

Division of Geological & Geophysical Surveys

PUBLIC-DATA FILE 95-30

**PRELIMINARY EVALUATION OF THE HYDROCARBON SOURCE ROCK  
POTENTIAL OF THE TINGMERKPUK SANDSTONE (NEOCOMIAN) AND  
RELATED ROCKS, NORTHWESTERN DE LONG MOUNTAINS,  
BROOKS RANGE, ALASKA**

by

C.G. Mull

August 1995

THIS REPORT HAS NOT BEEN REVIEWED FOR  
TECHNICAL CONTENT (EXCEPT AS NOTED IN TEXT) OR FOR  
CONFORMITY TO THE EDITORIAL STANDARDS OF DGGS.

Released by

STATE OF ALASKA  
DEPARTMENT OF NATURAL RESOURCES  
Division of Geological & Geophysical Surveys  
794 University Avenue, Suite 200  
Fairbanks, Alaska 99709-3645

**PRELIMINARY EVALUATION OF THE HYDROCARBON SOURCE ROCK POTENTIAL OF  
THE TINGMERKPUK SANDSTONE (NEOCOMIAN) AND RELATED ROCKS,  
NORTHWESTERN DE LONG MOUNTAINS, BROOKS RANGE, ALASKA**

**CONTENTS**

INTRODUCTION	1
GEOCHEMISTRY AND SOURCE ROCK POTENTIAL	4
TINGMERKPUK AREA	4
Kingak Shale (Neocomian)	4
TingmerkpuK Sandstone (Valanginian To Hauterivian)	6
Lower Brookian Shale (Hauterivian)	6
Torok Formation (Aptian-Albian)	9
SURPRISE CREEK AREA	9
Shubllk Formation	9
Kingak Shale	11
SUMMARY	11
TECTONIC IMPLICATIONS	13
REFERENCES CITED	
APPENDIX	
Description of DGSi analytical procedures and definition of terms	14

**FIGURES**

Figure 1. Map showing location of geochemical samples, DeLong Mountain quadrangle	2
2. Generalized composite stratigraphic columns, TingmerkpuK Mountain and Surprise Creek areas, northwestern DeLong Mountains	5
3. Generalized stratigraphic section of the TingmerkpuK Sandstone and related rocks on TingmerkpuK Mountain, showing geochemical data.	7
4. Correlation of maturation indices and zones of petroleum generation and destruction	8
5. Generalized stratigraphic column of the Surprise Creek area, showing geochemical data	10
6. Van Krevelen diagram showing organic facies of samples from northwestern DeLong Mountains	12

**TABLES**

Table 1. Table of geochemical data, TingmerkpuK and Surprise Creek areas, northwestern DeLong Mountains.	3
--	---

**PRELIMINARY EVALUATION OF THE HYDROCARBON SOURCE ROCK POTENTIAL  
OF THE TINGMERKPUK SANDSTONE (NEOCOMIAN) AND RELATED ROCKS,  
NORTHWESTERN DE LONG MOUNTAINS, BROOKS RANGE, ALASKA**

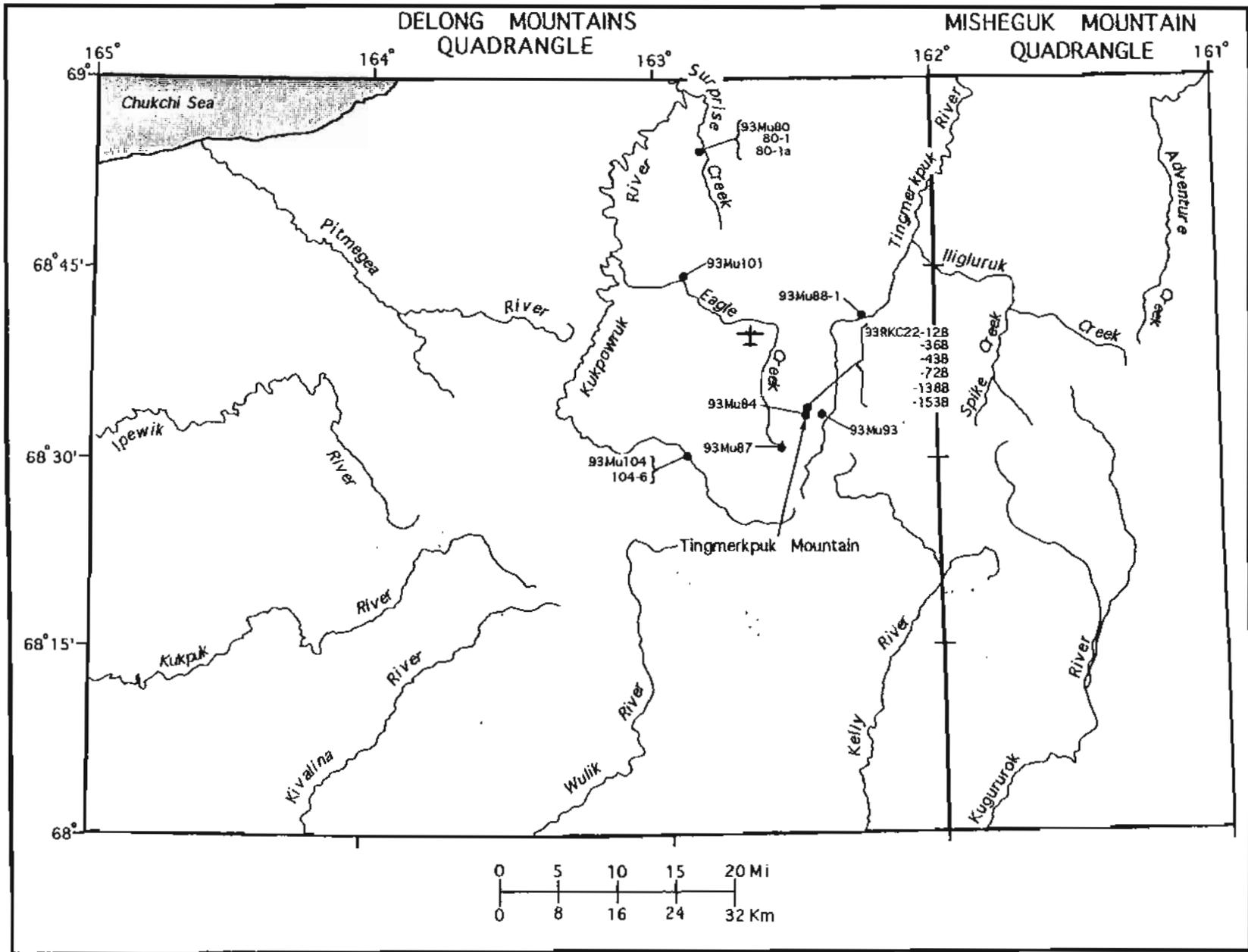
By C.G. Mull

INTRODUCTION

The Alaska Division of Geological and Geophysical Surveys, in collaboration with the Alaska Division of Oil and Gas, University of Alaska, Fairbanks, U.S. Geological Survey, and Bureau of Land Management is engaged in an ongoing study of the hydrocarbon potential of Neocomian sandstones in northwestern Alaska. As part of this collaborative effort, surface geological studies are being carried out in the northwestern DeLong Mountains of the western Brooks Range. The studies include involve mile to inch geological mapping in parts of the DeLong Mountains and Misheguk Mountain 1:250,000 quadrangles, study of depositional environments of the Neocomian rocks, and collection of samples for micropaleontologic, apatite fission track (AFTA), and organic geochemical analysis (fig.1). As a result of the field work to date, a measured section of the TingmerkpuK Sandstone (Neocomian) and a study of its depositional environment has been summarized by Crowder, Adams, and Mull (1994) and paleontologic data from megafossil collections and samples collected for micropaleontologic analysis are reported by Mickey, Haga, and Mull (1995).

