

Compositional Analysis of Upper Devonian Black Shales

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ABSTRACT

Mineral composition and the percent of total organic carbon (TOC) in black shales of Dunkirk and Hume formations were determined by X-ray diffraction, using Siemens D 500 X-ray diffractometer. Upper Devonian Black Shales of the Dunkirk and Hume Formations lie in the Upper Devonian Canadaway group. Dunkirk and Hume formations are potential source rocks for oil and gas-producing reservoirs. To examine the burial depth and temperature of the black shales, the extent of illite-smectite diagenesis was examined. Mineral composition of the black shales was determined quantitatively using the RockJock software. The analysis of the core samples of the Marcellus Formation and Geneseo Formation from the New York State Museum was also done. TOC was analyzed with a CM 5120 TOC analyzer. The principal clay minerals in all the samples are chlorite and 2M1 illite. There is a modest relationship between the percent of organic carbon and the weight percent of illite suggesting that the clay minerals have participated in hydrocarbon production. The degree of metamorphism experienced by the black shales was determined by measuring the Kübler index. The highest temperatures, over 360°C, appear to be related to large fractures in the black shale.

KEYWORDS

Black shale, hydrocarbons, Kübler index, illite, Dunkirk formation, TOC

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SUMMARY

The focus of this study is the black shales of the Dunkirk and Hume formations that occur within the Upper Devonian Canadaway Group. The study area covers most of Chautauqua, Cattaraugus and Allegany counties, as well as significant portions of Erie, Wyoming, Livingston and Steuben counties. The dimensions of this proposed study area are approximately 77°W to 79°45'W, and 42°N to 42°45'N. The study utilized both outcrop samples and well-cuttings from within the study area to determine variations of geochemical and lithological composition of the black shales across the depositional basin.

The clay mineral composition of the shale samples was determined primarily by X-ray diffraction using finely powdered samples of the shales in this study. The data were recorded using a Siemens D500 digital diffractometer. The mineral composition of each sample was determined by examining the diffraction pattern for the characteristic peaks of individual minerals. This was partly done using the search-match software incorporated in the Jade 7[®] software. Some minerals were present in small quantities and these were identified by a trial-and-error approach, using knowledge of the types of minerals to be expected in a black shale. Having determined the presence of a set of minerals, their abundance was determined using the RockJock[®] software. The abundance of each minerals was determined by a least squares process of matching the observed diffraction pattern with a mix of diffraction patterns of pure mineral components, each weighted by a factor representing the proportion of that particular mineral. The refinement terminated when the changes to the weighting factors became less than some predetermined value. The advantage of the RockJock[®] software is the ability to determine the relative abundances of clay minerals along with other minerals. Historically this has been a great challenge. The analyses of all the shale samples showed illite and chlorite as the dominant clay minerals with little or no smectite mixed in with the

illite. The lack of observable smectite suggests fairly high temperatures of burial, but such an observation gives little information about the temperature of equilibration.

There is a large literature describing the changes in clay minerals as they are heated during burial diagenesis. During diagenesis, preexisting smectite slowly changes to illite with the illite layers distributed in a largely random manner. The random nature of the interlayering results in a broad X-ray diffraction peak for the first order basal reflections. As the proportion of smectite decreases, the width of the basal reflection decreases, and the measurement of the width of the reflection has been referred to as the Kübler Index. This has led to attempts to correlate the peak width with burial temperature. These measurements were performed on the shale samples of this study yielding burial temperatures of 360° C. Thus, any hydrocarbon material in the black shales likely has been converted to natural gas rather than to liquid hydrocarbons.

INTRODUCTION

The main goal of this study was to determine if the Dunkirk and Hume formations are suitable for gas and oil exploration by examination of illite/smectite diagenesis, degree of metamorphism (Kübler analysis), and total organic carbon (TOC). To determine the burial depth and temperature of the black shales, the extent of smectite-to-illite transformation during diagenesis was examined. The presence or absence of smectitic clays was determined by comparison of the 001 illite peaks of air-dried (AD) samples and the samples saturated with ethylene-glycol (EG). Mineral composition of the black shales was determined quantitatively using the RockJock[®] software. The TOC was analyzed with a CM 5120 TOC analyzer. Mineralogical analysis of the core samples of the Marcellus Formation and Genesee Formation obtained from the New York State Museum was also done for comparison with the Dunkirk and Hume formations.

The Dunkirk Formation occurs at the base of the Canadaway Group, unconformably overlying the Wiscoy Formation in the eastern part of the basin, and the Hanover Formation in the west. The base of the Canadaway Group, and the Dunkirk Formation, coincides with the Frasnian-Famennian boundary 376.5Ma (Tucker et al., 1998). The global extinction event that occurred at the Frasnian-Famennian boundary is observable in examining the diverse bioassemblage within the stratigraphic units of the Wiscoy Formation continuing upsection to the near barren units of the Dunkirk Formation. Named by Clarke in 1903, the type locality occurs along the Lake Erie shore at Point Gratiot, near Dunkirk, New York. The Dunkirk Formation ranges in thickness from 6.2m in the east, to 36.6m along Lake Erie (Pepper and deWitt (1951). In areas west and southwest of New York State, the Dunkirk Formation correlates with the

Ohio and Huron shales.

The Hume Formation was named by Pepper and deWitt in 1951 as a member of the Perrysburg Formation. Smith and Jacobi (2000a) redefined the Canadaway Group removing the Perrysburg Formation and changing the Hume Black Shale Member to the Hume Formation. The Hume Formation's type locality is at Mills-Mills in the township of Hume along Wiscoy Creek. The thickness varies from 7.1m to 43.5m, the areas of maximum thickness coincide with the syndepositional active Clarendon-Linden Fault Zone, suggesting that the deposition of the Hume Formation is partially fault controlled (Smith and Jacobi, 1999, 2000b and 2001). Correlatives of the Hume Formation outside of New York State have not been reported, but may be an upper tongue of the Ohio or Huron shales.

Both the Dunkirk and Hume formations are transgressive black shale units; both mark the bases of 3rd order sequences (Figure 1).

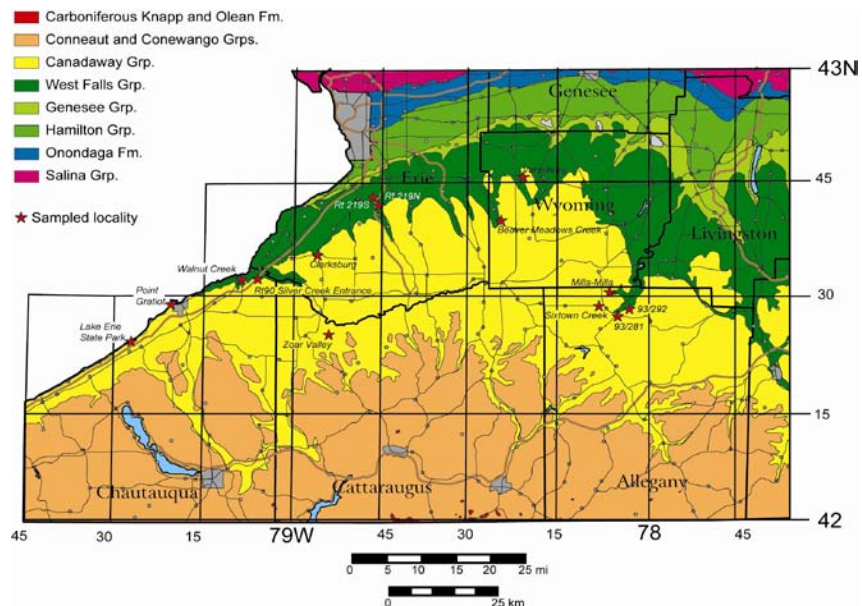


Figure 1: The sampling locations and geology of the study area (Smith, 2003).

The Dunkirk Formation marks a major eustatic transgression that is observed at Famennian outcrops around the world (Johnson et al., 1985). The transgression marked by the Hume Formation appears localized and work by Smith and Jacobi (1999, 2000b, 2001 and 2003) suggest that basin and deposition of the Hume Formation is likely controlled by syndepositional fault activity in the Clarendon-Linden Fault Zone.

The Canadaway Group and overlying Conneaut and Conewango Groups contained historically productive oil reservoirs in New York and Pennsylvania. The Dunkirk and Hume formations are the youngest black shales in the Upper Devonian and therefore may be the source rocks for the Upper Devonian oil reservoirs. Furthermore, the first known natural gas well was drilled into the Dunkirk Formation in 1821 in the town of Fredonia New York (Hill et al., 2002). Renewed interest targeting shale reservoirs suggests a reexamination of the Upper Devonian black shales. The geochemistry of petroleum reservoirs and source rocks typically examine the organic geochemistry and usually the lithologic composition of sandstone reservoirs. However, most source rocks are black shales, and yet little information regarding the mineralogical framework of the shales is available.

Section 2

BACKGROUND

Shales are one of the most common types of sedimentary rocks. Shales are deposited in low energy environments, in deep or marginal (shallow) seas and oceans, lake, swamp and lagoon environments. Diagenetic changes involve burial and low-grade metamorphic changes of deposited material. Black shales generally consist of feldspars, mostly albite and in some cases microcline, calcite and clay minerals such as illite, smectites, chlorites, and kaolinite, as well as pyrite and quartz (Yen and Chilingarian, 1976, Moore and Reynolds, 1997).

