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**GEOCHEMICAL INVESTIGATION OF
CARBONIFEROUS OIL SHALES ALONG
ROCKY BROOK, WESTERN NEWFOUNDLAND**

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ABSTRACT

Nine samples of oil shale from the Carboniferous Rocky Brook Formation along Rocky Brook in western Newfoundland were analyzed by Rock-Eval Pyrolysis. In conjunction with previously published data, various parameters were cross-plotted and interpreted along with other measured data to determine more accurately the thermal maturation levels and petroleum yield potential of these oil shale beds.

Thermal maturation of these Type I kerogens appears to vary from almost immature to moderately mature, well into the oil generation window, varying with the amount and distribution of the kerogen within each particular bed. Where TOC content exceeds 5%, petroleum potential is above the generally accepted 40 l/t minimum for economic interest. Beds containing less than 4% TOC exhibit a wide range of yields and in some cases may be attractive along with the more prolific zones.

INTRODUCTION

Oil shales have been described within the Carboniferous Deer Lake Basin of western Newfoundland for many years: a review of the geology and the limited geochemical data for these deposits prior to 1980 is contained in Macauley (1984). More recent mapping by Hyde (1979, 1982) has further refined the geology and Hyde presented an initial geochemical (Rock-Eval) study in 1984, wherein a wide range of hydrocarbon recoveries was reported from 16 samples. Kerogen color was indicated by Hyde to represent a greater maturation level than indicated from the Rock-Eval analyses although results of organic petrography were not included, nor were lithological descriptions of the individual samples. The kerogen was concluded to be Type I, for which Rock-Eval interpretations of maturity can be difficult, especially those based on Tmax values: further investigations (Kalkreuth and Macauley, 1984) now confirm that vitrinite reflectance values for Type I lacustrine oil shales can be severely depressed where light hydrocarbons have been generated, but no corresponding relationships are known for geochemical - kerogen color differences.

To gain further knowledge of this deposit, and to achieve a better understanding of the Type I kerogens within the Carboniferous of the Atlantic Provinces, nine additional samples were collected from the section exposed along Rocky Brook (Fig. 1). These have been analyzed by Rock-Eval pyrolysis and the kerogen content will be studied by both reflecting white light and fluorescent light microscopy.