In a pilot study to evaluate the hydrocarbon source rock potential of the Neocomian rocks of the western Arctic Slope, a suite of 16 shale samples collected from possible source rocks has been analyzed by DGS Inc.<sup>(1)</sup> Analyses were performed to determine three major aspects of the source rock potential: 1) organic content, 2) thermal maturity, and 3) kerogen type. Standard analyses include total organic carbon (TOC) and Rock-Eval pyrolysis to provide basic geochemical information that is used in screening samples for more detailed studies. The detailed studies include visual examination of kerogen, extract chromatography, and biomarker analyses; these analyses give a better indication of the type of kerogen in the rocks and the type and abundance of hydrocarbon that might be expected. A summary of the analytical techniques and definition of terms used by DGS is included as appendix 1. The results of the analyses and the analytical data sheets are given by Dow and Talukdar, 1994 [1995].

<sup>(1)</sup>DGSI, 8701 New Trails Drive, The Woodlands, Texas 77381.



2

Figure 1. Map showing location of geochemical samples, DeLong Mountains quadrangle

TINGMERKPUK AREA GEOCHEMISTRY  
Analyses by DGSJ

DGSJ #	DGSJ SAMPLE #	FORMATION	AGE	LOCATION	INDICATORS OF ORGANIC CONTENT				THERMAL MATURITY			INDICATORS OF KEROGEN TYPE								COMMENTS	
					TOC	S1	S2	S3	Ro	T Max	TAI *	S1/TOC	HI	OI	S2/S3	PI	% Lipids	% Humic	Pristane/ phytane		Kerogen type
TINGMERKPUK AREA																					
1	93 Mu 101	Torok Fm.	Aptian	Eagle Creek	1.3	0.31	0.41	0.34	1.47	479	3.0	24	32	26	1.21	0.43	55	45	2.4	Type III Gas source	
9	93 Mu 88-1	Torok Fm.	Aptian	TingmerkpuK River	1.08	0.15	0.36	0.08	1.19	475	-	14	34	8	8	0.29					
8	93 Mu 87	L. Brookian sh	Hauterivian- Barremian	Upper Eagle Creek	1.81	0.22	0.55	0.52	1.47	483	3.07	13	30	29	1.06	0.29					
10	93 Mu 93	L. Brookian sh	Hauterivian- Barremian	TingmerkpuK Mtn., S side	1.89	0.26	0.76	0.26	1.17	469	2.3-2.5	15	45	15	2.92	0.25	75	25	1.3	Mixed type II / III Oil and gas source	TMax unreliable
13	93 RKC 22-153-B	TingmerkpuK Ss.	Neocomian	TingmerkpuK Mtn. section	1.19	0.04	0.28	0.03	1.57	465	3.0-3.5	3	22	3	6.67	0.13	60	40	2.0	Mixed type II / III Oil and gas source	TMax unreliable
12	93 RKC 22-138-B	TingmerkpuK Ss.	Neocomian	TingmerkpuK Mtn. section	1.27	0.08	0.41	0.13	1.44	453	3.0-3.5	6	32	0	0	0.16					
16	93 RKC 22-72-B	TingmerkpuK Ss.	Neocomian	TingmerkpuK Mtn. section	1.32	0.05	0.41	0.08	1.46	455	3.0-3.5	4	31	0	0	0.11					
15	93 RKC 22-43-B	TingmerkpuK Ss.	Neocomian	TingmerkpuK Mtn. section	1.5	0.07	0.31	0.13	1.43	478	3.0-3.5	5	21	9	2.38	0.11					
14	93 RKC 22-38-B	Kingak Shale	Neocomian	TingmerkpuK Mtn. section	1.84	0.08	0.53	0.04	1.43	488	3.0-3.5	4	30	2	14.0	0.13	70	30	5.1	Mixed type II / III Oil and gas source	TMax unreliable
11	93RKC-22-12-B	Kingak Shale	Neocomian	TingmerkpuK Mtn. section	0.18	0.01	0.01	0.03	-	477**	?	8	0.33	17	0.33	0.5					
7	93Mu 84	Kingak Shale	Neocomian	SW TingmerkpuK Mtn.	0.41	0.01	0	0.11	-	449**	2.5-3.0	2	0	27	0	1					Maroon shale
2	93Mu 104	Kingak Shale	Neocomian	Kukpowruk River	0.35	0.03	0.05	0.06	-	426**	3.5?	8	14	17	0.83	0.38					Maroon shale
3	93Mu 104-B	Kingak Shale	Neocomian	Kukpowruk River	0.14	0.01	0	0.02	-	296**	-	7	0	14	0	1					Maroon shale
SURPRISE CREEK AREA																					
4	93 Mu 80	Kingak Shale	Neocomian	Surprise Ck.	1.87	0.14	0.57	0.23	0.92	461	-	7	30	12	2.48	0.2	65	35	2.0	Mixed type II / III Oil and gas source	TMax unreliable
5	93 Mu 80-1	Shublik Fm.	Upper Triassic	Surprise Ck.	4.63	2.14	1.7	0.34	0.74	445	-	46	367	7	50	0.11	85	15	2.7***	Type II Oil source	
6	93 Mu 80-1A	Shublik Fm.	Upper Triassic	Surprise Ck.	0.9	0.34	0.86	0.09	0.77	444	-	37	93	10	9.56	0.28	80	20	2.6***	Type II Oil source	
NOTES	TAI data from Micropaleo Consultants, Inc.				TOC < 0.5--non-source				Ro < 0.6 -- immature 0.6-2.0--mature			HI = S2/TOC X 100		OI = S3/TOC X 100		Pristane/phytane < 1--good marine source > 2--nonmarine source					
	** Invalid data due to low TOC				TOC 0.5-1.0--weak source rock				-- > 2.0--overmature			HI ca 800--Type I kerogen, algal		S2/S3 < 2.5--gas prone							
	*** Probably too high, affected by weathering				TOC 1.0-2.0--good source rock				T Max < 435--immature 435-460--mature > 460--overmature			HI ca 500--Type II kerogen, marine		S2/S3 2.5 to 5--oil and gas prone							
	See Appendix for description of analytical procedures				TOC > 2.0--excellent source rock							HI ca 200--Type III kerogen, terrestrial		S2 / S3 > 5--oil prone							
	See Dow and Talukdar (1995) for detailed data								TAI-- < 2.1--immature 2.1-3.3--mature > 3.3--overmature												

Table 1. Table of geochemical data, TingmerkpuK and Surprise Creek areas, northwestern DeLong Mountains. Data from Dow and Talukdar, 1995.

Table 1 summarizes the results of the pilot study; the data are grouped by stratigraphic unit, utilizing both formal and informal units recognized in the mapping of the area. Six samples are from a measured section of the Tingmerkpuk Sandstone and top of the Kingak Shale on Tingmerkpuk Mountain, seven samples are from scattered localities in the vicinity of Tingmerkpuk Mountain, and three samples are from the Surprise Creek area in the northern DeLong Mountains quadrangle. Samples reported in table 1 are by field station numbers which include the year of the collection, the initials of the collector, and a field sample number (example--93Mu 88, collected by Mull, and 93RKC 22-12, collected by Crowder). This pilot study provides only a preliminary evaluation of the source rock potential of the western DeLong Mountains and adjacent Colville basin will be used to guide future more detailed sampling and analyses in the area.

