 355°C for 72 h to estimate maximum yield, and the other experiment at 330°C for 72 h to estimate a first-order rate constant

Borehole/ sample	R_o [%]	HI	Maximum Yield [mg/g TOC]		Oil Yield at 330°C/72 h		$k_{330°C}$ [1/h]	E_a [kcal/mol]	lnA_0 (ln[1/h])	A_0 [1/m.y.]
			HI *vs.* HP*	355°C/72 h	[mg/g TOC]	X*				
Pakri 1	0.33	448	221.1	105.7	42.1	0.1903	2.931E-03	61.9	45.84	7.073E+29
B4-N1 comp.	0.56	364	179.6	118.7	47.2	0.2628	4.235E-03	57.5	42.50	2.508E+28
B7-1 comp.	0.74	289	142.6	86.0	37.4	0.2620	4.220E-03	57.5	42.53	2.594E+28
B6-2 comp.	0.86	302	148.8	117.1	54.5	0.3660	6.330E-03	52.6	38.85	6.547E+26

X – fraction of the reaction; k – rate constant; * – calculated on the basis of a maximum yield determined by the HP *versus RE* relationship (Equation 6); ** – calculated with a maximum yield determined by Equation 3, *** – calculated using Equation 4; other explanations as in Table 1
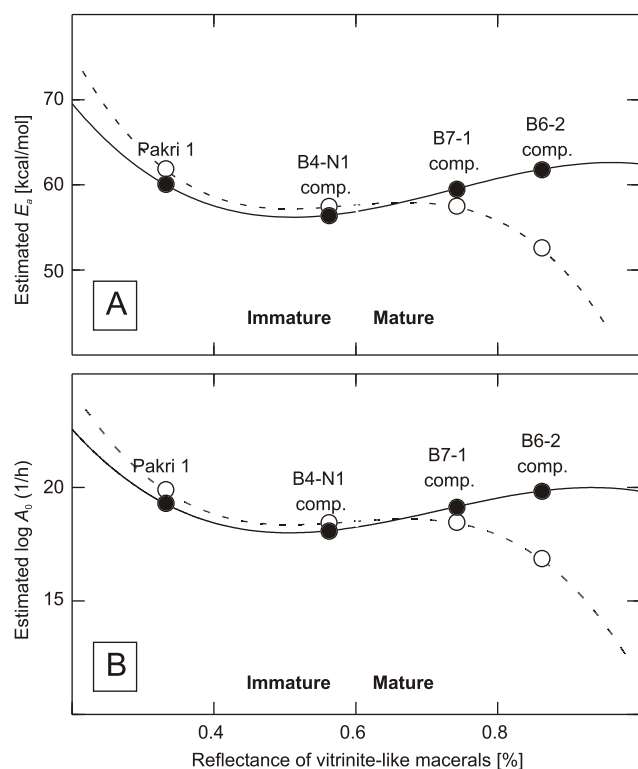
Fig. 7A – activation energies (E_a); B – log of frequency factors (A_0) estimated from kerogen S/(S + C) mole fractions (solid circles connected with solid line) and by *HP* experimentally determined $k_{330°C}$ (open circles connected with dashed line) *versus* reflectance of vitrinite-like macerals

samples having lower Rock-Eval HI values, which give lower maximum oil yields in Equation 6. This translates into higher rate constants at 330°C ($k_{330°C}$) resulting A_0 [1/m.y.] in lower kinetic parameters. Therefore, estimates of HP kinetic parameters based on S/(S + C) mole fractions of Type-II kerogen appear less sensitive to the thermal maturity of the source rock than those based on the two HP experiments. However, this conclusion should be restricted to Type-II kerogen and will not apply to Type-IIS kerogen because of significant changes in their S/(S + C) mole fractions with thermal maturation (Fig. 6).

GEOLOGICAL IMPLICATIONS

The geology and thermal history of the Baltic region are complex and complicated (e.g., Ulmishek, 1990; Brangulis *et al.*, 1992; Karnkowski, 2003; Modli ski and Podhala ska, 2010; Pokorski, 2010; Poprawa *et al.*, 2010) and they are impossible to describe by one general model. Therefore, in our study the geological implications of the estimated HP kinetic parameters were examined in simple 1-D burial histories for geological heating rates of 1 and 10°C/m.y. (Gretener and Curtis, 1982). They were adjusted to the geological and thermal conditions of the Polish part of the Baltic region for modelling of petroleum processes by Kosakowski *et al.* (2010) and Wróbel and Kosakowski (2010). Figure 8 shows oil-generation curves using the HP kinetic parameters estimated from the kerogen organic-sulfur contents of the Tremadocian and Upper Cambrian source rocks (Table 2) with geological time for these two heating-rate end members.