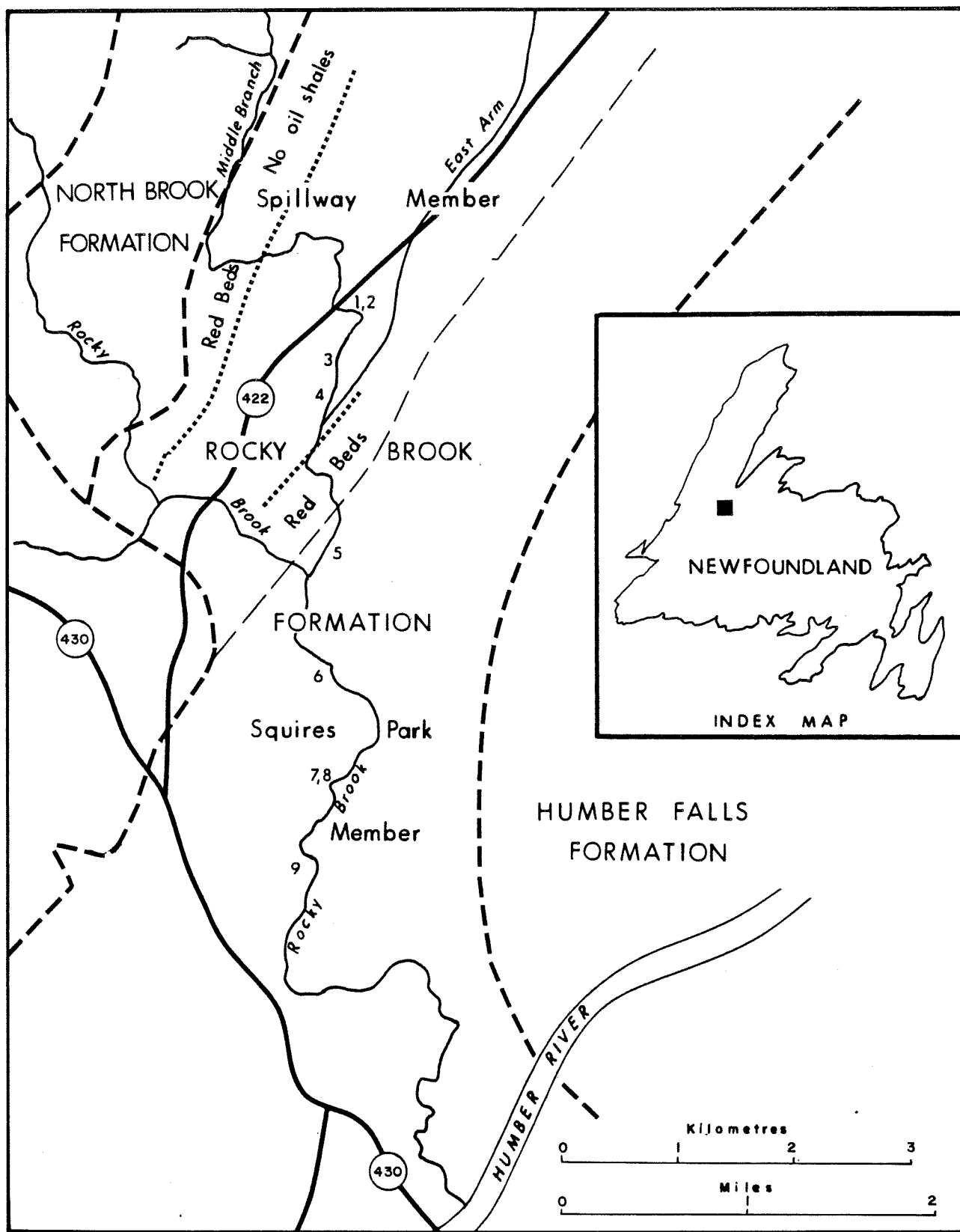


Figure 1. Sample location map, Rocky Brook, western Newfoundland.

PROCEDURES

Surface Samples

Hyde (1984) was able to divide the Rocky Brook Formation into an upper Squires Park Member and a lower Spillway Member, both containing oil shale beds, with a distinct red bed sequence separating the oil shale occurrences of the two members in the western part of the Deer Lake Basin. The formation was traversed upward in the section, starting where Highway 422 crosses Rocky Brook and following south-southeastward along the brook to the major bend just north of Highway 430 (Fig. 1); thus, samples were collected and numbered upward in the section; the data are here reported downward in sequence from the highest to the lowest to conform to the normal petroleum drilling results where the youngest sediments are penetrated first. Samples were also collected to ensure that all distinct lithological types would be analyzed.

Squires Park Member

Sample RB 9: from a 0.3 m (one foot) thick laminated bed; the lowest of five such beds present within a total 10 m interval

Sample RB 8: from a one metre thick massive bed; sample from near the base of the unit immediately above a sandstone

Sample RB 7: from a 0.1 m (4") thick finely laminated bed at the base of the above massive bed and separated by a 0.1 m thick sandstone

Sample RB 6: from a massive bed 0.3 m (1 foot) thick

Sample RB 5: from a 0.15 m (6") thick poorly laminated to massive bed immediately above the medial red bed sequence of the formation

Spillway Member

Red Bed sequence: not sampled

Sample RB 4: thinly laminated and splits easily, near confluence of East Brook arm of Rocky Brook

Sample RB 3: from a 0.15 m (6") thick bed, well laminated from 0.6 cm laminae at top to very finely laminated at base; sample from center of interval, with 0.15 cm sandstone laminae; although better laminated, splits less easily than sample 4 above

Sample RB 2: a thin bed, <5 cm, of very finely laminated oil shale

Sample RB 1: similar thin bed to sample 2 above, but much more massive

Within the total section, the oil shales are recognizable by a distinctive white weathered surface. Most occur in thin beds of a few centimetres with a maximum observed oil shale bed thickness of approximately one metre. The most abundant occurrence noted was in the section containing sample RB 9, where some 15% of the section was estimated to consist of oil shale.

Rock-Eval Pyrolysis

All samples were processed at the Institute of Sedimentary and Petroleum Geology (ISPG), Calgary, on a Rock-Eval analyzer. Using a standard program, the S1 peak was obtained at 300°C, the S2 was measured during heating at 25°C/min. and collected to a temperature of 600°C. The S3 peak was collected to a temperature of 390°C. Total organic carbon (TOC) content was determined by burning all residual organic carbon in a separate oxidation oven built into the analyzer and operated at 600°C in air. In order to ensure uniform results and that all the organic carbon was burned, samples were ground to a particle size of approximately 150 microns.

Rock-Eval analytical data reported by Hyde (1984) were also determined at the ISPG. At that time, TOC data were determined in a Leco WR12 carbon analyzer after the pulverized samples (150 micron) had been treated in both cold and hot 6N hydrochloric acid to remove mineral carbon (Macauley et al., 1985).

GEOCHEMISTRY

Results from the investigations by Hyde (1984) identified the kerogen as Type I, but the degree of thermal maturation was somewhat indefinite as both Tmax and Production Indices from the Rock-Eval pyrolyses indicated lower maturation levels than those from kerogen color determinations and vitrinite reflectance values from other beds within the gross oil shale bearing section. Several low Hydrogen Indices and related poor hydrocarbon yields were also anomalous results from four of his sixteen samples.

Rock-Eval analyses from this study confirm the kerogen character, but still leave some doubt as to the degree of thermal maturation. More detailed organic petrological studies involving maceral determinations under white light reflectance, and the measurement of both wavelength intensities and the Red/Green Quotient under ultraviolet irradiation by W. Kalkreuth at ISPG, will hopefully resolve this problem. Utilization of the same samples for both geochemical and organic microscopic analysis was successful for similar type oil shale beds of the Albert Formation in New Brunswick (Kalkreuth and Macauley, 1984).