## GEOCHEMISTRY AND SOURCE ROCK POTENTIAL

Potential hydrocarbon source rocks in the foothills of the western DeLong Mountains include shales from the Otuk and Shublik Formations (Triassic), Kingak Shale (Jurassic to Neocomian), Tingmerkpuk Sandstone (Neocomian), unnamed lower Brookian shale (Neocomian), unnamed Brookian turbidites (Aptian?), and Torok Formation (Aptian-Albian). (See Mickey, Haga, and Mull, 1995, for a summary of the paleontologic dating of these rocks.) In the pilot geochemical study, samples were collected from the Shublik Formation, Kingak Shale, Tingmerkpuk Sandstone, lower Brookian shale, and Torok Formation (fig. 2). Although the Otuk Formation is present on some of the thrust sheets in the Tingmerkpuk Mountain area, outcrops are poor, and no fresh unweathered samples could be collected for geochemical analysis.

### TINGMERKPUK AREA

#### Kingak Shale (Neocomian--Valanginian)

The Kingak Shale in the northwestern DeLong Mountains is generally not well exposed, but consists of an estimated 100-140 m of black fissile clay shale that overlies the Otuk Formation. Earlier workers in the western DeLong Mountains included this shale as part of the Ipewik Formation (Crane and others, 1981; Curtis and others, 1990) but it is here mapped as Kingak Shale owing to its similarity to the Kingak in the subsurface.

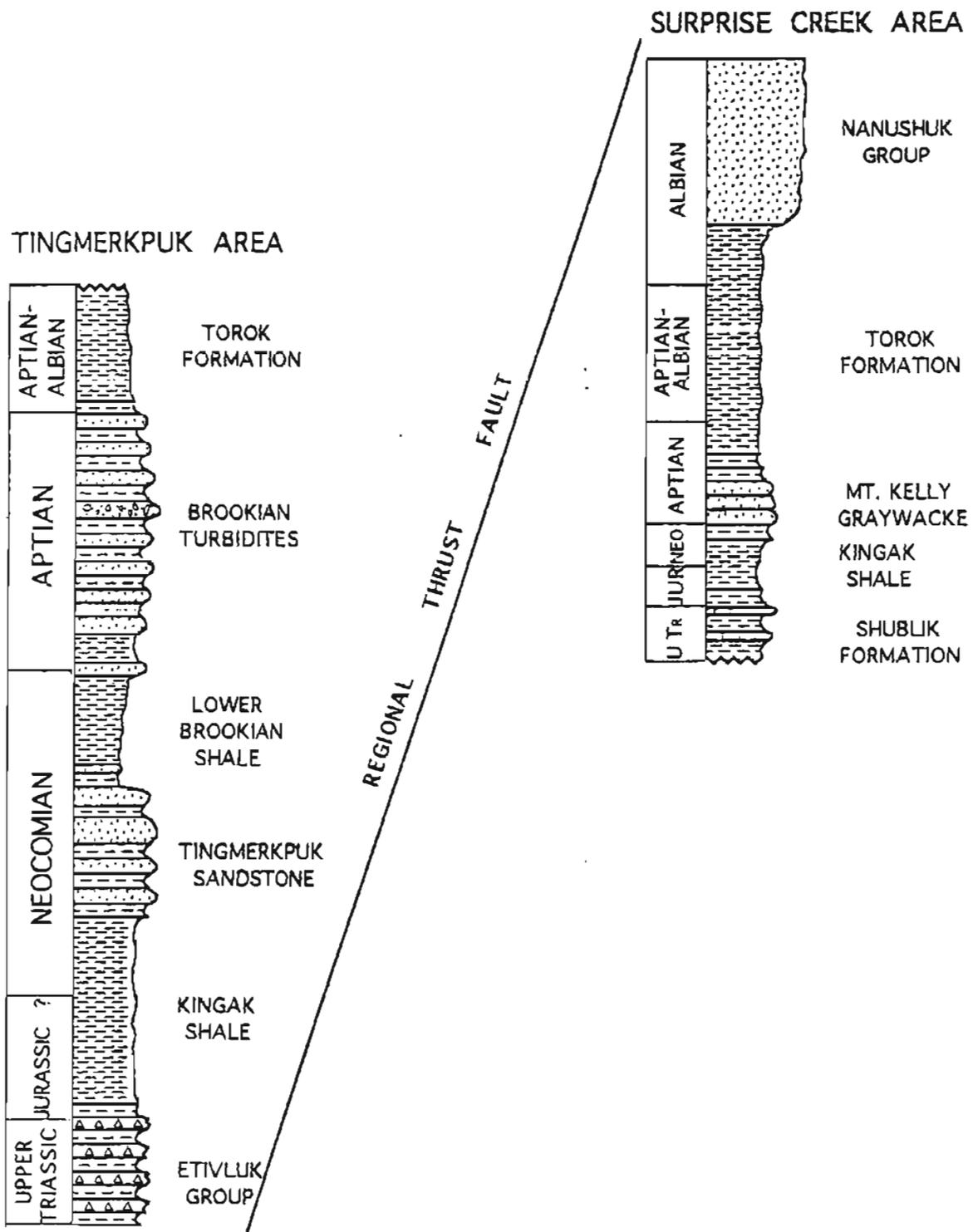


Figure 2. Generalized composite stratigraphic columns, Tingmerkpuk Mountain and Surprise Creek areas, northwestern DeLong Mountains

A well exposed section of the top of the Kingak and the overlying Tingmerkpuk Sandstone (fig.3) is present at Tingmerkpuk Mountain, in the eastern DeLong Mountains quadrangle (Crowder, Mull, and Adams, 1994). A sample from the top of the Kingak at Tingmerkpuk Mountain is a good source rock (1.84% TOC) and is probably characteristic of the Kingak as a whole. Visual kerogen examination and extract chromatography indicate that the Kingak contains a mixed organic facies (type II / III) with a significant amount of terrigenous organic matter relative to the lipid-rich organic matter; this organic facies is normally considered to be an oil and gas prone facies. However, the indicators of thermal maturity ( $468^{\circ}$  T<sub>Max</sub>, 1.43% Ro, and 3.0-3.5 TAI) show that the Kingak in the Tingmerkpuk Mountain area (as well as the shale in the overlying Tingmerkpuk Sandstone) is thermally overmature for generation of oil, and is now capable of generating only gas (fig.4). Small amounts of maroon to greenish gray shale are locally present in the Kingak in the Tingmerkpuk Mountain area; these intervals have low total organic carbon (< 0.5% TOC), and were probably oxidized at the time of deposition. Maroon shale is not characteristic of most of the Kingak, which consists dominantly of black fissile clay shale.

#### Tingmerkpuk Sandstone (Valanginian to Hauterivian)

The Tingmerkpuk Sandstone in the Tingmerkpuk Mountain area consists of about 130 m of quartzose sandstone deposited as turbidites in a deep marine environment (Crowder, Adams, and Mull, 1994). Four samples of black fissile clay shale interbedded with the Tingmerkpuk Sandstone on Tingmerkpuk Mountain (fig. 3) have 1.2-1.5% TOC and are good source rocks. Visual kerogen examination and extract chromatography indicate that shale in the Tingmerkpuk is similar to the Kingak and contains a mixed type II / III, oil and gas prone organic facies with a significant amount of terrigenous organic matter. However, the Tingmerkpuk is also thermally overmature (1.43-1.57% Ro) and is now in the zone of gas generation below the oil window.

#### Lower Brookian shale (Hauterivian)

A thick but poorly exposed section (probably > 250 m.) of black fissile clay shale overlies the Tingmerkpuk Sandstone in the Tingmerkpuk Mountain area. This shale is lithologically similar to the shale in the Tingmerkpuk and Kingak and appears to represent the Neocomian background sedimentation. It contains thin micaceous sandstone interbeds that represent the onset of Brookian deposition in this part of the Colville basin. Two samples of the lower Brookian shale are very good source rocks (1.69-1.81% TOC) and also contain a mixed type II / III organic facies with somewhat more lipid-rich kerogen (70-75%) than in the Tingmerkpuk and Kingak. This shale has a somewhat lower thermal maturity (1.17-1.47% Ro) than the Tingmerkpuk, and is in the zone of wet gas generation, near the floor for oil generation.