Clay minerals are a part of the phyllosilicate group. They are layer silicates that consist of tetrahedral and octahedral sheets. Clay layers are bound together by interlayer cations or a sheet of hydroxides. Interlayer cations or hydroxides are bound with ionic or hydrogen bonds, which are much weaker than covalent bonds within the layers. This type of bonding dictates the platy habit of clay crystals. Smectites or expandable clays can facilitate organic matter in the interlayer space. This is significant for the preservation of the organic matter during the deposition of black shales. This behavior is due to the small layer charge, and the expansion causes a visible shift in the X-ray diffraction (XRD) pattern where the 001 peak shifts from 12 to 15 Å. The 001 peak is of interest because it contains information about the type(s) of clay layers present in the sample and the manner in which they are stacked. Conversely, illite is a non-expandable clay mineral, with a 0.89 layer charge which is usually compensated by the presence of a monovalent cation, most commonly K. Moreover, illite is characterized by a 10 Å basal reflection.

Clay mineral composition of shales provides information about the diagenesis and burial temperatures. During burial as the depth and temperature increase, the smectite converts to illite and either chlorite forms or the crystallinity of the illite increases, or both (Moore and Reynolds, 1997). During this process, water or organic matter trapped in the interlayer of smectites is released. The loss of water has been suggested to play a role in the movement of hydrocarbon material from the clay-rich part of the sediment column to a reservoir rock with greater porosity. During this flushing action, it is possible that some secondary porosity is created in the source rock.

Several mechanisms for this change have been suggested (Hower, 1976, Booles and Franks, 1979). Models for this transformation have been suggested by MacEwan, the fundamental particle model and a two solid solution model (Moore and Reynolds, 1997). The role of pressure in the conversion of smectite to illite is less well established. In theory, the change from smectite to illite should not have a net volume change and thus pressure would not play a significant role.

KÜBLER INDEX

Kübler index (KI), represents the measure of the degree of the illite “crystallinity”, and its relation to the degree of metamorphism in the very low grade (sub-greenschist facies) metamorphic zone. With the increase of temperature and/or depth the “crystallinity” or the sharpness of the 10Å illite peak increases. In other words smectite converts to illite leaving ultimately illite with the 2M1 polymorph. This method involves the measurement of full width at half-maximum height (FWHM) above the background of the 10Å illite peak on the XRD pattern of random oriented samples (2μ fraction) (Figure 2).

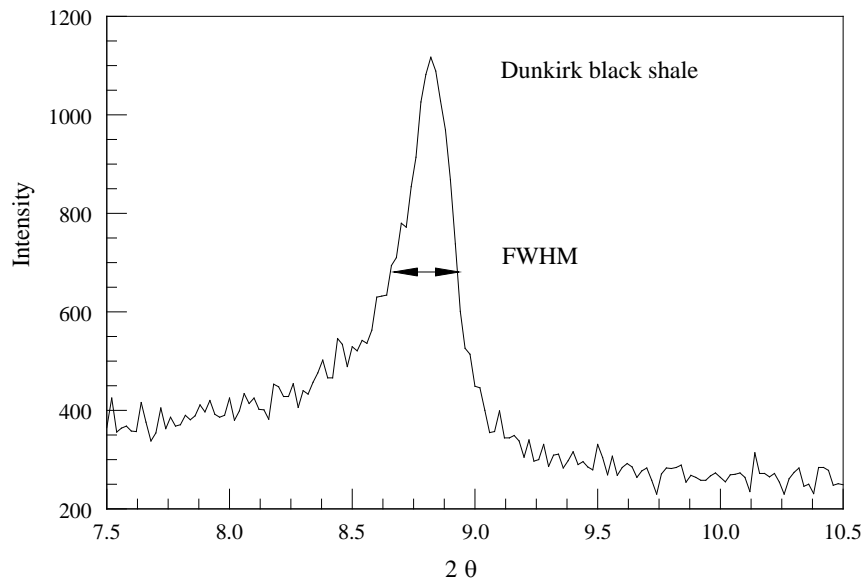


Figure 2: The double arrow indicates the measurement of the full width at half maximum (FWHM) for the 001 reflection of illite.

KI is used to determine the metamorphic grade of low metamorphic rocks. In this range three metamorphic zones can be distinguished based on the KI and the illite polytype: diagenesis, anchizone and epizone. Temperatures for these zones are: 280°C, 280-360°C and over 360°C respectively (Moore and Reynolds, 1997).

Sample thickness and sample preparation affect the illite “crystallinity” measurements. Krumm and Buggisch (1997) suggested discarding the weathered portion of the material in question to avoid the peak broadening. They have also suggested wet grinding to protect the smaller grain size particles from shearing. For clay bearing samples ultrasonic treatment should not exceed 20 minutes. Further sonifying results in peak broadening (Krumm and Buggisch, 1997). While the measurement of the KI is easily and accurately done, the temperatures derived from such measurements are related to studies of low-grade metamorphic terrains. This naturally introduces some uncertainty and to the exact burial temperatures.

Section 3

METHODOLOGY

Samples were collected in Alleghany, Chautauqua, Cattaraugus and Wyoming counties (Table 1). After collection, they were crushed and prepared in the lab for qualitative (mineral identification), quantitative (quantities of each mineral present) and TOC analysis. The procedures are described below.

Site	Location	Outcrop	USGS Topo Quad
South Branch of Eighteenmile Creek	Clarksburg, NY, along New Oregon Rd., and also the intersection of New Oregon Rd. and Rt. 75	Dunkirk Fm.	Langford and Hamburg
Point Gratiot	Point Gratiot Park, Dunkirk NY, Off Rt 5, sampled along lake shore cliffs	Dunkirk Fm.	Dunkirk
Lake Erie State Park	Lake Erie State Park, Off Rt. 5, 3.2 km north of Brocton NY	Dunkirk Fm.	Brocton
Walnut Creek	Main St, Silver Creek, NY. Outcrop forms cliffs along eastern bank of Walnut Creek	Pipe Creek Fm.	Silver Creek
Interstate 90 On Ramp	Silver Creek, NY, On ramp to Interstate from Silver Creek	Dunkirk Fm.	Silver Creek
219 South	Boston, NY Roadcut on west side, 1.3 km south of Mayer Rd.	Dunkirk Fm.	Hamburg
219 North	Boston, NY, prior to Boston exit ramp, Roadcut on east side, 0.7 km north of Eiss Rd.	Dunkirk Fm.	Hamburg
Sixtown Creek	West of Rt 19, where the Finger Lakes Trail crosses Buffalo Rd.	Hume	Houghton
Mills-Mills	Small south flowing tributary to Wiscoy Creek, west of Mills-Mills Rd.	Hume	Portageville
Ballard Rd, North	First west flowing tributary to the Genesee River, south of Knibloe Rd.	Dunkirk Fm.	Fillmore
Beil's Farm (Ballard Rd South)	First northwest flowing tributary to the Genesee River, south of Snyder Hill/Bottsford Hollow Rd	Dunkirk Fm.	Fillmore
Zoar Valley	Confluence of the South Branch and Cattaraugus Creek. Outcrop along east side of creek.	Hume	Gowanda

Table 1: A summary of the localities where black shale samples were collected.

Targeted amount of samples were about 1 kilogram. During collection we have tried to remove the top most weathered layer. However, samples from throughway outcrops such as the ones from 219N and 219S were extremely weathered.

Collection of the Dunkirk samples from the type locality Point Gratiot beach was done along and between the fracture planes. This was done to determine if there is a relationship between the fractures and the distribution of the organic matter in the black shales. The assumption that the fractures control the movement of the organic matter was investigated. The sample localities are shown in Figure 1.

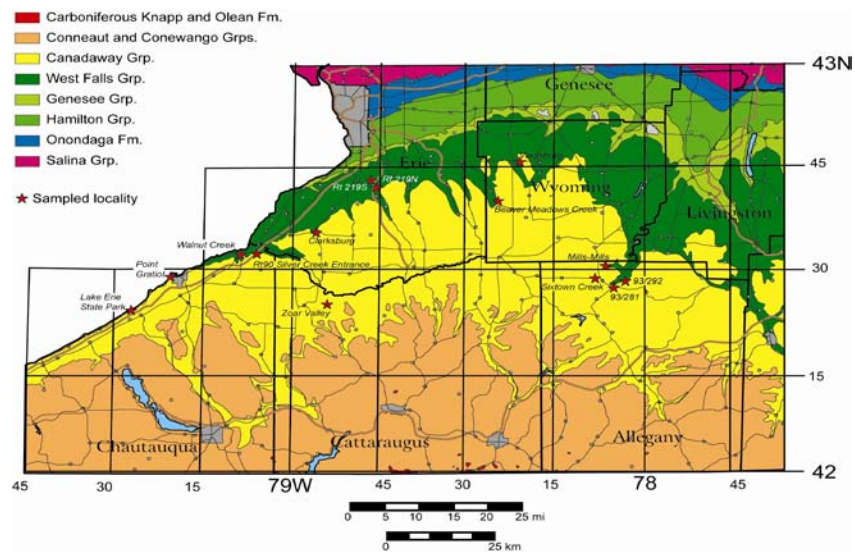


Figure 1: The sampling locations and geology of the study area (Smith, 2003).