Results from the Rock-Eval analyses of this study are presented in Table I, and, in order to provide easy comparison with the earlier data, Hyde's (1984) results are reproduced in Table II. Yield ratios and Production Indices have been calculated and some additional plots have been made herein from both his data and those of this study.

<u>Sample</u>	<u>TOC</u> Wt%	<u>Tmax</u> °C	<u>S1</u>	<u>S2</u> mg/g	<u>S3</u>	<u>HI</u>	<u>OI</u>	<u>S1+S2</u> kg/t	<u>PI</u>	<u>Ratio</u> kg/t /%TOC
Squires Park Member										
RB 9	9.65	449	3.44	93.21	1.40	965	14	96.65	.04	10.01
	9.48	448	3.37	88.14	1.82	929	19	91.51	.04	9.65
RB 8	2.92	439	0.64	23.55	0.64	806	21	24.19	.03	8.28
	2.84	444	0.56	22.83	0.74	803	26	23.39	.02	8.23
RB 7	15.43	451	3.20	153.78	2.71	996	17	156.98	.02	10.17
	14.99	451	3.06	148.19	1.44	988	9	151.25	.02	10.09
RB 6	1.86	433	0.46	11.58	0.67	636	36	12.04	.04	6.47
	1.86	435	0.42	11.33	0.50	609	26	11.75	.04	6.31
RB 5	3.41	443	0.68	26.95	0.67	790	19	27.63	.02	8.10
	3.55	444	0.59	28.20	0.65	794	18	28.79	.02	8.10
Spillway Member										
RB 4	2.81	441	0.34	13.50	0.65	480	23	13.84	.02	4.92
	3.13	436	0.37	13.58	0.56	433	17	13.95	.03	4.45
RB 3	8.15	450	0.77	72.41	1.12	888	13	73.18	.02	8.97
	8.11	449	0.76	68.60	1.32	845	16	69.36	.01	8.55
RB 2	13.19	448	3.12	122.85	1.76	931	13	125.97	.02	9.55
	13.31	446	3.09	121.38	2.40	911	18	124.47	.02	9.35
	13.44	446	3.05	122.61	1.67	912	12	125.66	.02	9.34
RB 1	3.08	438	0.60	21.63	0.47	702	15	22.23	.03	7.25
	2.85	442	0.49	20.35	0.29	714	10	20.84	.02	7.31

Table I: Rock-Eval analytical data.

<u>Sample</u>	<u>TOC</u> Wt%	<u>Tmax</u> °C	<u>S1</u>	<u>S2</u> mg/g	<u>S3</u>	<u>HI</u>	<u>OI</u>	<u>S1+S2</u> kg/t	<u>PI</u>	<u>Ratio</u> kg/t /%TOC
Float										
OS-1	9.67	437	0.96	75.30	2.53	778	26	76.26	.01	7.89
OS-2	15.93	450	2.80	129.40	1.90	812	11	132.20	.02	8.11
OS-4	14.91	446	2.19	119.86	1.82	803	12	122.05	.02	8.12
Squires Park Member										
82-521A	2.77	438	0.26	4.63	0.67	167	24	4.89	.01	1.80
82-124	3.54	441	1.46	15.60	0.96	440	27	17.06	.08	4.82
82-126A	5.08	444	1.40	32.00	1.03	629	20	33.40	.04	6.58
82-128	5.45	444	0.96	33.45	1.46	610	26	34.21	.03	6.28
82-131	5.23	445	1.41	34.47	1.05	659	20	35.88	.04	6.86
82-132	9.73	448	1.86	81.23	1.30	834	13	83.09	.02	8.54
82-143A	5.92	444	1.05	41.81	0.89	706	15	42.86	.03	7.24
82-176	9.62	448	0.44	57.75	1.05	600	10	58.19	.01	6.05
82-190	3.67	440	0.26	11.15	0.72	303	19	11.41	.02	3.11
82-192	8.32	445	0.43	65.00	1.73	781	20	67.43	.01	8.10
Spillway Member										
82-46	8.88	448	1.58	72.04	1.35	811	15	73.62	.02	8.29
82-47	8.02	451	1.34	64.56	1.20	804	14	65.90	.02	8.21
82-172	3.72	442	0.82	9.93	0.82	706	15	10.75	.08	2.89

Table II: Rock-Eval analytical data, from Hyde (1984).