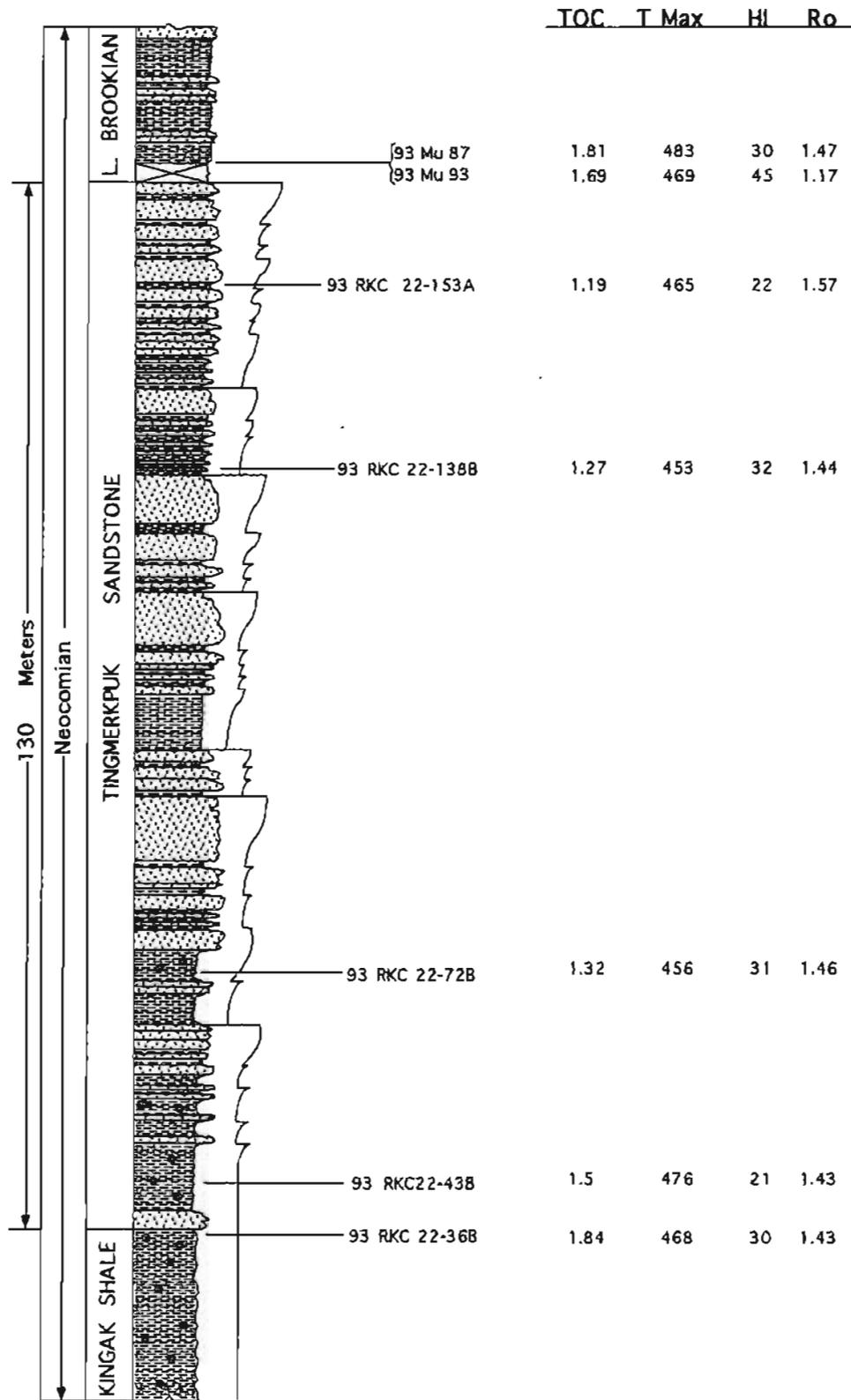
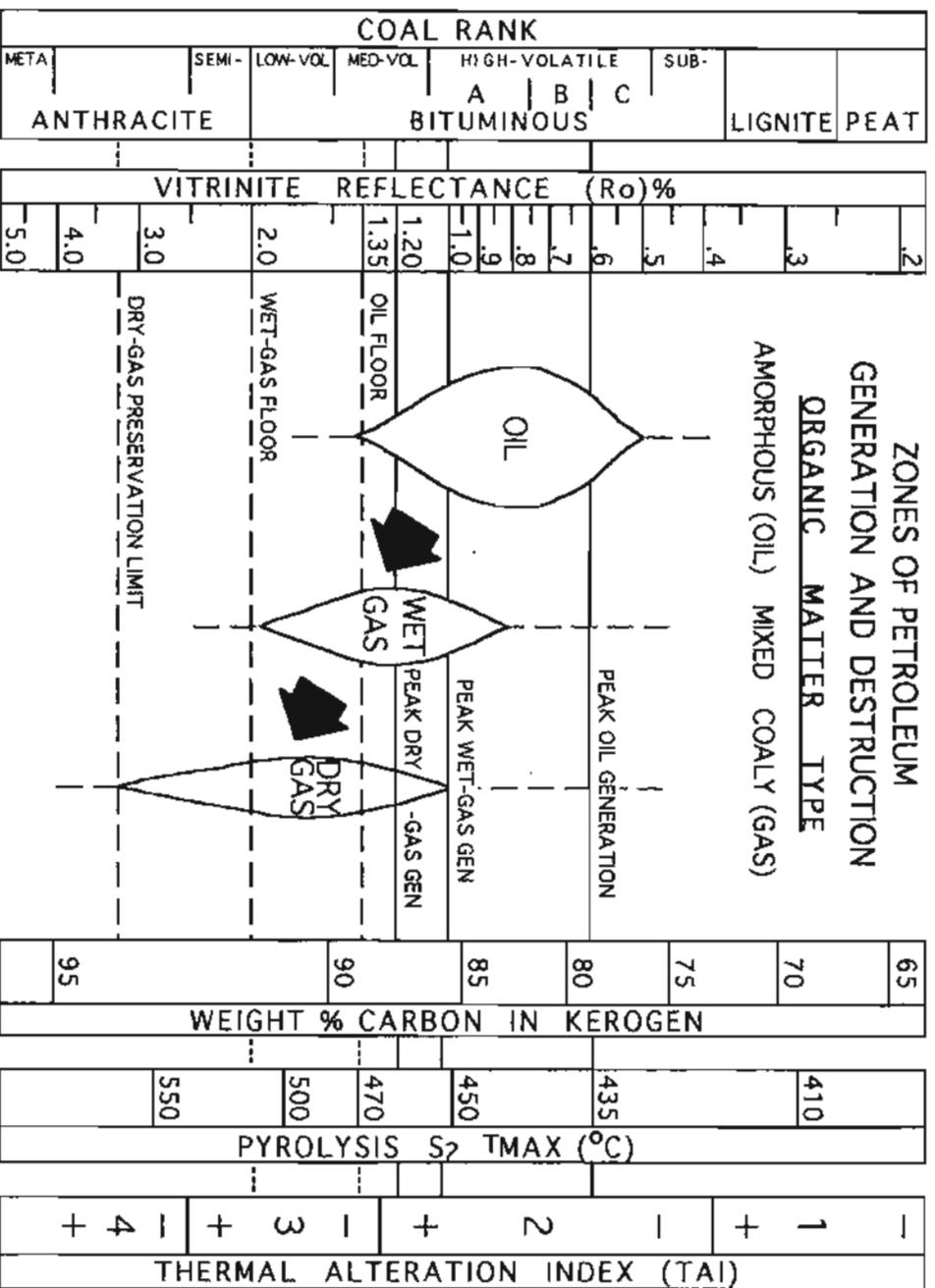


Figure 3. Generalized stratigraphic section of the Tingmerkpuk Sandstone and related rocks on Tingmerkpuk Mountain, showing geochemical data. Stratigraphic section generalized from Crowder and others, 1994.