The small standard deviations for the HP kinetic parameters of the Tremadocian source rocks (Table 2) are reflected in the narrow timing differences between the maximum, mean, and minimum curves at both heating rates (Fig. 8). The mean curve indicates that 10% of oil generation (TR = 0.10) from Tremadocian source rocks would have started between 485 and 360 Ma depending on the heating rate. As indicated by the larger standard deviation for the HP kinetic parameters of the Upper Cambrian source rocks (Table 2), a greater difference occurs between the minimum, mean, and maximum transformation curves than between those of the Tremadocian source rocks (Fig. 8). It is noteworthy that the Upper Cambrian source rocks will mature earlier (i.e., at lower thermal maturities) than the overlying Tremadocian source rocks. The magnitude of this difference will depend on the specific kinetic parameters of the Upper Cambrian source rocks, which show the greatest variability. As an example, at a heating rate of 10°C/m.y., the mean Tremadocian source rock will have an oil transformation ratio of 0.02 at 486 Ma and its underlying Upper Cambrian source rock could have an oil transformation ratio of 0.13, 0.50 or 1.0 depending on whether its kinetic parameters followed the minimum, mean, or maximum curves, respectively (Fig. 8A). At the lower heating rate, the mean Tremadocian source rock will have an oil transforma-
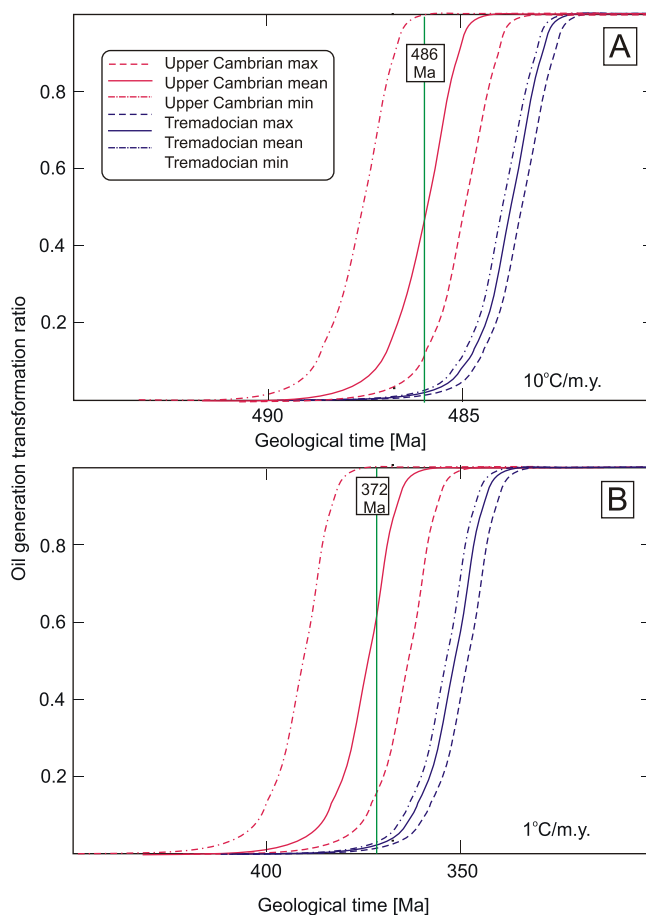

Fig. 8A – oil transformation ratios calculated for estimated minimum, mean and maximum HP kinetic parameters for Tremadocian and Upper Cambrian source rocks subjected to geological heating rates of 10°C/m.y. and B – 1°C/m.y. *versus* geological time

Kinetic parameters are in Table 3

tion ratio of 0.02 at 372 Ma and its underlying Upper Cambrian source rock could have a transformation ratio of 0.15, 0.61, or 1.0 depending on whether its kinetic parameter followed the minimum, mean, or maximum curves, respectively (Fig. 8B). Testing this prediction requires having natural data of both units in close proximity to one another that are in the maturing stages of oil generation. The samples from the B4-1 and B4-N1 bore-holes provide this situation, with a Tremadocian sample from B4-1 borehole and an Upper Cambrian sample from the neigh-boring B4-N1 borehole (Table 1 and Fig. 1). Lewan (1985, Fig. 5) has reported a good correlation between oil transforma-tion ratios (X) and kerogen atomic H/C ratios that is independent of kinetic parameters for Type-II and -IIS kerogen. Recalculat-ing his polynomial expression to solve for oil transformation ra-tio (X) gives:

$$X = 2.662(\text{H/C})^3 - 4.992(\text{H/C})^2 + 0.785(\text{H/C}) + 1.653 \qquad [7]$$

Using this expression, the atomic H/C ratios for the two samples give oil transformation ratios of 0.097 for the Tremadocian sample and 0.191 for the Upper Cambrian sam-ple. These are significant differences considering the differ-ence in depth between the samples is only ~90 m in the two neighbouring boreholes. Although more subsurface data for these two source rocks in the maturing stages of oil generation are needed, the available data does indicate that, based on the estimated HP kinetics, the Upper Cambrian source rocks gen-erate oil notably earlier than the Tremadocian source rocks.