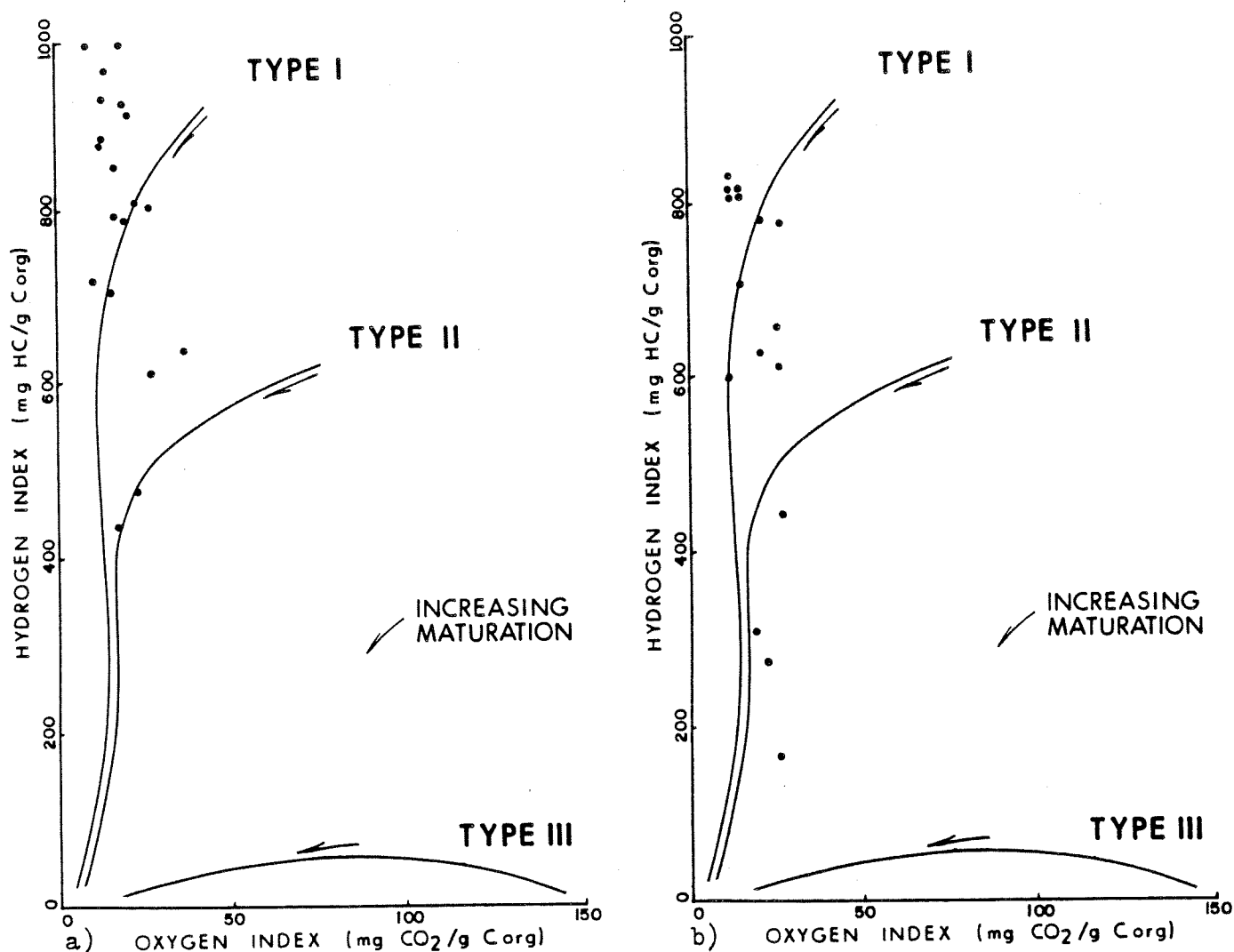


Figure 2. Hydrogen Index versus Oxygen Index: (a) this study, (b) Hyde (1984).

Hydrogen (HI) - Oxygen (OI) indices: Cross-plots of HI against OI for the data herein (Fig. 2a) and those of Hyde (Fig. 2b) both define the kerogen as Type I with HI generally above 600 and OI in the 10 to 25 range. Only five of 25 samples (one with dual run) have HI values below 600. In contrast, the similar Albert oil shales at Albert Mines, New Brunswick, exhibit an equivalent range of HI values, but are much more deficient in Oxygen with OI values generally less than 10 (Macauley and Ball, 1982).

In an attempt to determine controlling factors for the range of HI values, and the directly correlative hydrocarbon yields, HI was cross-plotted against two other significant parameters, TOC and Tmax.

TOC: Organic carbon content ranges from a low of 1.86 to a high of 15.43%, representing a broad spectrum of oil shale quality. From both sets of available data (Fig. 3), TOC and HI are related differently above and below 4 to 5% TOC. Above 5% TOC, HI increases at a rate of 15/%TOC. The visually averaged