(Dow and Talukdar, DGSJ, 1994.)

Figure 4. Correlation of various maturation indices and zones of petroleum generation and destruction.

### Torok Formation (Aptian-Albian)

The lower Brookian shale section in the Tingmerkpuk Mountain area appears to grade upward into a thick section (probably > 1000 m.) of Brookian turbidites that consist of numerous muscovite-bearing graywacke sandstones interbedded with thick silty mudstone (fig. 2). Owing to the abundance of terrigenous detritus, these rocks appear to have very little organic content, and were not analyzed in the pilot study. The upper part of the Brookian turbidite section includes the Mt. Kelly Graywacke Tongue of the Fortress Mountain Formation, which grades upward more than 3 km of prodelta mudstone and silty mudstone of the Torok Formation. Two samples of the lower part of the Torok have 1.06-1.3% TOC and are fair source rocks. Visual kerogen examination and extract chromatography indicate that the Torok contains dominantly type III gas-prone organic matter with a high percentage (45%) of terrigenous organic matter relative to the lipid-rich organic matter. The Torok is also thermally overmature for generation of oil and is now in the zone of gas generation.

### **SURPRISE CREEK AREA**

An anomalous section composed of about 150 m of Shublik Formation, Kingak Shale, lower Brookian turbidites, and lower part of the Torok Formation (fig. 5) is exposed in a faulted sharp anticline on Surprise Creek in the northeastern DeLong Mountains quadrangle 40 km north of Tingmerkpuk Mountain (fig. 1). The section is anomalous because the exposure of these older rocks is located in an area that is regionally underlain by several kilometers of Torok Formation that grades upward into thick deltaic deposits of the Nanushuk Group (Chapman and Sable, 1960). Although exposures are incomplete at Surprise Creek, the section of Torok that underlies the Nanushuk Group appears to be very thin. The tight anticline probably represents part of a fault propagation fold with several kilometers of uplift.

### Shublik Formation (Triassic)

The Shublik Formation at Surprise Creek consists of > 25 m of thinly interbedded black organic-rich shale, fossiliferous limestone containing abundant *Monotis* and *Halobia* sp. pelecypods, and gray marl. The lithology is generally typical of the Shublik Formation in the subsurface of the Arctic Slope and in outcrop in the northeastern Brooks Range. It contrasts sharply with the coeval Otuk Formation, which underlies the Kingak Shale in the Tingmerkpuk Mountain area and contains abundant chert and silicified shale and limestone.

Two samples of the Shublik at Surprise Creek were analyzed. A shale contains 4.63% TOC; its thermal maturity indicators (445° T Max and 0.74% Ro) show that the rock is thermally

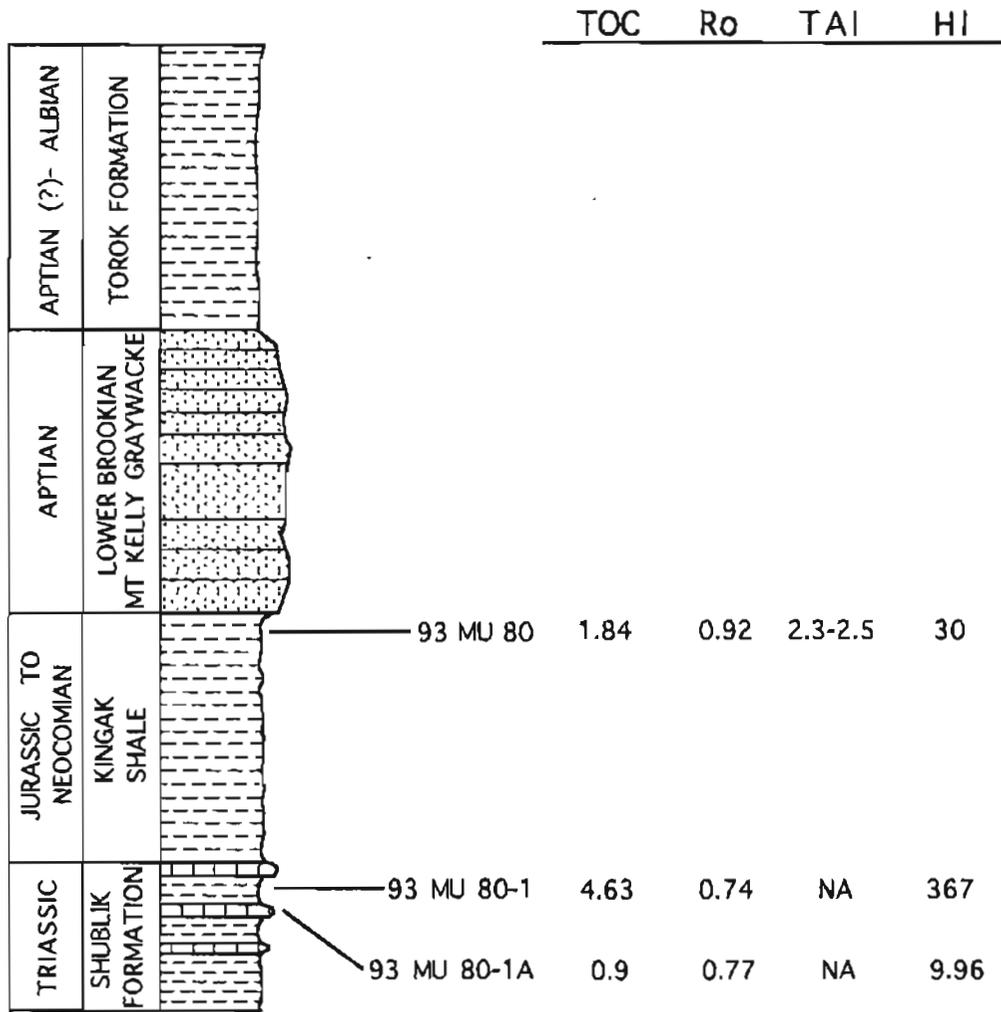


Figure 5. Generalized stratigraphic column of the Surprise Creek area, showing geochemical data.

mature and close to peak oil generation stage. Visual kerogen and extract chromatography show that this is a rich oil-prone source rock. Its hydrogen index (HI) of 367 plotted against oxygen index (OI) on a Van Krevelyn diagram shows that it contains Type II kerogen which will generate oil (fig. 6). This is confirmed by a high oil prone S2/S3 ratio (50) and visual kerogen examination showing that the Shublik contains 80-85% lipid-rich kerogen. A sample of marl from the Shublik has lower TOC (0.9%) but contains migrated bitumen and confirms the level of thermal maturity and the oil-prone nature of the source rock,

### Kingak Shale

About 30 m of poorly exposed and deeply weathered black fissile clay shale of the Kingak Shale overlies the Shublik at Surprise Creek. A sample from near the top of the Kingak contains 1.87% TOC, which classifies it as a good source rock. Its thermal maturity (0.92% Ro) shows that the Kingak is at peak oil generation stage. Visual kerogen and extract chromatography indicate that this sample of the Kingak contains a Type II / III organic facies that is an oil and gas source similar to the Kingak in the Tingmerkpuk Mountain area.

### SUMMARY

The pilot geochemical study shows that Lower Cretaceous oil and gas source rocks are present in the northwestern DeLong Mountains. In the thrust sheets in the Tingmerkpuk Mountain area, shales in the Kingak Shale, Tingmerkpuk Sandstone, lower Brookian shale, and Torok Formation are thermally overmature and probably generated and expelled oil and gas earlier in their history. The kerogen content of these rocks suggests that at a lower stage of thermal maturity the Kingak, Tingmerkpuk, and lower Brookian shales should generate both oil and gas; the Torok Formation appears to be dominantly a gas source.