Approximately 500g of sample were crushed in a jaw crusher. Crushing was repeated until the size of the shale chips was reduced to approximately 5 millimeter. It was important to analyze fresh, relatively unweathered minerals, therefore the sample at this stage was sieved through a 32-mesh (500 microns opening) sieve. Sieving was done so that the weathered portion of the sample

would unlikely be used in the analysis (Krumm and Buggisch, 1991). After sieving, fines that accumulated in the bottom pan were discarded. The unweathered portion of the sample was then pulverized to about a few millimeter size.

In order to get a representative and unbiased portion of the sample for the analysis, the pulverized sample was put through a splitter until each portion consisted of approximately 10g of shale. One portion, for the clay fraction analysis, of approximately 10g was left for an overnight soak in distilled water. The other portion was again put through the splitter, weighed and prepared for the quantitative analysis.

EXPERIMENTAL

The X-ray diffraction analyses were done on the Siemens D500 diffractometer, CuK α , graphite monochromator. The receiving Soller slit was removed for all X-ray diffraction analyses. This was done so as to have the same settings as the diffractometer where the RockJock standards were run. Two kinds of samples were prepared. One consisted of carefully prepared bulk samples. The key to an accurate quantitative determination of the minerals in rock samples by X-ray diffraction depends strongly on having the sample in the form of small, uniform particles. This is best accomplished using a micronizing mill from McCrone Research Associates. The apparatus consists of a cylindrical plastic container filled with smaller cylinders of fused aluminum oxide. The coarsely ground sample is added along with a few milliliters of methanol. The loaded cylinder is rapidly vibrated which allows the alumina cylinders to vigorously rub against each other thus grinding the powder. The methanol assures that the powder is ground without heating. The slurry is removed after a 5-minute treatment and the alcohol is allowed to evaporate. The X-ray sample is assembled by side loading the powder into a sample holder. The RockJock software is based on having a sample containing an internal standard (a known quantity of pure zinc oxide), knowledge of the minerals present and using a library of diffraction patterns of a range of minerals commonly found in rock and especially shale rocks. The experimental pattern is compared to a calculated one based on the minerals identified in the sample. The software optimizes the fit of experimental and calculated scans by adjusting the proportion of each of the minerals known to be in the sample.

Presence of smectites was analyzed qualitatively by saturating the oriented clay fraction with ethylene glycol (EG) and comparing the EG and the air-dried (AD) XRD patterns. The diffraction was done in two ranges: 5° to 10.5° 2 θ and 16.5° to 19.5° 2 θ . These ranges were chosen to provide two

peaks which are sensitive to the presence of smectite intermixed with illite. The first range covers the combination peak of 001 for illite and 002 for EG smectite. The second peak is a combination of the 002 of illite and the 003 of EG smectite. Środoń (1980) has shown that the difference in 2θ ($\Delta 2\theta$) between these peaks is a good measure of the quantity of illite and smectite in a sample. Scans were done with the step of 0.02° and a count of 5 seconds. A typical XRD scan for an oriented clay sample is shown in Figure 2. The effect of EG saturation is shown in Figure 3 where the two scans of the same oriented clay fraction (AD and EG) are plotted at the same scale. Both scans match with the exception of the top of the two peaks. This is an artifact of peak shape rather than a shift in 2θ .

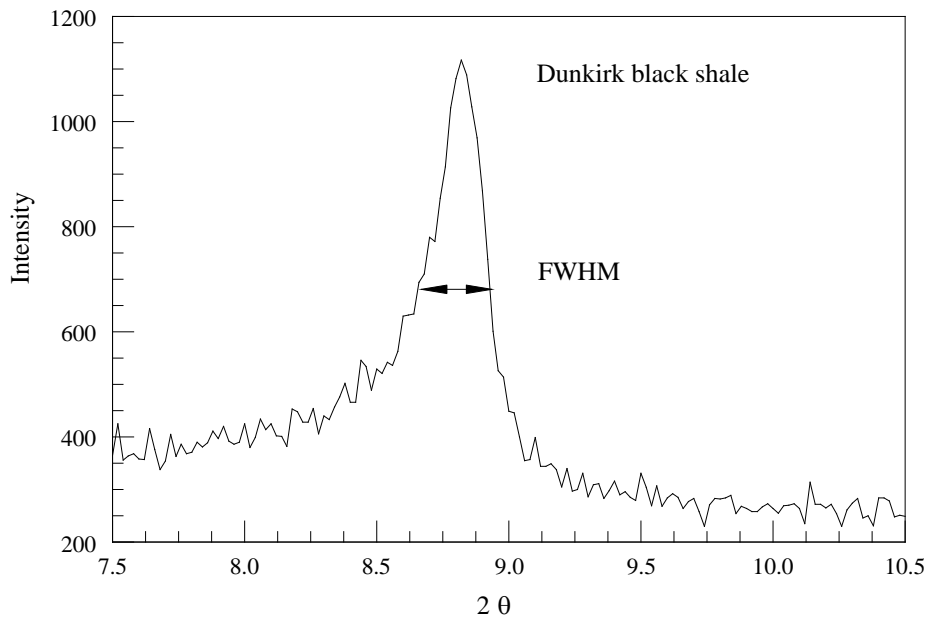


Figure 2: The double arrow indicates the measurement of the full width at half maximum (FWHM) for the 001 reflection of illite.

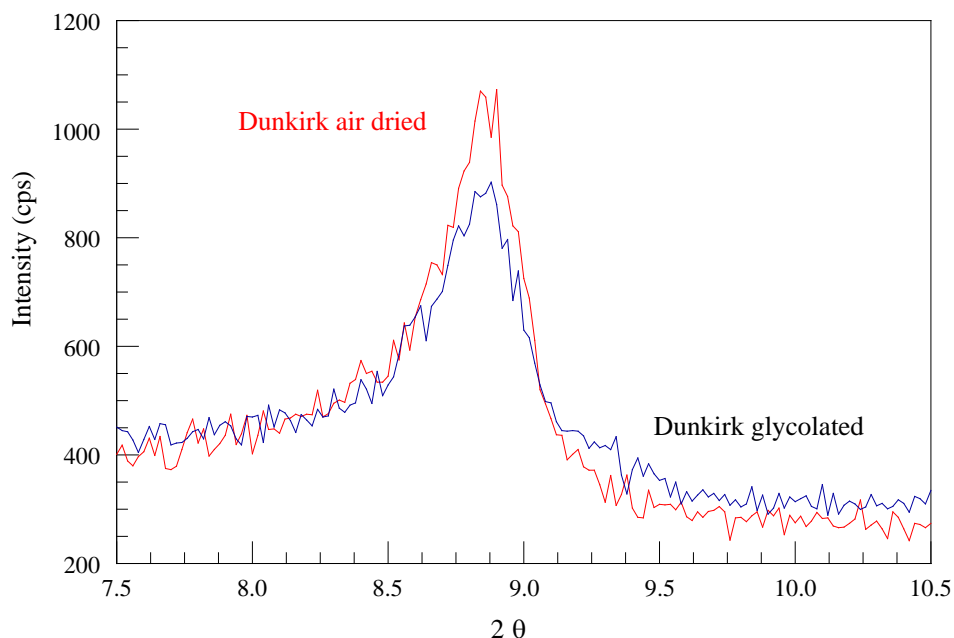


Figure 3: A comparison between the red line of an air dried oriented clay sample and the same sample after exposure to ethylene glycol vapor shown as the black line. The ethylene glycol causes any smectite layers in the illite to expand resulting in a shift of the clay peak to larger d-spacings (smaller 2θ values). The clay sample is from the Dunkirk formation.

One of the main problems in the quantitative analysis of clay rich samples in the past was the occurrence of preferred orientation of clay minerals, variable chemical composition of clay minerals, variable crystallographic structures and defects in the mineral structures (Środoń et al., 2001). The problem of preferred orientation can be avoided by the preparation of samples with random orientation. The procedure is explained in the RockJock manual (Eberl, 2003).

Total carbon was determined with a CM 5120 analyzer by heating a weighed sample of powdered black shale to 950° C in an oxygen atmosphere. The evolved gas was passed through a solution which changed color depending on the amount of carbon dioxide present in the gas. This analysis

yields total carbon (i.e. carbon from carbonates and organic matter). To obtain a precise TOC measurement the total inorganic carbon (TIC) was also measured on the CM 5120 analyzer by acidifying a weighed sample of the same black shale and the carbon dioxide was determined as in the TC process. The TOC was determined by subtracting the TIC from the TC values.

Section 4

RESULTS

Qualitative mineral analysis

The mineral composition of the samples collected for this study was determined by searching for characteristic peaks in the X-ray diffraction scans of unoriented powders. For example, a peak at 14 Å is indicative of chlorite or kaolinite, a peak at 10 Å indicates illite, a peak at 3.37 Å indicates quartz, and so on. The minerals which are present at moderate to high percentages (e.g., quartz) are readily identified. Those which are present at levels of a few percent become more difficult to identify (e.g., sphalerite) are more difficult to identify. A lower limit of identification is probably about 2 wt%. There are standard tables which help in the identification of minerals present; we used the table included in the RockJock software.