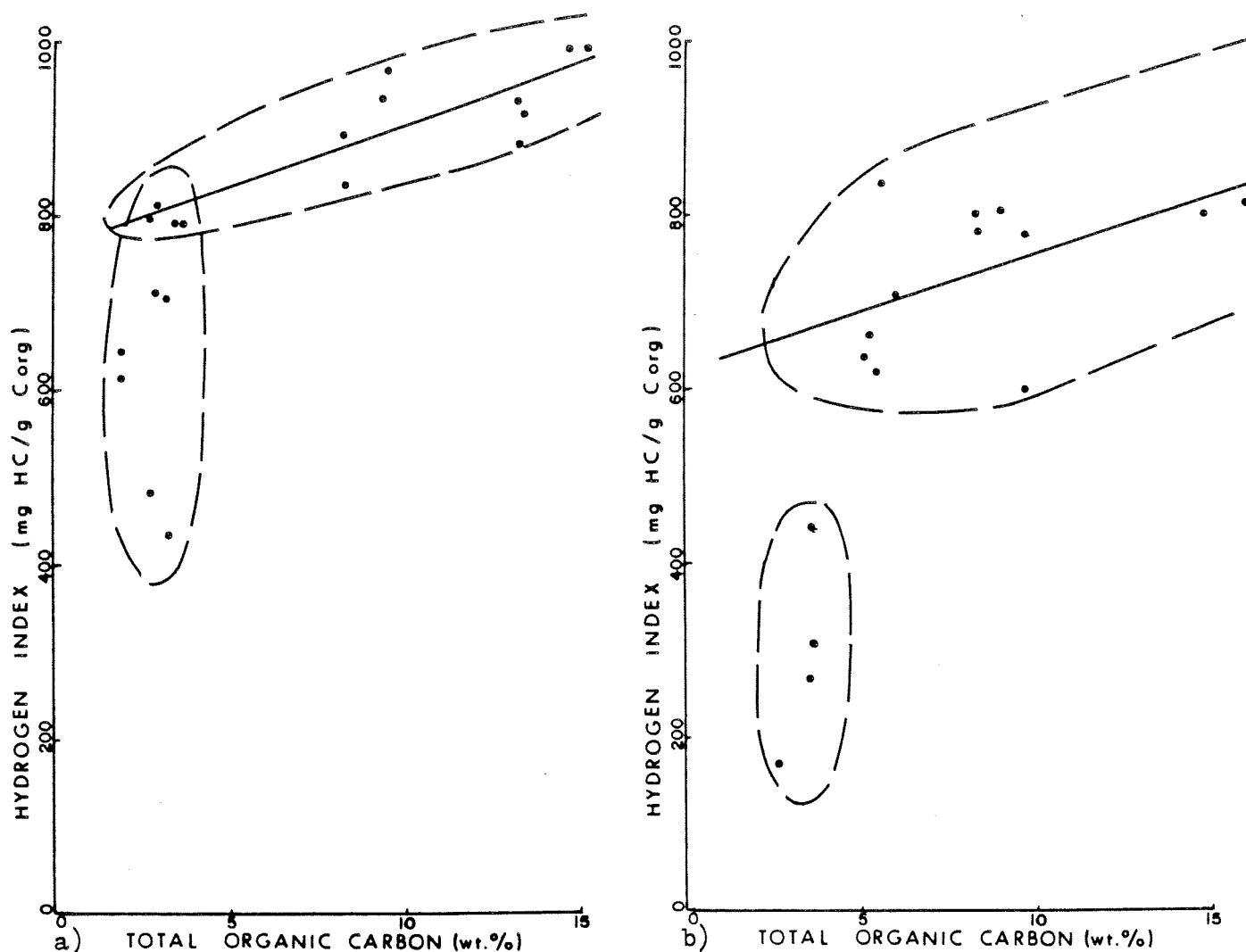


Figure 3. Hydrogen Index versus total organic carbon: (a) this study, (b) Hyde (1984).

lines are offset for the two data bases, but the difference in the analytical methods used to determine the TOC content may be the cause of this variation. Below 4% TOC, HI varies markedly and cannot be related directly to TOC. Low carbon content samples commonly have excellent HI values much above 600, whereas others, many with slightly better TOC contents, have extremely low Hydrogen release.

Several causes may account for this phenomenon. A change in the character of the kerogen to include Type III materials is possible, but is here discounted as there is no apparent increase in the Oxygen indices as should occur with humic detritus. A mineral-matrix effect is considered to be the probable cause whereby the kerogen becomes too finely and intimately intermixed with the inorganic grains for the hydrocarbon products to escape readily.

Tmax: Tmax ranges from 433 to 451°C over all the available data. Type I kerogen does not normally pyrolyze below 445 to

450°C (Espitalié et al, 1984). Some consideration must be given to the range of Tmax values for these oil shales. Tmax has therefore been cross-plotted against the Hydrogen Index (HI) (Fig. 4) to attempt a more comprehensive interpretation of both these parameters. No direct relationship is apparent between Tmax and HI; however, above a Tmax of 442°C, HI values are clustered along axes indicating increasing HI with increasing Tmax. Below 442°C, an indistinct relationship can be drawn similar to that between HI and TOC. Because the HI-Tmax relationship is even less distinct than that for HI-TOC, Tmax has also been cross-plotted against TOC values (Fig. 5). A distinct relationship is here again evident with a high Tmax above 442°C where TOC exceeds 5% and a broad range of Tmax values relating to TOC below 4%. The analogy to the TOC-HI relationship (Fig. 3) is clear.

Production indices (PI): Production indices in the range 0.01 to 0.08, generally 0.02 to 0.04 (Tables I, II), indicate virtual thermal immaturity.

Yield Potential: For those samples containing >5% TOC, the yield ratio is in the range 8 to 10 kg/t/%TOC (Tables I, II). This is comparable to the yields obtained from the moderately mature Albert oil shales in New Brunswick (Macauley et al., 1985). Actual yields can thus be considerably greater than 100 kg/t for the higher TOC intervals (Fig. 6). A comparison of the sample descriptions and the hydrocarbon recoveries indicates increasing potential as the oil shale becomes more finely laminated and papery: the thicker, more massive beds (1 cm or thicker) have the least potential. There is no relationship between potential yield and the stratigraphic position in the section.