CONCLUSIONS

The best approach to determine oil-generation kinetics by hydrous pyrolysis is with a complete set of temperature and time experiments as discussed by Lewan and Ruble (2002) and Lewan *et al.* (2006). This complete experimental series may re-quire 14 to 18 HP experiments, i.e. the large amount of imma-ture sample and experimental time. To circumvent these re-quirements, two methods for estimating HP kinetic parameters were evaluated: (i) using the S/(S + C) mole fractions of imma-ture kerogen and their relationship to previously established HP kinetic parameters to estimate activation energies (E_a) and frequency factors (A_0) and (ii) based on results from two hy-drous pyrolysis experiments to determine a rate constant at 330°C ($k_{330°C}$). Using the first method, the Baltic Upper Cam-brian and Tremadocian immature source rocks had mean esti-mated E_a values of 52.7 ±3.9 and 61.1 ±1.5 kcal/mol and logA_0 values of 16.91 ±1.29 and 19.66 ±0.49 (log [1/h]), respectively. Because of these parameters, depending on S/(S + C) ratio, can

change with maturation, estimations made by this method should be restricted to immature source rocks unless prior knowledge of how their kerogen S/(S + C) mole fractions be-have with increasing maturity is obtained.

The estimated HP kinetic parameters for the two immature samples by the second method were in good agreement with those estimated by the first method. The Upper Cambrian source rocks had an estimated E_a value of 57.5 kcal/mol and A_0 value of 2.594×10^{28} m.y.$^{-1}$. The Tremadocian source rocks had a mean estimated E_a value of 61.9 kcal/mol and A_0 value of 7.073×10^{29} m.y.$^{-1}$. However, the estimated HP kinetic parame-ters for the mature samples consistently gave lower values than those estimated from the first method based on kerogen S/(S + C) mole fractions.

Both methods of estimating HP kinetic parameters for source rocks with Type-II kerogen are applicable when small amounts of sample and limited time restrict determinations by a complete series of hydrous pyrolysis experiments at various times and temperatures. The values estimated for the Baltic source rocks predict that Upper Cambrian source rocks will generate expelled oil at notably lower thermal maturities than overlying Tremadocian source rocks. This prediction from the estimated HP kinetic parameters is in part confirmed by sam-ples from neighbouring boreholes.

REFERENCES

AMRANI A., LEWAN M. D. and AIZENSHTAT Z. (2005) – Stable sulfur isotope partitioning during simulated petroleum formation as deter-mined by hydrous pyrolysis of Ghareb Limestone, Israel. Geochim. Cosmochim. Acta, **69**: 5317–5331.

BEHAR F., LEWAN M. D., LORANT F. and VANDENBROUCKE M. (2003) – Comparison of artificial maturation of lignite in hydrous and nonhydrous conditions. Org. Geochem., **34**: 575–600.

BHARATI S., LARTER S. and HORSFIELD B. (1992) – The unusual po-tential of the Cambrian Alum Shale in Scandinavia as determined by

quantitative pyrolysis methods. In: Generation, Accumulation and Production of Europe's Hydrocarbons II (ed. A. M. Spencer). Spec. Publ. Eur. Ass. Petrol. Geosc., **2**: 103–110. Springer-Verlag Berlin Heidelberg.

BHARATI S., PATIENCE R. L., LARTER S. R., STANDEN G. and POPLETT I. J. F. (1995) – Elucidation of the Alum Shale kerogen structure using a multi-disciplinary approach. Org. Geochem., **23**: 1043–1058.

BRANGULIS A. P., KANEV S. V., MARGULIS A. S. and HASETON T. M. (1992) – Hydrocarbon geology of the Baltic republics and the adjacent Baltic Sea. In: Generation, Accumulation and Production of Europe's Hydrocarbons II (ed. A. M. Spencer). Spec. Publ. Eur. Ass. Petrol. Geosc., **2**: 111–115. Springer-Verlag Berlin Heidelberg.