Analysis of samples from the Surprise Creek area show that the Triassic Shublik Formation contains thermally mature, rich oil-prone source rock characterized by lipid-rich kerogen. The Neocomian Kingak Shale at Surprise Creek is also thermally mature and contains mixed marine and terrigenous kerogen that is an oil and gas prone source. Both units in this area are at peak oil generation thermal maturity.

The presence of thermally mature rocks at the surface in the northwestern DeLong Mountains in contrast to the thermally overmature rocks elsewhere is anomalous. The Shublik Formation at Surprise Creek is characteristic of the Shublik in the subsurface of the northern Arctic Slope and Colville basin, and contrasts sharply with the coeval Otuk Formation in the

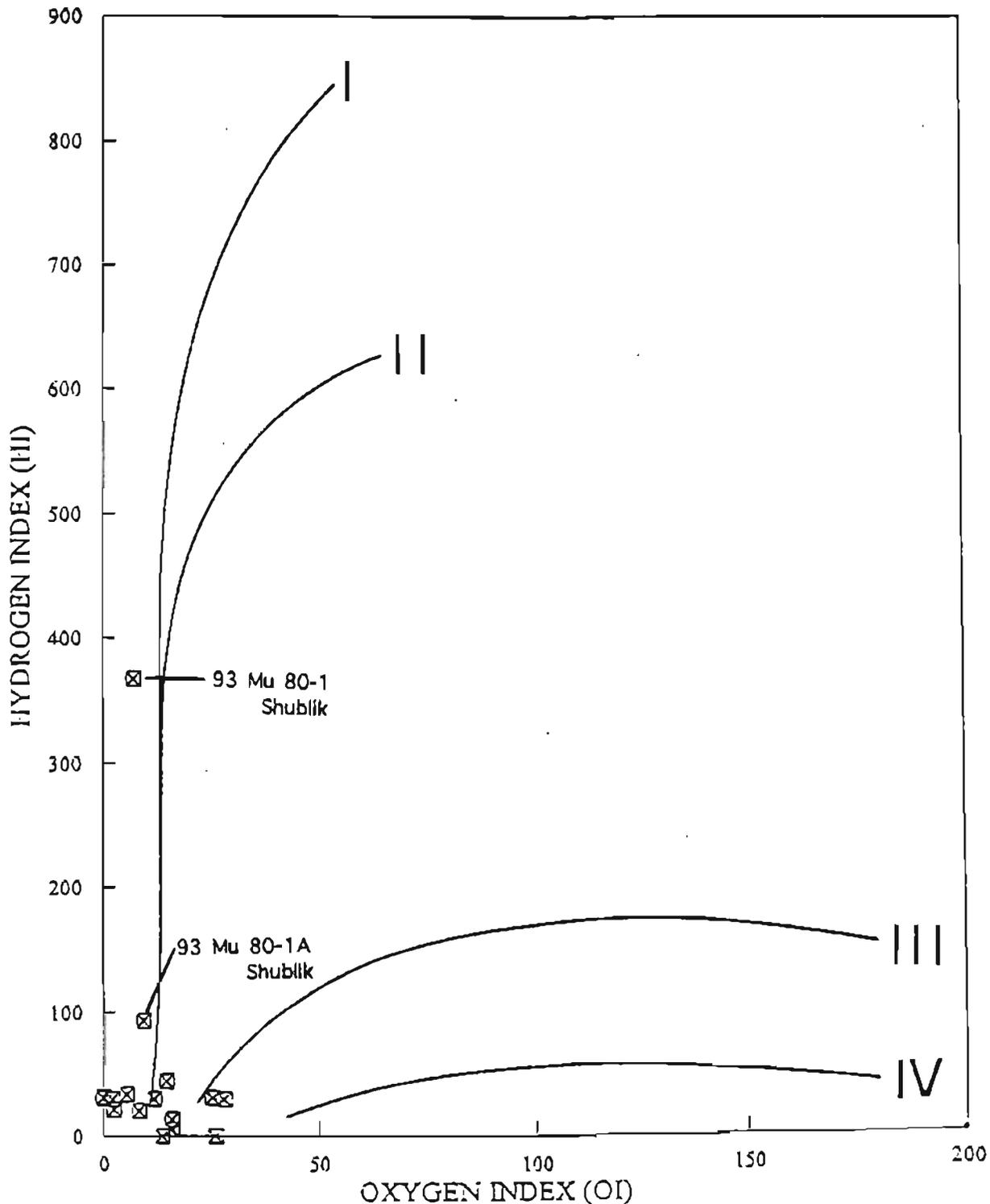


Figure 6. Van Krevelen diagram showing organic facies of samples from northwestern DeLong Mountains. Type I will generate oil, type II will generate oil and gas, type III will generate mostly gas, and type IV will generate little or no hydrocarbon. Note that the Shublik Formation contains type II kerogen. Other rock units in the northwestern DeLong Mountains outcrops are type II/III oil and gas prone rocks, but low hydrogen indices indicate that most of these have already generated and expelled hydrocarbons. See table I for hydrogen index (HI) and oxygen index (OI) data used on diagram.

DeLong Mountains to the south. Data from the Tunalik #1 well, 175 km north of Surprise Creek, show that the base of the oil window there is at less than 4 km. (12,000 ft.) in rocks of Neocomian age. Seismic data on the western Arctic Slope show that the Shublik regionally dips south from the Tunalik well and is at a depth of over 6 km (18,000 ft) in the southern part of the Colville basin, where it should be thermally overmature for either oil or gas.

### TECTONIC IMPLICATIONS

Uplift of the Shublik Formation, Kingak Shale, and Mt. Kelly Graywacke in a tight faulted anticline is evident in the mapping at Surprise Creek. The thermal maturity data show that the section is thermally mature, in contrast to the thermal overmaturity that is characteristic of the rocks in the thrust belt to the south. In addition, the data from the pilot study show that the thermal maturity of the Shublik and Kingak at Surprise Creek is lower than even some of the Torok Shale in adjacent parts of the Colville basin. These data suggest that the Surprise Creek outcrops have not been subjected to the same burial history that has affected most of the rocks in the area. The relationships imply early uplift and reduced burial and heating for some areas in the foreland of the Brooks Range thrust belt. The lateral extent of this anomalously cool stratigraphic section in the northern Brooks Range foothills is unknown and awaits further geochemical studies.

### REFERENCES CITED

- Chapman, R.M., and Sable, E.G., 1960, Geology of the Utukok-Corwin region, northwestern Alaska: U.S. Geological Survey Professional Paper 303-C, p. 47-174.
- Crane, R.C., Wiggins, V.D., and Tailleir, I.L., 1981, Ipewik Formation: A unique Jurassic-Neocomian sequence in the Brooks Range, Alaska: Unpublished manuscript, 15p.
- Crowder, R. K., Adams, K.E., and Mull, C.G., 1994, Measured stratigraphic section of the Tingmerkpuk Sandstone (Neocomian), western Brooks Range, Alaska: Alaska Division of Geological and Geophysical Surveys Public-data file report 94-29, 5 p, 1 sheet.
- Curtis, S.M.; Ellersieck, Inyo; Mayfield, C.F.; and Tailleir, I.L., 1990, Reconnaissance geologic map of the DeLong Mountains A-1 and B-1 quadrangles and part of C-1 quadrangle, Alaska: U.S. Geological Survey Map 1-1930, scale 1:63,360, two sheets.
- Dow, W.G., and Talukdar, S.C., 1995, Geochemical analysis of outcrop samples, western DeLong Mountains, Brooks Range, Alaska: Alaska Division of Geological and Geophysical Surveys Public-data file report 95-30, 40 p.
- Mickey, M.B., Haga, Hideyo, and Mull, C.G., 1995, Paleontologic data: Tingmerkpuk Sandstone and related units, northwestern DeLong Mountains, Brooks Range, Alaska: Alaska Division of Geological and Geophysical Surveys Public-data file report 95-31, 42 p.