Kerogen Classification and Maturation

Hydrogen-Oxygen index relationships indicate that the kerogen is Type I, characteristic of continental lacustrine deposits. From his detailed lithological studies, Hyde (1979) has concluded that the Rocky Brook section is of continental fluvial-lacustrine origin, following closely the earlier interpretations of Belt (1968). Hyde (1984) commented that the kerogen is orange/brown, amorphous and intimately intermixed with fine-grained dolomite. Further organic petrographical investigations are warranted and are in progress at ISPG, Calgary.

In accordance with the theorized mineral-matrix effect, Hydrogen indices are of limited interpretive value where TOC content is less than 4%: above 5% TOC, HI values cover a wide range, from 600 to almost 1,000, with these variations directly correlative to TOC content. Although values approaching 1,000 theoretically indicate a maximum possible hydrogen content, similar results were obtained from moderately mature New Brunswick oil shales (Kalkreuth and Macauley, 1984). Any interpretation of thermal maturity, other than that there is still a significant potential for petroleum generation, is difficult to reach from the HI data.

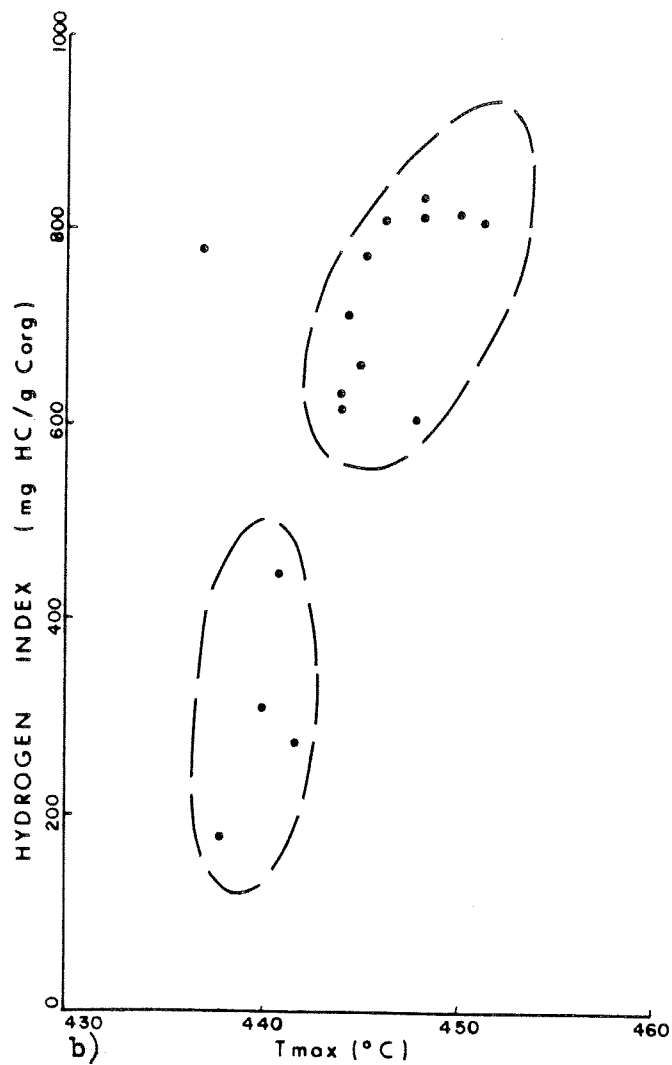
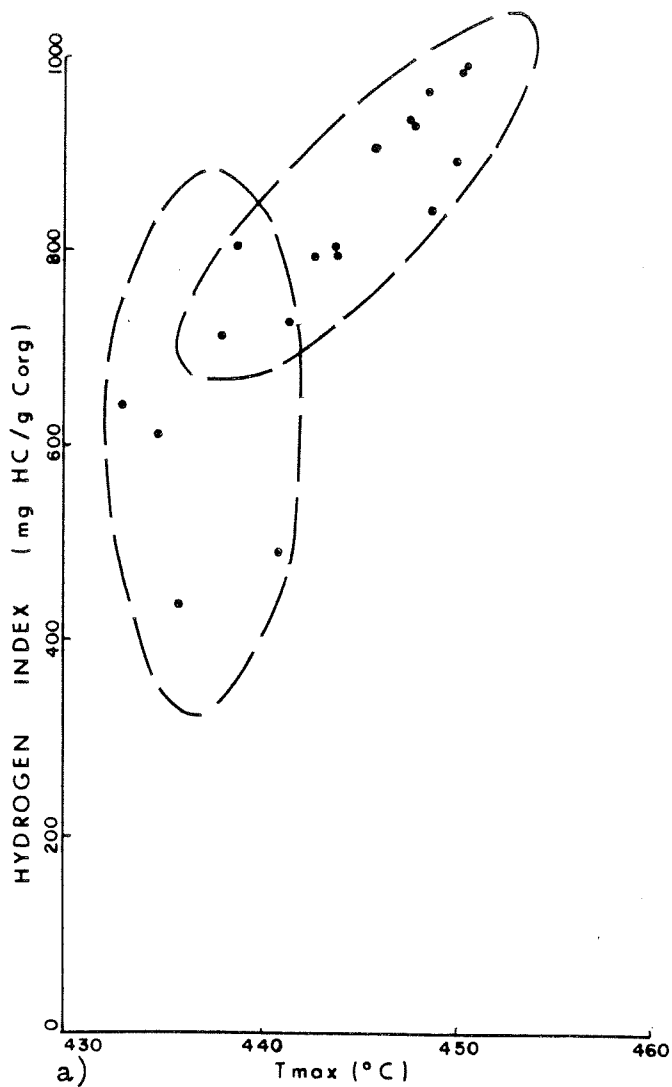