Quantitative mineral analysis

To calculate the results quantitatively, the RockJock software compares the measured XRD pattern with the internal standards for minerals identified in the sample. Mineral composition of the Dunkirk and Hume samples is similar (Table 2). The samples contain up to 50wt% of quartz. Feldspars such as albite and intermediate microcline, and pyrite are present in minor quantities. Calcite and dolomite are present in minor quantities or not present at all. Calcite and dolomite are present only in some of the samples from Point Gratiot, the type locality for the Dunkirk Formation, and the Marcellus and Geneseo formations (Table 2). The ash layers found in the field are about 5cm thick and can be seen every 0.5 – 1 m at the Finger Lakes trail. The RockJock result for the ash layer sample A1 does not have a good agreement. This sample was analyzed more than once to eliminate human error. Nevertheless, the degree of fit between the calculated and measured results was higher than the one for the black shale samples. Also, the results show the presence of

jarosite, a clay mineral associated with volcanism and hydrothermal vents. This may be because ash cooled fast and the materials are poorly crystallized. If that is the case, high degree of fit is to be expected because the agreement between the measured XRD pattern and the standards from the internal database will not be good. The mineral compositions determined quantitatively for the samples of Marcellus, Geneseo, Dunkirk and Hume formations are shown in the tables below.

Mineral present	M1	M2	M3	G1	G2	GD1	GD2
Quartz	26.6	23.7	18.2	29.9	30.5	26.9	28.9
Intermediate Microcline feldspar	4.8	3.7	3.6	2.7	2.6	2.3	3.3
Albite feldspar (Cleavelandite)	4.7	2.2	1.3	2.8	3.4	2.6	3.8
Calcite	2.9	13.4	22.7	2.8	2.9	0.4	1.9
Dolomite	1.2	1.5	1.0	0.9	0.9		
Disordered Kaolinite	2.7	4.0	2.3	0.7	1.5	3.5	3.1
2M1 illite (SG4)	30.5	30.2	26.6	33.5	32.5	35.8	32.7
Chlorite Tusc	7.3	7.9	9.0	11.9	12.0	17.2	14.9
Pyrite	8.0	5.2	3.2	2.1	2.1	1.4	1.5
Marcasite	0.9						
TOTAL	89.57	91.8	87.80	87.26	88.53	90.07	90.06

Table 2: The mineral composition of the Marcellus and Geneseo shale samples as determined by the RockJock® software.

Mineral present	D1	D2	D3	D4	D5	D6	D7	D8	D9
Quartz	25.2	45.6	45.7	43.4	42.8	45.6	42.9	45.2	37.3
Intermediate Microcline feldspar	1.9	2.9	2.8	2.3	2.8	2.1	2.6	2.9	3.1
Orthoclase feldspar			0.2						
Albite feldspar (Cleavelandite)	1.9	4.4	4.1	3.9	3.7	3.3	3.5	4.0	2.8
Calcite				0.3					0.1
Dolomite		0.6	0.5	1.0	0.3				0.2
Disordered Kaolinite	4.8	2.8	2.5	3.0	2.4	2.8	2.5	3.0	2.3
2M1 illite (SG4)	44.8	22.7	23.9	24.5	25.9	28.9	26.3	25.3	27.3
Chlorite CCa-1				1.5	0.9		1.7	1.0	
Chlorite CCM					2.3			3.0	
Chlorite CO			8.1						
Chlorite Tusc	13.2		5.7	6.5	4.5	7.2	5.0	2.5	9.7
Mg-Chlorite (Clinochlore)		1.2	4.3		0.9	5.2	1.3		
Pyrite	3.5	2.3	1.9	1.8	3.7	2.5	4.7	1.7	2.7
Marcasite			1.2	1.1	1.1	1.0	1.0	1.0	1.0
TOTAL	95.36	82.38	100.97	89.33	91.35	98.42	91.66	89.68	86.6

Table 2 cont.: The mineral composition of the Dunkirk samples as determined by the RockJock® software.

Mineral present	D10	D11	D12	D13	D14	D15	PC1	D16	D17
Quartz	41.2	39.8	47.1	42.6	41.4	39.1	26.5	47.9	40.5
Intermediate Microcline feldspar	2.1	3.3	1.9	2.8	2.8	2.5	1.9	3.9	2.6
Orthoclase feldspar							1.5		
Albite feldspar (Cleavelandite)	3.1	3.1	3.9	3.6	3.4	4.0	1.8	4.5	5.2
Calcite	0.1			0.2	0.1				
Dolomite	0.1				0.1				
Disordered Kaolinite	2.7	2.1	2.9	2.0	3.0	3.5	3.2	3.8	4.8
2M1 illite (SG4)	31.0	28.6	26.6	31.7	30.7	30.0	29.5	30.3	32.6
Chlorite CCa-1						2.2			1.6
Chlorite CCM						2.5	3.1	0.8	4.0
Chlorite Tusc	10.1	9.0	9.9	10.7	10.3	4.0	3.7	6.9	5.2
Mg-Chlorite (Clinochlore)							4.2	3.5	0.6
Pyrite	2.8	2.1	1.8	1.9	2.0	1.8	2.6	1.3	2.2
Marcasite	1.0	1.1	0.6	0.7	1.0	1.1	0.9	0.7	0.8
TOTAL	94.2	89.1	94.8	96.3	94.9	90.74	78.99	103.60	100.0

Table 2 cont.: The mineral composition of Dunkirk shale samples (cont.).

Mineral present	D18	D19	D20	D21	D22	H1	H2	H3	H4	A1
Quartz	50.1	42.1	28.8	39.3	43.7	50.4	53.6	35.4	41.0	36.1
Intermediate Microcline feldspar	2.4	1.7	2.3	2.1	2.2	1.2	2.0	2.1	2.4	1.9
Albite feldspar (Cleavelandite)	5.3	3.3	2.9	4.6	5.0	7.8	7.8	4.4	5.2	4.4
Disordered Kaolinite	3.5	3.1	1.2	2.1	3.9	7.2	3.3	4.0	3.7	5.0
2M1 illite (SG4)	22.9	34.6	31.1	29.5	27.2	21.0	19.7	36.3	26.4	44.9
Chlorite CCa-1									3.0	
Chlorite CCM						4.2		5.4		8.4
Chlorite CO										
Chlorite Tusc	9.5	13.0	13.3	13.0	11.7	5.1	11.7	6.7	6.9	7.7
Mg-Chlorite (Clinochlore)						3.1	1.8	2.1		
Pyrite	2.1	2.6	4.9	2.7	1.7	1.7	0.7	2.3	2.0	0.6
Marcasite			0.4	0.6	0.6			0.9	0.4	
Halite										0.9
Jarosite										1.6
TOTAL	95.7	100.3	84.9	94.0	96.0	101.9	100.5	99.57	91.0	111.49

Table 2 cont.: Mineral composition of Dunkirk shale samples (cont.) along with samples from the Hume formation.

The dominant clay minerals are 2M1 illite and one or more chlorites. There are also small amounts of kaolinite present in most of the samples. RockJock software is designed to analyze samples with high clay content. However, the clay mineral XRD patterns for 1M, 1Md and 2M1 illite are similar and the peaks have low intensity compared to other minerals e.g. quartz. Consequently, the program would calculate a certain percent of 1Md and 1M illite. The quantitative analysis was simplified by the fact that the only one illite polytype present (2M1) was determined from the qualitative analysis. The amounts and types of chlorites vary in the samples. This is not unusual since chlorites are known to have extremely variable composition. The most

prominent chlorite matches the chlorite from Tuscany in the RockJock standards database. This type of chlorite has broad, low intensity peaks.

Total organic carbon

The measured amount of TOC is presented in Figure 4 below. The samples shown in the figure represent the TOC distribution in the Dunkirk (on the left of the ash sample) and the Hume formations (to the right of the ash sample) with the exception of the Pipe Creek Formation sample and the sample that represents the possible ash layer sampled from the Finger Lakes Trail.

Kübler index

There are no shifts of 001 illite peak in the samples (Figure 3) which leads to the conclusion that smectite is not present in any of the samples; therefore, the diagenesis of smectite to illite was completed. Further, application of the Środoń (1980) method of estimating smectite content by means of the difference in the positions of two diffraction peaks showed no measurable smectite content. Consequently the only type of illite present in the samples is the 2M1 illite polytype, the final product of the I/S diagenesis.