**APPENDIX**

**Description of DCSI Analytical Procedures**

## ORGANIC CARBON AND PYROLYSIS DATA

Total Organic Carbon (TOC) and Rock-Eval pyrolysis data provide basic geochemical information and are frequently used to select samples for more detailed studies, particularly kerogen microscopy, extract chromatography and biomarker analyses. Well data can be plotted to make geochemical logs. Unless otherwise specified by a client, DGSI uses LECO TOC then Rock-Eval II pyrolysis as the standard analytical sequence and Rock-Eval is recommended for samples with greater than 0.4% TOC. Samples for LECO TOC and Rock-Eval pyrolysis are ground to pass through a 60 mesh sieve to assure homogeneity.

### LECO ORGANIC CARBON AND TOTAL SULFUR

Total Organic Carbon is best determined by direct combustion. Approximately 0.15 grams of sample are carefully weighed, treated with concentrated HCl to remove carbonates, and vacuum filtered on glass fiber paper. The residue and paper are placed in a ceramic crucible, dried, and combusted with pure oxygen in a LECO EC-12 or LECO CS-444 carbon analyzer at about 1,000°C. A laboratory standard is run every five samples. Total, insoluble, mineral plus organic sulfur can be determined by the CS-444 analyzer during the carbon analysis. Total carbonate can be determined from sample and acid residue weight differences or by LECO combustion TOC differences before and after acid digestion.

### ROCK-EVAL II PYROLYSIS

Rock-Eval II pyrolysis is used to determine kerogen type, kerogen maturity and the amount of free hydrocarbons. About 0.1 grams of the same ground sample used for LECO TOC are carefully weighed in a pyrolysis crucible and then heated to 300°C to determine the amount of free hydrocarbons,  $S_1$ , that is thermally distilled. Next, the amount of pyrolyzable hydrocarbons,  $S_2$ , is measured when the sample is heated in an inert environment which rises from 300° to 550°C at a heating rate of 25°C/minute.  $S_1$  and  $S_2$  are reported in mg HC/g sample.  $T_{max}$ , a maturity indicator, is the temperature of maximum  $S_2$  generation. When  $S_2$  values are less than 0.2 mg HC/g sample, the  $S_2$  maximum typically has poor definition and thus,  $T_{max}$  cannot be reliably determined (Peters, 1986). Carbon dioxide generated during the  $S_2$  pyrolysis, an indicator of kerogen oxidation, is collected up to a temperature of 390°C and reported as  $S_3$  in units of mg  $CO_2$ /g sample. A laboratory standard is run every 10 samples. Hydrogen Index (HI =  $S_2 \cdot 100/TOC$ ) and Oxygen Index (OI =  $S_3 \cdot 100/TOC$ ) are used as kerogen type indicators when plotted on a van Krevelen type diagram.

### ROCK-EVAL II PYROLYSIS PLUS TOC

Rock-Eval II Plus TOC is used to determine both Rock-Eval data ( $S_1$ ,  $S_2$ ,  $S_3$ ,  $T_{max}$ ) and TOC of a 0.1 gram ground sample. With this instrument, the pyrolysis stage ( $S_2$ ) ramps to 600°C at which point the sample is switched to an oxidation oven where the sample is oxidized at 600°C for 5 minutes in air to measure the residual organic matter ( $S_4$ ). A laboratory standard is run every 10 samples.  $S_1$ ,  $S_2$ ,  $S_3$ , and  $S_4$  are summed appropriately to calculate TOC. True TOC will be greater than this calculated sum for samples with maturity greater than about 1.0%  $R_o$  because the Rock-Eval final temperature is inadequate for complete combustion (Peters, 1986). This instrument is preferred when there is insufficient sample to run TOC and pyrolysis separately, or when all samples in a study are to be analyzed for both TOC and Rock-Eval data without prior TOC screening.

## VISUAL KEROGEN ANALYSIS TECHNIQUES

Visual kerogen analysis employs a Zeiss Universal microscope system equipped with halogen, xenon, and tungsten light sources or a Jena Lumar microscope equipped with halogen and mercury light sources. Vitrinite reflectance and kerogen typing are performed on a polished epoxy plug of unfloated kerogen concentrate using reflected light from the halogen source. The digital indicator is calibrated using a glass standard with a reflectance of 1.02% in oil. This calibration is linearly accurate for reflectance values ranging from peat ( $R_o$  0.20%) through anthracite ( $R_o$  4.0%).

Reflectance values are recorded only on good quality vitrinite, including obvious contamination and recycled material. The relative abundance of normal, altered, lipid-rich, oxidized, and coked vitrinite is recorded. When good quality, normal vitrinite is absent, notations are made indicating how the maturity is affected by weathering, oxidation, bitumen saturation, or coking. When normal vitrinite is absent or sparse, other macerals may be substituted. Solid bitumen, for example is present in many samples. Although it often has a different reflectance than vitrinite, Jacob's calibration chart can be used to obtain an estimated vitrinite reflectance equivalent. Graptolites have about the same reflectance as vitrinite and can often be used to obtain maturity data in early Paleozoic rocks that have no vitrinite.

Unstructured lipid kerogen changes in texture and color during the maturation process. Typically, unstructured kerogen at low maturity is reddish brown and amorphous. Somewhere between  $R_o$  0.50 to 0.65%, the kerogen takes on a massive texture and is gray in color. At higher maturity, generally above  $R_o$  1.30%, unstructured kerogen is light gray and micrinized.

Kerogen typing and maturity assessments from the polished plug are enhanced by utilizing fluorescence from blue light excitation. The xenon or mercury lamp is used with an excitation filter at 495 nm coupled with a barrier filter of 520 nm. With the Jena microscope we also have the option of observing fluorescence under ultra violet excitation. The intensity of fluorescence in the epoxy mounting medium (background fluorescence) correlates well with the onset of oil generation and destruction. The identification of structured and unstructured liptinite is also enhanced with the use of fluorescence in those samples having a maturity less than  $R_o$  1.3%. The relative abundance and type of pyrite is also recorded.

TAI is performed using tungsten or halogen light source that is transmitted through a glass slide made from the unfloated kerogen concentrate. Ideally, TAI color is based on sporinite of terrestrial origin. When sporinite is absent, TAI is estimated from the unstructured lipid material. Weathering, bitumen admixed with the unstructured material and micrinization can darken the kerogen and raise the TAI value. The character of the organic matter in transmitted light is correlated with observations made in reflected light for kerogen typing.

Kerogen typing and maturity assessments from the slide preparation are also reinforced by using different light sources. The slide is first observed in transmitted light to obtain TAI color and organic matter structure or type. The light is then switched to reflected halogen light to observe structure and amount of pyrite, and finally to reflected blue light excitation from the xenon or mercury source

for fluorescence. The fluorescence of structured and unstructured liptinite is not masked by the epoxy fluorescence as it is in the reflected light mode because the mounting medium is non-fluorescent. Remnant lipid structures (e.g. sporinite and alginite) within the unstructured kerogen can often be identified in blue light.

Maturity calculations are made from the vitrinite reflectance histograms. Decisions as to which reflectance measurements indicate the maturity of the sample are based not only on the histogram but on all of the kerogen descriptive elements as well. Because it is not done at the time of measurement, alternate maturity calculations can be made if kerogen data and geological information dictate.

In summary, vitrinite reflectance measurements are performed on a polished plug in reflected light, TAI is performed on a slide in transmitted light, and kerogen typing is estimated from both preparations using a combination of reflected, transmitted, and fluorescent light techniques. Fluorescence in blue light is used to enhance the identification of structured and unstructured lipid material, solid bitumens, and drilling mud contaminants. Fluorescence also correlates with the maturity and state of preservation of the sample. Maturity calculations from measured reflectance data are made from the histograms and are influenced by all of the kerogen data.