BUCHARDT B., CLAUSEN J. and THOMSEN E. (1986) – Carbon isotope composition of Lower Paleozoic kerogen: effects of maturation. Org. Geochem., **10**: 127–134.

BUCHARDT B. and LEWAN M. D. (1990) – Reflectance of vitrinite-like macerals as a thermal maturity index for Cambrian–Ordovician Alum Shale, southern Scandinavia. Am. Ass. Petrol. Geol. Bull., **74**: 394–406.

BURNHAM A. K. (1998) – Comment on "Experiments on the role of water in petroleum formation". Geochim. Cosmochim. Acta, **62**: 2207–2210.

BURNHAM A. K. and BRAUN R. L. (1999) – Global kinetics analysis of complex materials. Energy and Fuels, **13**: 1–22.

CURTIS J. B., KOTARBA M. J., LEWAN M. D. and WIĘCŁAW D. (2004) – Oil/source rock correlations in the Polish Flysch Carpathians and Mesozoic basement and organic facies of the Oligocene Menilite Shales: insights from hydrous pyrolysis experiments. Org. Geochem., **35**: 1573–1596.

ESPITALIÉ J., DEROO G. and MARQUIS F. (1985) – La pyrolyse Rock Eval et ses applications. Revue Inst. Fran. Petrol., **40**: 755–784.

GRETENER P. E. and CURTIS C. D. (1982) – Role of temperature and time on organic metamorphism. Am. Ass. Petrol. Geol. Bull., **66**: 1124–1129.

GROTEK I. (2006) – Thermal maturity of organic matter from the sedimentary cover deposits from Pomeranian part of the TESZ, Baltic Basin and adjacent area (in Polish with English summary). Pr. Państw. Inst. Geol., **186**: 253–270.

HIGLEY D. K., LEWAN M. D., ROBERTS L. N. R. and HENRY M. (2009) – Timing and petroleum sources for the Lower Cretaceous Mannville Group oil sands of northern Alberta based on 4-D modeling. Am. Ass. Petrol. Geol. Bull., **93**: 203–230.

HUNT J. M. (1996) – Petroleum geochemistry and geology. W. H. Freeman and Company, New York.

IDIZ E. F., TANNENBAUM E. and KAPLAN I. R. (1990) – Pyrolysis of high-sulfur Monterey kerogens. In: Geochemistry of Sulfur in Fossil Fuels (eds. W. L. Orr and C. M. White). Am. Chem. Soc. Symp. Ser., 429: 575–591. Washington, DC.

JOHANNES I., KRUUSEMENT K. and VESKI R. (2007) – Evaluation of oil potential and pyrolysis kinetics of renewable fuel and shale samples by Rock-Eval analyzer. J. Anal. Appl. Pyrol., **79**: 183–190.

KARNKOWSKI P. H. (2003) – Modelling of hydrocarbon generating conditions within Lower Palaeozoic strata in the western part of the Baltic Basin (in Polish with English summary). Prz. Geol., **51** (9): 756–763.

KOSAKOWSKI P., WRÓBEL M. and POPRAWA P. (2010) – Hydrocarbon generation and expulsion modelling of the lower Paleozoic source rocks in the Polish part of the Baltic region. Geol. Quart., **54** (2): 241–256.

KOTARBA M. J., CURTIS J. B. and LEWAN M. D. (2009) – Comparison of natural gases accumulated in Oligocene strata with hydrous pyrolysis gases from Menilite Shales of the Polish Outer Carpathians. Org. Geochem., **40**: 769–783.

KOTARBA M. J., KOSAKOWSKI P., WRÓBEL M. and WIĘCŁAW D. (2010) – Petroleum system and hydrocarbon exploration potential of the Lower Paleozoic strata of the Polish Baltic region. Marine and Petrol. Geol., **29** (in press).

LEVENTHAL J. S. (1991) – Comparison of organic geochemistry and metal enrichment in two black shales: Cambrian Alum Shale of Sweden and Devonian Chattanooga Shale of United States. Mineralium Deposita, **26**: 104–112.

LEWAN M. D. (1985) – Evaluation of petroleum generation by hydrous pyrolysis experimentation. Philos. Trans. R. Soc., London, Ser. A., **315**: 123–134.

LEWAN M. D. (1993*a*) – Laboratory simulation of petroleum formation: Hydrous pyrolysis. In: Organic Geochemistry (eds. M. Engel and S. Macko): 419–442. Plenum Publ. Corp. New York.

LEWAN M. D. (1993*b*) – Identifying and understanding suppressed vitrinite reflectance through hydrous pyrolysis. The Society for Organic Petrology, Abstracts and Program, **3**: 1–3.