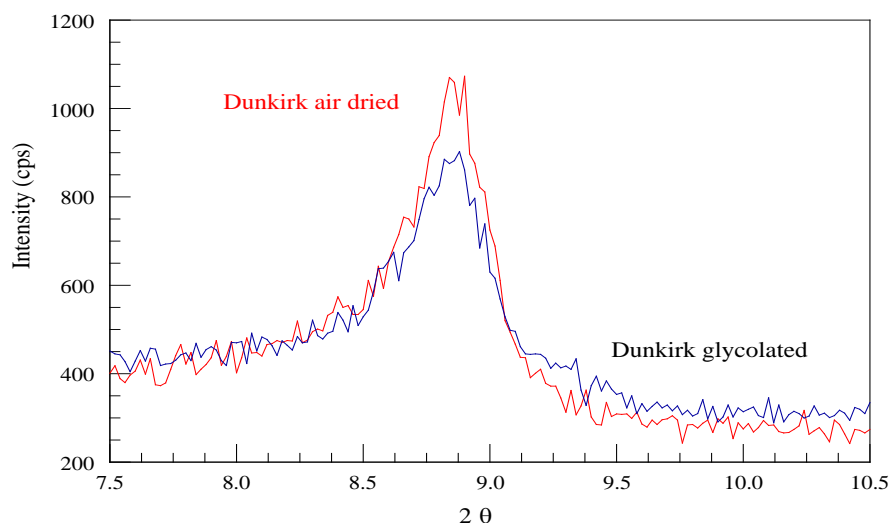


Figure 3: A comparison between the red line of an air dried oriented clay sample and the same sample after exposure to ethylene glycol vapor shown as the black line. The ethylene glycol causes any smectite layers in the illite to expand resulting in a shift of the clay peak to larger d-spacings (smaller 2 θ values). The clay sample is from the Dunkirk formation.

All the clay fraction samples had Kübler indexes that fall into the range of epizone/anchizone boundary. Most of the samples fall in the 0.24-0.29 range. Results of the Kübler analysis are presented in the Figure 5 below. Silver creek location represents the Pipe creek Formation. Finger Lakes trail, Mills and Zoar Valley samples represent the Hume Formation, and the other localities represent the Dunkirk Formation. KI values between 0.42-0.36 represent diagenesis, 0.36-0.24 anchizone/epizone transition and lower than 0.24 represents epizone.

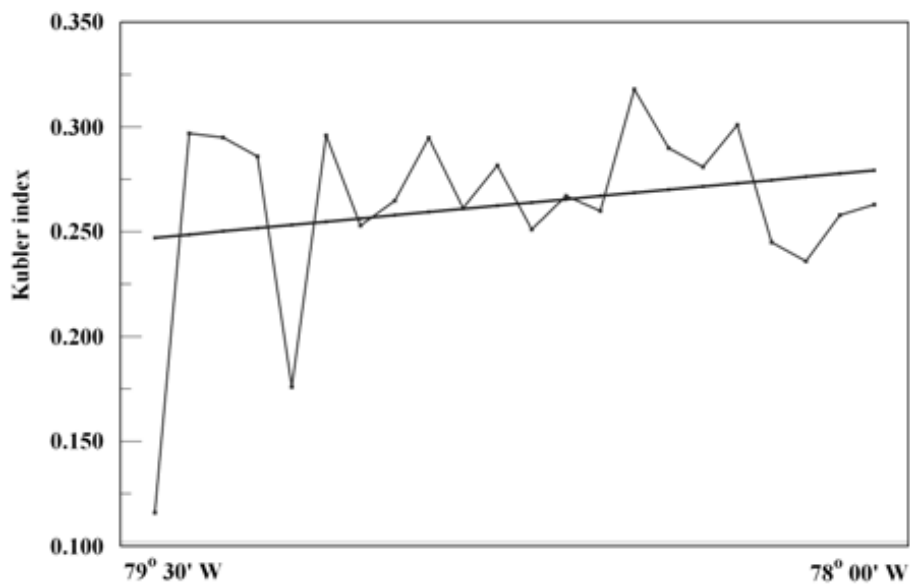


Figure 5: An east-west profile showing a modest trend in the Kübler index for Dunkirk shale samples.

Section 5

DISCUSSION

The presence of 2M1 illite and chlorite along with the absence of smectites implies that the I/S diagenesis was completed. If one considers Howers' theory that the small amounts of feldspars, especially intermediate microcline which contains potassium, can be explained by the smectite to illite transformation. This would be the case because the K bearing feldspar would be used during illitization of smectites. Boles' and Franks' theory states that the cannibalization of smectites is followed by the formation of large amounts of quartz. That is also the case for Dunkirk and Hume samples (Table 2).

Mineral present	M1	M2	M3	G1	G2	GD1	GD2
Quartz	26.6	23.7	18.2	29.9	30.5	26.9	28.9
Intermediate Microcline feldspar	4.8	3.7	3.6	2.7	2.6	2.3	3.3
Albite feldspar (Cleavelandite)	4.7	2.2	1.3	2.8	3.4	2.6	3.8
Calcite	2.9	13.4	22.7	2.8	2.9	0.4	1.9
Dolomite	1.2	1.5	1.0	0.9	0.9		
Disordered Kaolinite	2.7	4.0	2.3	0.7	1.5	3.5	3.1
2M1 illite (SG4)	30.5	30.2	26.6	33.5	32.5	35.8	32.7
Chlorite Tusc	7.3	7.9	9.0	11.9	12.0	17.2	14.9
Pyrite	6.0	5.2	3.2	2.1	2.1	1.4	1.5
Marcasite	0.9						
TOTAL	89.57	91.8	87.80	87.26	88.53	90.07	90.06

Table 2: The mineral composition of the Marcellus and Genesee shale samples as determined by the RockJock® software.

Mineral present	D1	D2	D3	D4	D5	D6	D7	D8	D9
Quartz	25.2	45.6	45.7	43.4	42.8	45.6	42.9	45.2	37.3
Intermediate Microcline feldspar	1.9	2.9	2.8	2.3	2.8	2.1	2.6	2.9	3.1
Orthoclase feldspar			0.2						
Albite feldspar (Cleavelandite)	1.9	4.4	4.1	3.9	3.7	3.3	3.5	4.0	2.8
Calcite				0.3					0.1
Dolomite		0.6	0.5	1.0	0.3				0.2
Disordered Kaolinite	4.8	2.8	2.5	3.0	2.4	2.8	2.5	3.0	2.3
2M1 illite (SG4)	44.8	22.7	23.9	24.5	25.9	28.9	26.3	25.3	27.3
Chlorite CCa-1				1.5	0.9		1.7	1.0	
Chlorite CCM					2.3			3.0	
Chlorite CO			8.1						
Chlorite Tusc	13.2		5.7	6.5	4.5	7.2	5.0	2.5	9.7
Mg-Chlorite (Cinocllore)		1.2	4.3		0.9	5.2	1.3		
Pyrite	3.5	2.3	1.9	1.8	3.7	2.5	4.7	1.7	2.7
Marcasite			1.2	1.1	1.1	1.0	1.0	1.0	1.0
TOTAL	95.36	82.38	100.97	89.33	91.35	98.42	91.66	89.68	86.6

Table 2 cont.: The mineral composition of the Dunkirk samples as determined by the RockJock® software.

Mineral present	D10	D11	D12	D13	D14	D15	PC1	D16	D17
Quartz	41.2	39.8	47.1	42.6	41.4	39.1	26.5	47.9	40.5
Intermediate Microcline feldspar	2.1	3.3	1.9	2.8	2.8	2.5	1.9	3.9	2.6
Orthoclase feldspar							1.5		
Albite feldspar (Cleavelandite)	3.1	3.1	3.9	3.6	3.4	4.0	1.8	4.5	5.2
Calcite	0.1			0.2	0.1				
Dolomite	0.1				0.1				
Disordered Kaolinite	2.7	2.1	2.9	2.0	3.0	3.5	3.2	3.8	4.8
2M1 illite (SG4)	31.0	28.6	26.6	31.7	30.7	30.0	29.5	30.3	32.6
Chlorite CCa-1						2.2			1.6
Chlorite CCM						2.5	3.1	0.8	4.0
Chlorite Tusc	10.1	9.0	9.9	10.7	10.3	4.0	3.7	6.9	5.2
Mg-Chlorite (Cinocllore)							4.2	3.5	0.6
Pyrite	2.8	2.1	1.8	1.9	2.0	1.8	2.6	1.3	2.2
Marcasite	1.0	1.1	0.6	0.7	1.0	1.1	0.9	0.7	0.8
TOTAL	94.2	89.1	94.8	96.3	94.9	90.74	78.99	103.60	100.0

Table 2 cont.: The mineral composition of Dunkirk shale samples (cont.).

Mineral present	D18	D19	D20	D21	D22	H1	H2	H3	H4	A1
Quartz	50.1	42.1	28.8	39.3	43.7	50.4	53.6	35.4	41.0	36.1
Intermediate Microcline feldspar	2.4	1.7	2.3	2.1	2.2	1.2	2.0	2.1	2.4	1.9
Albite feldspar (Cleavelandite)	5.3	3.3	2.9	4.6	5.0	7.8	7.8	4.4	5.2	4.4
Disordered Kaolinite	3.5	3.1	1.2	2.1	3.9	7.2	3.3	4.0	3.7	5.0
2M1 illite (SG4)	22.9	34.6	31.1	29.5	27.2	21.0	19.7	36.3	26.4	44.9
Chlorite CCa-1									3.0	
Chlorite CCM						4.2		5.4		8.4
Chlorite CO										
Chlorite Tusc	9.5	13.0	13.3	13.0	11.7	5.1	11.7	6.7	6.9	7.7
Mg-Chlorite (Cinocllore)						3.1	1.8	2.1		
Pyrite	2.1	2.6	4.9	2.7	1.7	1.7	0.7	2.3	2.0	0.6
Marcasite			0.4	0.6	0.6			0.9	0.4	
Holite										0.9
Jarosite										1.6
TOTAL	95.7	100.3	84.9	94.0	96.0	101.9	100.5	99.57	91.0	111.49

Table 2 cont.: Mineral composition of Dunkirk shale samples (cont.) along with samples from the Hume formation.