Figure 4. Hydrogen Index versus T_{max} : (a) this study, (b) Hyde (1984).

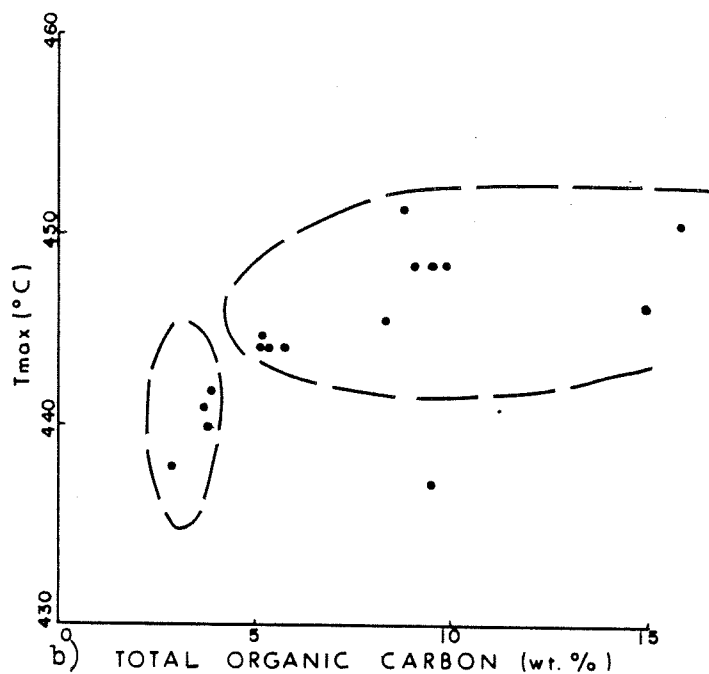
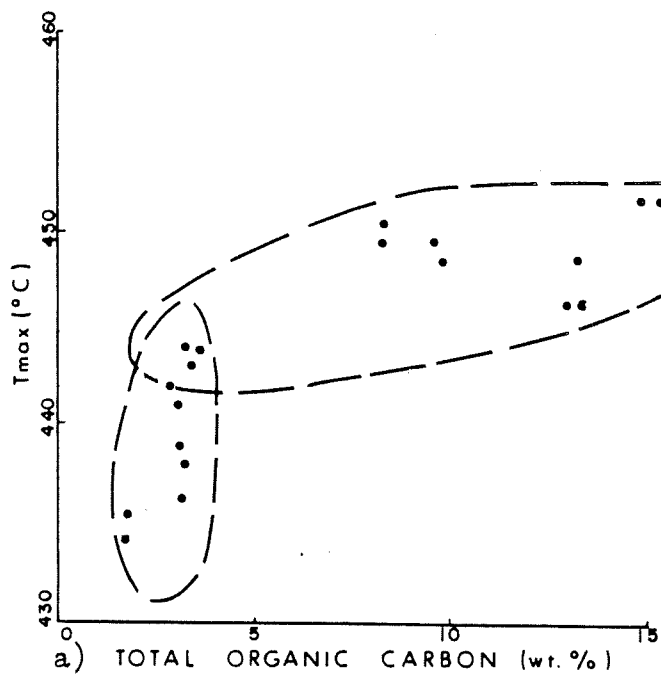


Figure 5. T_{max} versus total organic carbon: (a) this study, (b) Hyde (1984).