### VISUAL KEROGEN ANALYSIS GLOSSARY

Several key definitions are included in this glossary in order to make our reports more self-explanatory. In our reports, we refer to organic substances as macerals. Macerals are akin to minerals in rock, in that they are organic constituents that have microscopically recognizable characteristics. However, macerals vary widely in their chemical and physical properties, and they are not crystalline.

1. UNSTRUCTURED KEROGEN, or sometimes called structureless organic matter (SOM) and bituminite; it is widely held that unstructured kerogen represents the bacterial breakdown of lipid material. It also includes fecal pellets, minuta particles of algae, organic gels, and may contain a humic component. As described on the first page of this section, unstructured lipid kerogen changes character during maturation. The three principal stages are amorphous, massive, and micrinized. Amorphous kerogen is simply without any structure. Massive kerogen has taken on a cohesive structure, as the result of polymerization during the process of oil generation. At high maturity, unstructured kerogen becomes micrinized. Micrinite is characterized optically by an aggregation of very small (less than one micron) round bodies that make up the kerogen.
2. STRUCTURED LIPID KEROGEN consists of a group of macerals which have a recognized structure, and can be related to the original living tissue from which they were derived. There are many different types, and the types can be grouped follows:
  - a. Alginite, derived from algae. It is sometimes very useful to distinguish the different algal types, for botryococcus and pediatrum are associated with lacustrine and non-marine source rocks, while algae such as tasmanites, gloecapsomorpha, and nostocopsis are typically marine. Acritarchs and dinoflagellates are marine organisms which are also included in the algal category.

- b. Cutinite, derived from plant cuticles, the remains of leaves.
- c. Resinite, (including fluorinite) derived from plant resins, balsams, latexes, and waxes.
- d. Sporinite, derived from spores and pollen from a wide variety of land plants.
- e. Suberinite is derived from the corky tissue of land plants.
- f. Liptodetrinite is that structured lipid material that is too small to be specifically identified. Usually, it is derived from alginite or sporinite.
- g. Undifferentiated. At times, one can readily distinguish structured lipid material from the unstructured without being able to make a specific determination of the structured material.

The algae are an important part of many oil source rocks, both marine and lacustrine. Alginite has a very high hydrogen index in Rock-Eval pyrolysis. Resins, cuticles, and suberinite contribute to the waxy, non-marine oils that are found in Africa and the Far East. At vitrinite reflectance levels above  $R_o$  1.2 - 1.4%, structured lipid kerogen changes structure and it becomes very difficult to distinguish them from vitrinite.

3. SOLID BITUMEN, also called migrabitumen and solid hydrocarbon. In 1992, the International Committee for Coal and Organic Petrology (ICCP) has decided to include solid bitumen in the Exsudatlnite group. Solid bitumens are expelled hydrocarbon products which have particular morphology, reflectance and fluorescence properties which make it possible to identify them. They represent two classes of substances: one which is present at or near the place where it was generated, and second as a substance which is present in a reservoir rock and may have migrated a great distance from its point of origin. The solid bitumens have been given names, such as gilsonite, impsomite, grahamite, etc., but they represent generated heavy hydrocarbons which remain in place in the source rock or have migrated into a reservoir and mature along with the rock. Consequently, it is possible to use the reflectance of solid bitumens for maturation determinations when vitrinite is not present.
4. HUMIC TISSUE, that is organic material derived from the woody tissue of land plants. The most important of this group is:
  - a. Vitrinite is derived from woody tissue, which has been subjected to a minimum amount of oxidation. Normally, it is by far the most abundant maceral in humic coals, and because the rate of change of vitrinite reflectance is at a more even pace than it is for other macerals, it offers the best means of obtaining thermal maturity data in coals and other types of sedimentary rocks.

Because the measurement of vitrinite is so important, care is taken to distinguish normal (fresh, unaltered) vitrinite from other kinds of vitrinite. Rough vitrinite does not take a good polish and therefore may not yield good data. Oxidized vitrinite may have a reflectance higher or lower than fresh vitrinite; this is a problem often encountered in outcrop samples. Lipid-rich vitrinite, or saprovitrinite, has a lower reflectance than normal vitrinite, and will produce an abnormally low thermal maturity

value. Coked vitrinite is vitrinite that has structures found in vitrinite heated in a coke oven. Naturally coked vitrinite is the product of very rapid heating, such as that found adjacent to intrusions. Where it is possible to do so, vitrinite derived from an uphole portion of a well will be identified as caved vitrinite. Recycled vitrinite is the vitrinite of higher maturity which clearly can be separated from the indigenous first-cycle vitrinite population. Often, the recycled vitrinite merges in with the inert group.

- b. Inertinite is made up of woody tissue that has been matured by a different pathway. Early intense oxidation, usually involving charring, fungal attack, biochemical gelification, creates the much more highly reflecting fusinite and semi-fusinite. Sometimes the division between vitrinite and fusinite is transitional. Sclerotinite, fungal remains having a distinct morphology are considered to be inert. An important consideration is that the inerts, as the name implies, are largely non-reactive, "dead carbon", and they have an extremely low hydrogen index in Rock-Eval pyrolysis.

#### 5. OTHER ORGANIC MATERIAL

- a. In the table, we have put lipid-rich, caved and recycled vitrinite in this section so that we could show the percentages of these macerals; they are described above.
  - b. Exsudatinite. Oil and oily exudates fall in this group. Exsudatinite differs from the solid bitumens on the basis of mobility and solubility. We prefer to maintain this distinction although the ICCP has now included the solid bitumens in with the Exsudatinite group.
  - c. Graptolites are marine organisms that range from the Cambrian to the lower Mississippian; it has been found that they have a reflectance similar to that of vitrinite. Because vitrinite is lacking in early Paleozoic rocks, the proper identification and measurement of graptolites is important in these sediments.
6. PYRITE. Various forms of pyrite can be readily identified under the microscope. Euhedral is pyrite with a definite crystalline habit. Framboidal is pyrite in the form of grape-like clusters which are made up of euhedral to subhedral crystals. Framboidal pyrite is normally found in sediments with a marine influence; for example, coals with a marine shale roof rock usually contain framboidal pyrite. Massive pyrite is pyrite with no particular external form; often this is pyrite that forms rather late in the pore spaces of the sediment. Replacement/infilling is self-explanatory.

## WHOLE EXTRACT GAS CHROMATOGRAPHY

About 50 grams of sample are crushed, passed through a 20 micron sieve, accurately weighed, and soxhlet extracted for 16 hours with dichloromethane. Other solvents can be substituted if desired. The solvent is evaporated and the residue weighed to obtain the weight percent of total organic extract. The advantage of whole extract chromatography over saturate chromatography is more of the lighter fraction ( $C_{10} - C_{15}$ ) is preserved. A minor disadvantage is the nonsaturate compounds are retained and complicate the chromatograms in relatively immature extracts.

A sample of whole extract is injected directly into a Varian model 3400 gas chromatograph fitted with a Quadrex 50 meter fused silica capillary column. The GC is programmed from 40°C to 340°C at 10°C/minute with a 2 minute hold at 40°C and a 20 minute hold at 340°C. Analytical data are processed with a Nelson Analytical model 3000 chromatographic data system and IBM computer hardware. This software system facilitates data processing and graphic display as well as electronic data transmittal. All standard calculations are made including pristane/phytane ratio, carbon preference index, and other key parameters.

Whole extract gas chromatography provides information on organic facies and thermal maturity of source rocks and migrated petroleum. It serves as a basis for oil-rock correlations. It is recommended primarily to evaluate known or suspected source beds, oil shows, samples with anomalous pyrolysis  $S_1$  values and to identify possible contamination products.