LEWAN M. D. (1998*a*) – Reply to the comment by A. K. Burnham on "Experiments on the role of water in petroleum formation". Geochim. Cosmochim. Acta, **62**: 2211–2216.

LEWAN M. D. (1998*b*) – Sulfur-radical control on petroleum formation rates. Nature, **391**: 164–166.

LEWAN M. D. (2002) – New insights on timing of oil and gas generation in the central Gulf Coast interior zone based on Hydrous-Pyrolysis kinetic Parameters. Gulf Coast Ass. Geol. Soc. Transactions, **52**: 607–620.

LEWAN M. D. and BUCHARDT B. (1989) – Irradiation of organic matter by uranium decay in the Alum Shale, Sweden. Geochim. Cosmochim. Acta, **53**: 1307–1322.

LEWAN M. D., KOTARBA M. J., CURTIS J. B., WIĘCŁAW D. and KOSAKOWSKI P. (2006) – Oil generation kinetics for organic facies with Type-II and -IIS kerogen in the Menilite Shales of the Polish Carpathians. Geochim. Cosmochim. Acta, **70**: 3351–3368.

LEWAN M. D. and RUBLE T. E. (2002) – Comparison of petroleum generation kinetics by isothermal hydrous and nonisothermal open-system pyrolysis. Org. Geochem., **33**: 1457–1475.

MODLIŃSKI Z. and PODHALAŃSKA T. (2010) – Outline of the lithology and depositional features of the lower Paleozoic strata in the Polish part of the Baltic region. Geol. Quart., **54** (2): 109–121.

NELSON B. C., EGLINTON T. I., SEEWALD J. S., VAIRAVAMURTHY M. A. and MIKNIS F. P. (1995) – Transformations in organic sulfur speciation during maturation of Monterey Shale: Constraints from laboratory experiments. In: Geochemical Transformations of Sedimentary Sulfur (eds. M. A. Vairavamurthy and M. A. A. Schoonen). Am. Chem. Soc. Symp. Ser., **612**: 138–166. Washington, DC.

ORR W. L. (1986) – Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oils. Org. Geochem., **10**: 499–516.

ORR W. L. and SINNINGHE DAMSTÉ J. S. (1990) – Geochemistry of sulfur in petroleum systems. In: Geochemistry of Sulfur in Fossil Fuels (eds. W. L. Orr and C. M. White). Am. Chem. Soc. Symp. Ser., **429**: 2–29. Washington, DC.

PITMAN J. K., STEINSHOUER D. and LEWAN M. D. (2004) – Petroleum generation and migration in the Mesopotamian Basin and Zagros fold belt of Iraq: results from a basin modelling study. GeoArabia, **9**: 41–72.

POKORSKI J. (2010) – Geological section through the lower Paleozoic strata of the Polish part of the Baltic region. Geol. Quart., **54** (2): 123–130.

POPRAWA P., KOSAKOWSKI P. and WRÓBEL M. (2010) – Burial and thermal history of the Polish part of the Baltic region. Geol. Quart., **54** (2): 131–142.

ROBERTS L. N. R., LEWAN M. D. and FINN T. M. (2004) – Timing of oil and gas generation of petroleum systems in the Southwestern Wyoming Province. Mountain Geologist, **41**: 87–118.

RUBLE T. E., LEWAN M. D. and PHILP R. P. (2001) – New insights on the Green River petroleum system in the Uinta basin from hydrous pyrolysis experiments. Am. Ass. Petrol. Geol. Bull., **85**: 1333–1372.

SCHLEICHER M., KÖSTER J., KULKE H. and WEIL W. (1998) – Reservoir and source-rock characterisation of the Early Palaeozoic interval in the Peribaltic Syneclise, northern Poland. J. Petrol. Geol., **21**: 33–56.

TAYLOR G. H., TEICHMÜLLER M., DAVIS A., DIESSEL C. F. K., LITTKE R. and ROBERT P. (1998) – Organic Petrology. Gebrüder Borntraeger, Berlin-Stuttgart.

ULMISHEK G. (1990) – Geologic evolution and petroleum resources of the Baltic Basin. In: Interior Cratonic Basins. (eds. M. W. Leighton, D. R. Kolata, D. F. Oltz and J. J. Eidel). Am. Ass. Petrol. Geol. Mem., **51**: 603–632.

WRÓBEL M. and KOSAKOWSKI P. (2010) – 2-D modelling of petroleum processes of the lower Paleozoic strata in the Polish part of the Baltic region. Geol. Quart., **54** (2): 257–266.