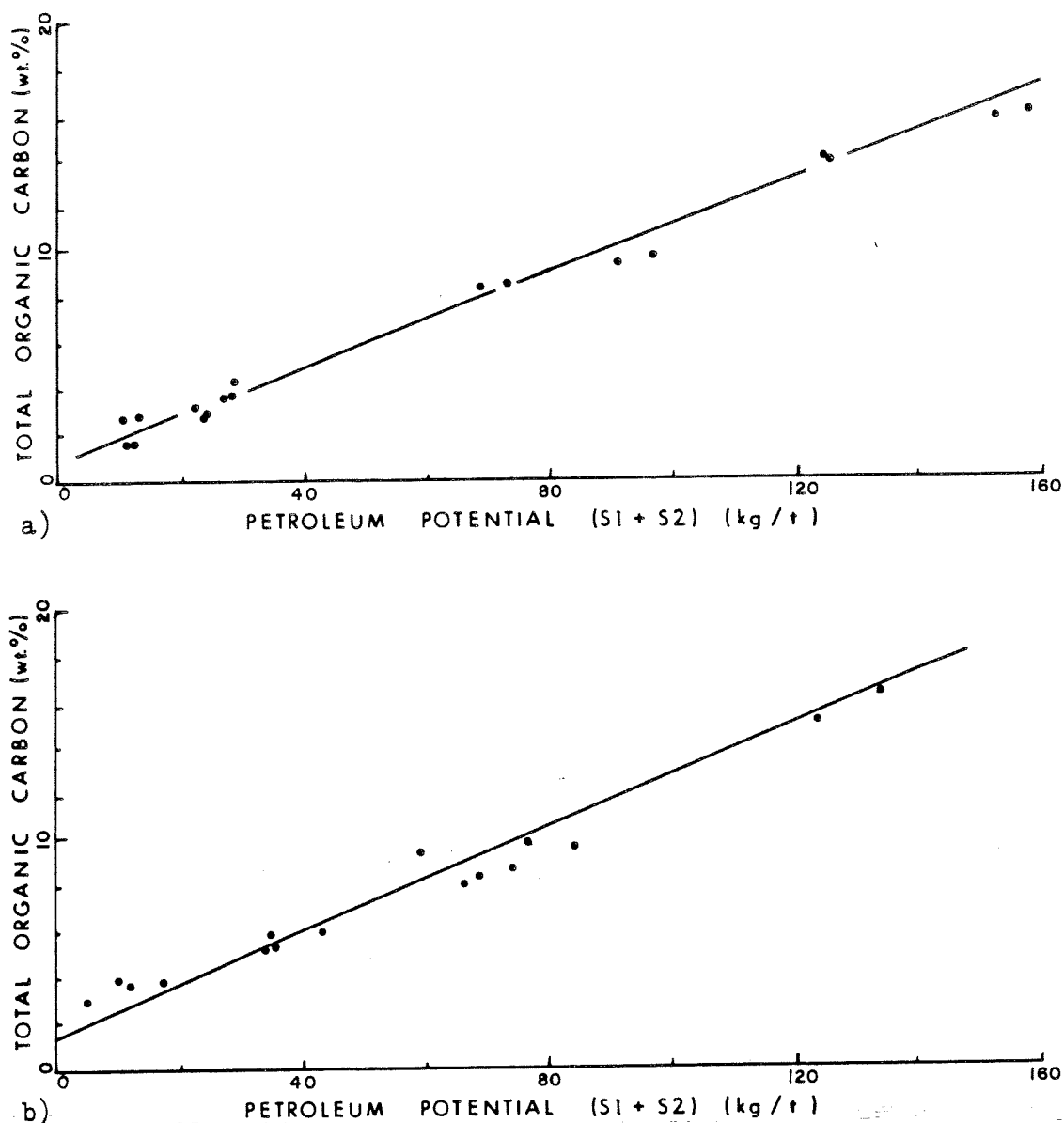


Figure 6. Total organic carbon versus petroleum potential:
(a) this study, (b) Hyde (1984).

Tmax indicates that some of the samples are within the petroleum generation "oil window", but that some may still be relatively immature. Compared to the reported range of vitrinite reflectance values and color variations reported by Hyde (1984), a range of maturation levels within the beds, related to the TOC content, and probably controlled by the distribution of the kerogen within the inorganic mineral matrices, can be deduced. The highest TOC samples produce both the highest Tmax and HI values. Tmax is thought to be more indicative of maturation level under these conditions of optimum recovery.

Production indices indicate virtual thermal immaturity and are thus difficult to explain in the light of the other indicators. Possibly only gas has been generated, an explanation offered for low PI values in torbanites (combined sapropelic and humic kerogen) in the Stellarton area, Nova Scotia (Macauley

et al., 1985), but this is not a plausible explanation for a Type I kerogen. Alternatively, the generated light hydrocarbons may have escaped through surface exposure as only surface samples have been analyzed. No loss of light hydrocarbons is indicated in Carboniferous Type I deposits for surface samples or for core exposed to the elements for over 10 years (Macauley and Ball, 1982), nor is any loss indicated for Ordovician Collingwood Type II oil shales in southwestern Ontario (studies in progress by the writer). No theory is here put forward for this enigma.

SUMMARY

Oil shales of the Carboniferous Rocky Brook Formation were deposited as Type I sapropelic kerogen within a continental lacustrine environment.

Thermal maturation probably ranges from virtually immature to moderate maturity well into the oil generation window, with the degree of maturation varying with the amount and distribution of the kerogen within the mineral matrices of each particular bed. Further investigations by organic petrographic microscopy may assist greatly in the proper assessment of maturation within these oil shales.

Beds with TOC content above 5% will have Petroleum Potential near to or above the generally accepted minimum 40 litres/tonne (10 gallons/ton) for economic interest, but presently known bed thicknesses are insufficient for such interest. Any future discovery of thicker beds may reach the resource parameters necessary for development potential.

In some cases, beds with less than 4% TOC may represent potential petroleum resource in combination with the more prolific intervals because of good yield factors. Evaluation of low organic carbon beds would of necessity be on a bed by bed basis: individual beds will vary laterally as well as vertically.

Acknowledgements

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