In either theory, (Hower, 1976 and Boles and Franks, 1979) temperature is needed for the transformation of smectite to illite to take place. Burial depths and temperatures were determined based on the conodont alteration index (CAI) by Weary et al. Weary et al. determined the CAI for Western and Central New York to be between 2 and 3.5. They have also stated that these values are within the range of thermal maturity indices cited for the “window” of oil and natural gas generation and preservation. The burial depths determined by Weary et al. were from 1.8 to 2.4 km assuming the geothermal gradient 20° to

30° C/km the burial temperatures should not exceed 100° C. However, the CAI indicates much higher temperatures than those from the overburden pressure, (Weary et al). Absence of smectite and the presence of 2M1 illite imply that burial temperatures exceeded 360° C. This was also confirmed by KI analysis. Most of the samples fall in the 0.24-0.3, which represents the transition from anchizone to epizone. However, most of the KI values are closer to the epizone boundary (Table 3). Figure 5 shows the trend in the Kübler indices throughout the sampling area from west to east. It can be seen that the thermal maturity decreases eastward as the Kübler indices increase. Consequently, the samples in the westernmost part of the sampling area have experienced the highest temperatures.

<u>Sample</u>	<u>KI</u>	<u>Low Metamorphic Zone</u>
Clarksburg	0.290	Anchizone/Epizone
Point Gratiot	0.116	Epizone
Point Gratiot	0.297	Anchizone/Epizone
Point Gratiot	0.295	Anchizone/Epizone
Point Gratiot	0.286	Anchizone/Epizone
Point Gratiot	0.176	Epizone
Point Gratiot	0.296	Anchizone/Epizone
Point Gratiot	0.253	Anchizone/Epizone
Point Gratiot	0.265	Anchizone/Epizone
Point Gratiot	0.295	Anchizone/Epizone
Point Gratiot	0.261	Anchizone/Epizone
Point Gratiot	0.282	Anchizone/Epizone
Point Gratiot	0.251	Anchizone/Epizone
Point Gratiot	0.267	Anchizone/Epizone
Beil Property	0.263	Anchizone/Epizone
219 S	0.281	Anchizone/Epizone
219 N	0.301	Anchizone/Epizone
Lake Erie State Park	0.260	Anchizone/Epizone
Walnut creek	0.318	Anchizone/Epizone
Varisburg	0.236	Anchizone/Epizone
Varisburg	0.258	Anchizone/Epizone
Beaver/Meadow creek	0.245	Anchizone/Epizone
Silver creek	0.303	Anchizone/Epizone
Finger Lakes trail ash layer	0.239	Anchizone/Epizone
Finger Lakes trail	0.309	Anchizone/Epizone
Mills Mills	0.269	Anchizone/Epizone
Zoar Valley	0.290	Anchizone/Epizone

Table 3: Kübler Index values for samples from the Dunkirk and Hume formations. The Silver Creek sample is from the Pipe Creek Formation.

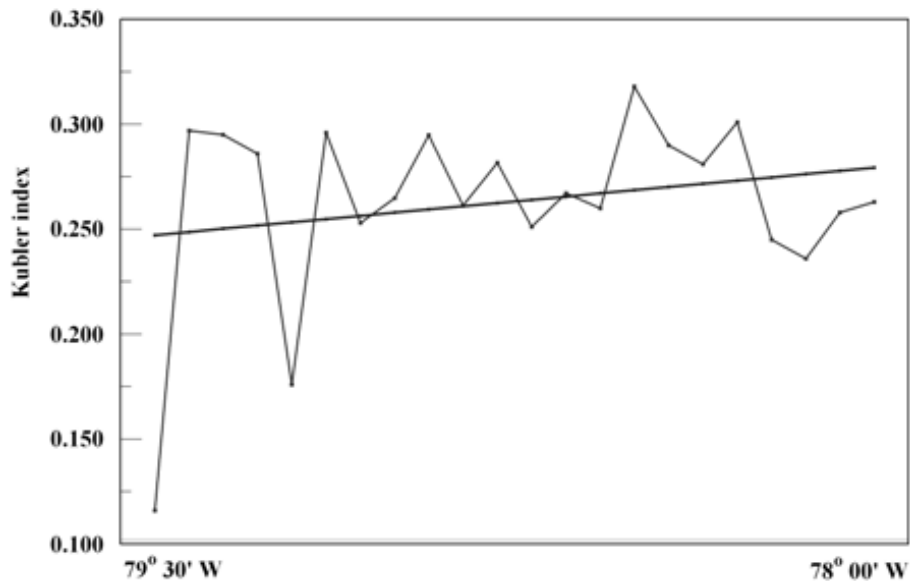


Figure 5: An east-west profile showing a modest trend in the Kübler index for Dunkirk shale samples.

The percent of TOC varies between 0.3 and 4.8 percent (Figure 6). The sample with the smallest amount of organic matter was collected from the ash layer in the Sixtown Creek. Two samples that fall into the epizone were sampled along the fractures at the Point Gratiot Beach. This suggests that there might be a relationship between the distribution of fractures and organic matter. In the Dunkirk Formation, the amount of TOC decreases southwards. The amount of the illite is highest in the Cattaraugus County and it decreases in the Alleghany and the Chautauqua County. If we assume that the parent sediment of the Dunkirk Formation contained roughly the same quantity of organic matter at the moment of burial and that the smectite clay was the repository of this organic matter, then there should be a relation between the amount of illite formed and the TOC. Figure 6 shows what appears to be such an inverse relationship between the percents of illite and TOC.

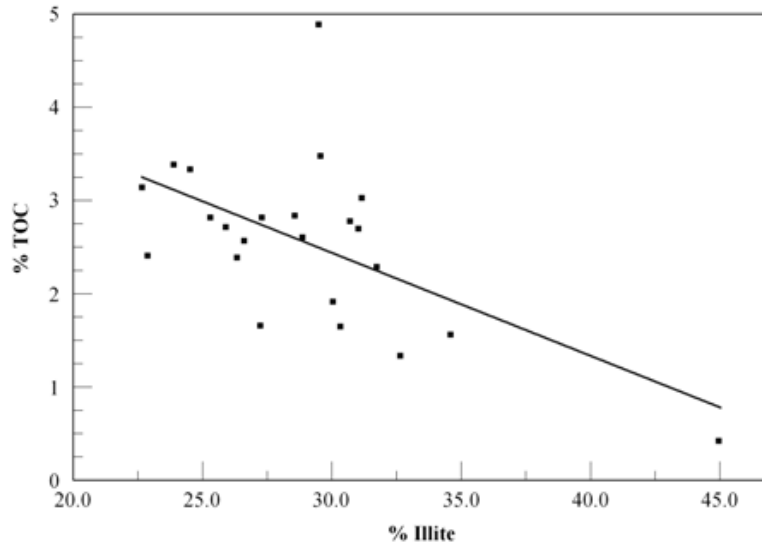


Figure 6: A regression line fitted to the TOC and weight percent of illite in the shale samples of this study.

If such a relation is real, then a mineralogical analysis such as reported here might be a useful exploration tool for natural gas deposits in black shales.

Section 6

CONCLUSIONS

Absence of smectites and presence of 2M1 illite polytype tells us that the diagenesis of smectite to illite was completed. This implies temperatures higher than 360°C. Kübler analysis yields epizone/anchizone boundary for most samples. The range of temperatures for this boundary is 280-360°C.

There seems to be an inverse relationship between the distributions of the TOC and the illite. However, it is essential to collect more data especially from the mid section of the sampling area to prove that relationship. Another factor that seems to control the distribution of TOC are fractures. It appears that samples that were closest to the fracture planes experienced the highest temperatures. The reason for this could be the migration of hydrothermal fluids through fractures. However, to prove this more data has to be acquired.

Based on the illite/smectite diagenesis, burial temperature, and Kübler index Dunkirk and Hume can be interpreted as source rocks; moreover, they could be suitable exploration targets.

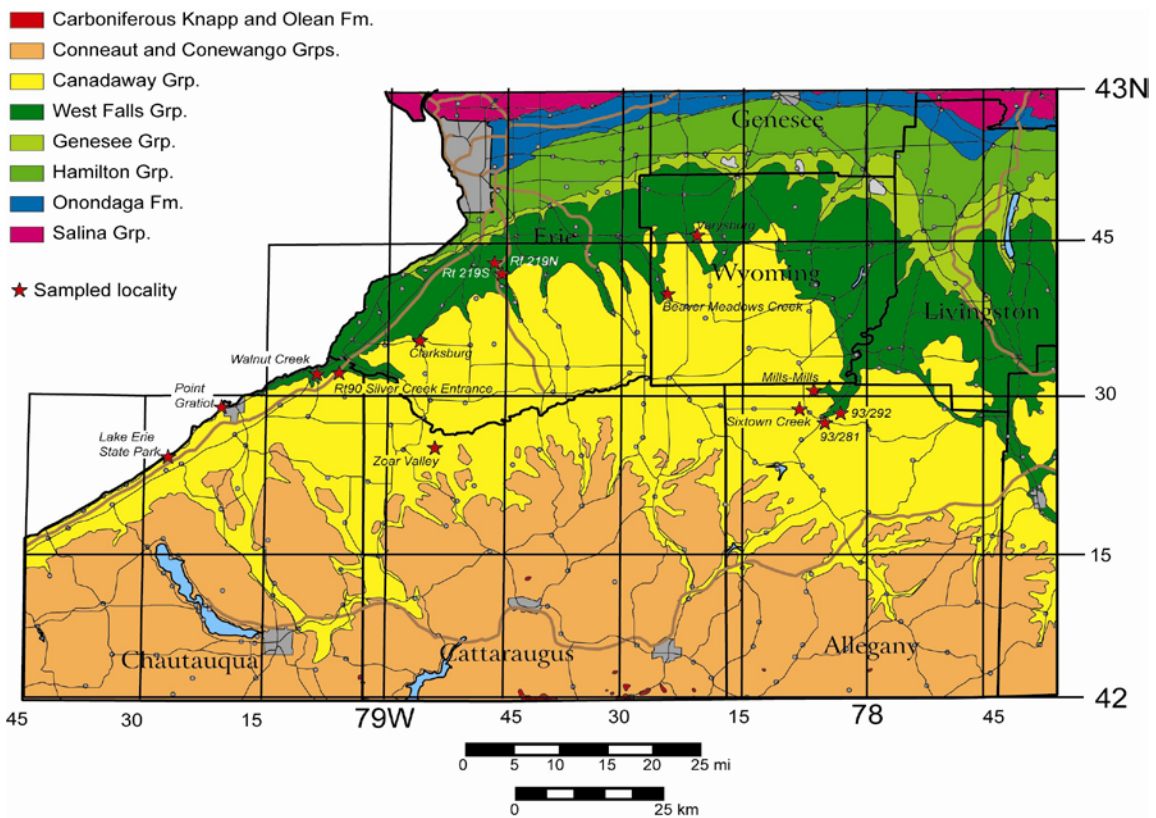


Figure 1: The sampling locations and geology of the study area (Smith, 2003).

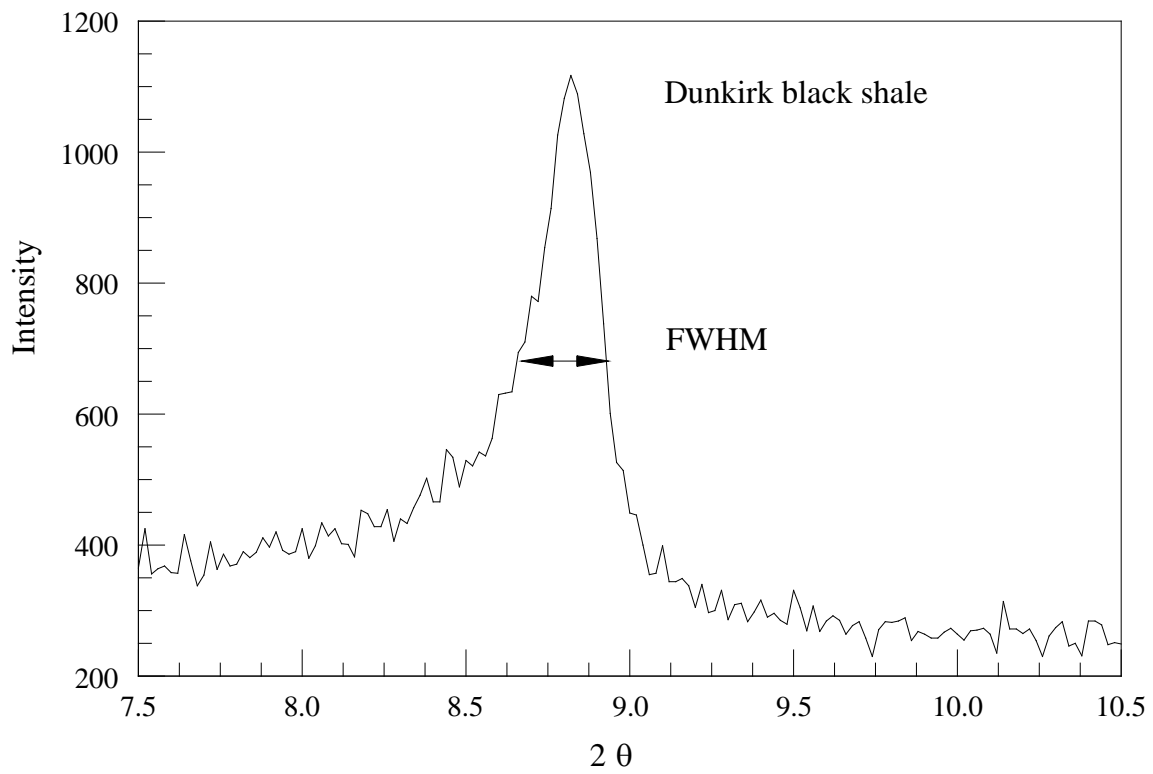


Figure 2: The double arrow indicates the measurement of the full width at half maximum (FWHM) for the 001 reflection of illite.

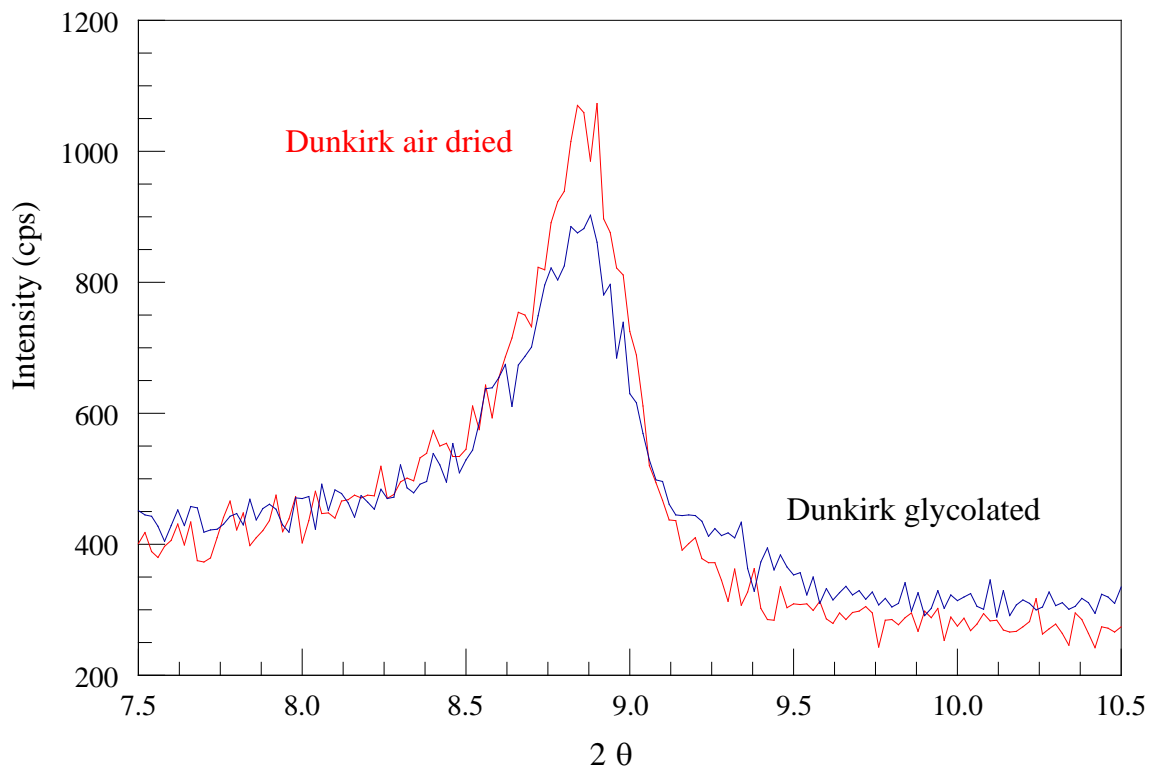


Figure 3: A comparison between the red line of an air dried oriented clay sample and the same sample after exposure to ethylene glycol vapor shown as the black line. The ethylene glycol causes any smectite layers in the illite to expand resulting in a shift of the clay peak to larger d-spacings (smaller 2 θ values). The clay sample is from the Dunkirk formation.

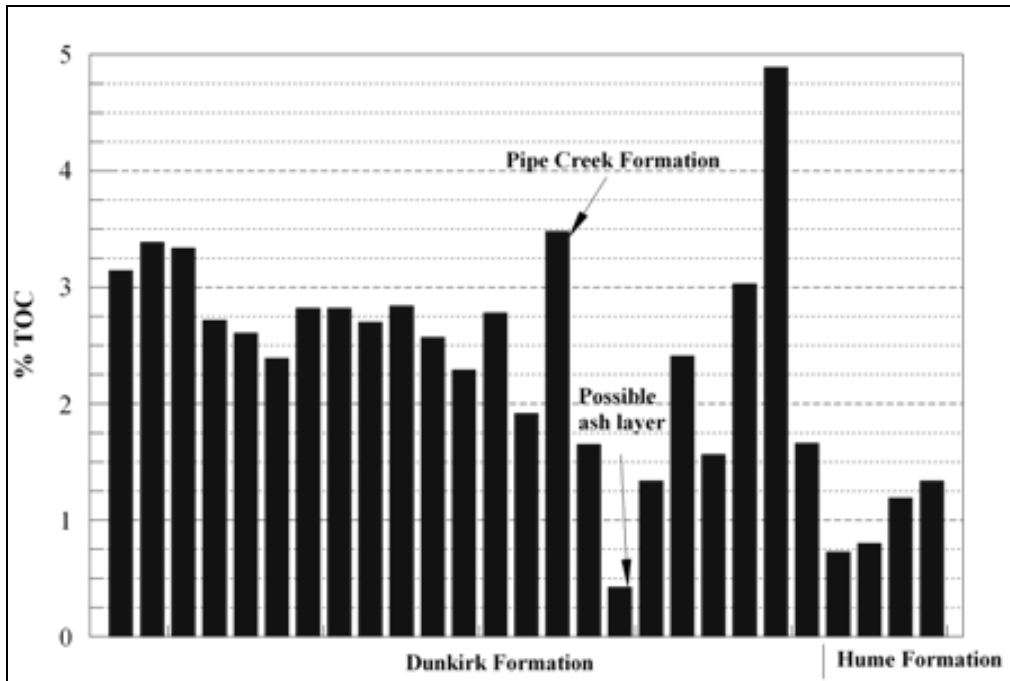


Figure 4: The variation of TOC among the samples from the Dunkirk, Pipe Creek and Hume formations.

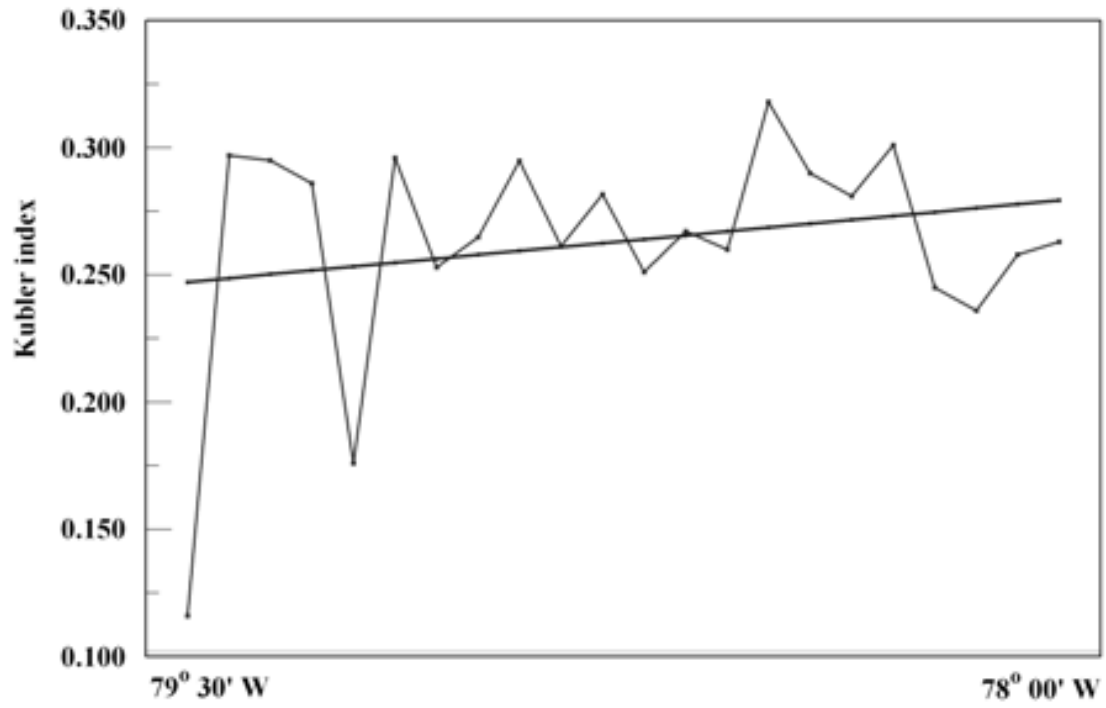


Figure 5: An east-west profile showing a modest trend in the Kübler index for Dunkirk shale samples.

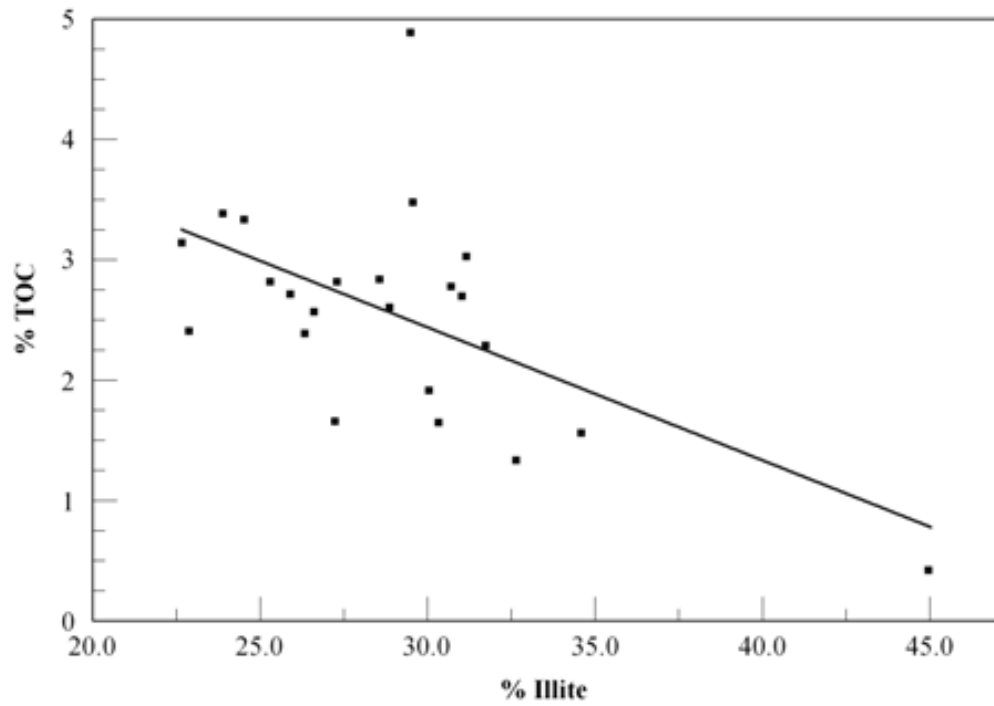


Figure 6: A regression line fitted to the TOC and weight percent of illite in the shale samples of this study.

Site	Location	Outcrop	USGS Topo Quad
South Branch of Eighteenmile Creek	Clarksburg, NY, along New Oregon Rd., and also the intersection of New Oregon Rd. and Rt. 75	Dunkirk Fm.	Langford and Hamburg
Point Gratiot	Point Gratiot Park, Dunkirk NY, Off Rt 5, sampled along lake shore cliffs	Dunkirk Fm.	Dunkirk
Lake Erie State Park	Lake Erie State Park, Off Rt. 5, 3.2 km north of Brocton NY	Dunkirk Fm.	Brocton
Walnut Creek	Main St, Silver Creek, NY. Outcrop forms cliffs along eastern bank of Walnut Creek	Pipe Creek Fm.	Silver Creek
Interstate 90 On Ramp	Silver Creek, NY, On ramp to Interstate from Silver Creek	Dunkirk Fm.	Silver Creek
219 South	Boston, NY Roadcut on west side, 1.3 km south of Mayer Rd.	Dunkirk Fm.	Hamburg
219 North	Boston, NY, prior to Boston exit ramp, Roadcut on east side, 0.7 km north of Eiss Rd.	Dunkirk Fm.	Hamburg
Sixtown Creek	West of Rt 19, where the Finger Lakes Trail crosses Buffalo Rd.	Hume	Houghton
Mills-Mills	Small south flowing tributary to Wiscoy Creek, west of Mills-Mills Rd.	Hume	Portageville
Ballard Rd, North	First west flowing tributary to the Genesee River, south of Knibloe Rd.	Dunkirk Fm.	Fillmore
Beil's Farm (Ballard Rd South)	First northwest flowing tributary to the Genesee River, south of Snyder Hill/Bottsford Hollow Rd	Dunkirk Fm.	Fillmore
Zoar Valley	Confluence of the South Branch and Cattaraugus Creek. Outcrop along east side of creek.	Hume	Gowanda

Table 1: A summary of the localities where black shale samples were collected.

Mineral present	M1	M2	M3	G1	G2	GD1	GD2
Quartz	26.6	23.7	18.2	29.9	30.5	26.9	28.9
Intermediate Microcline feldspar	4.8	3.7	3.6	2.7	2.6	2.3	3.3
Albite feldspar (Cleavelandite)	4.7	2.2	1.3	2.8	3.4	2.6	3.8
Calcite	2.9	13.4	22.7	2.8	2.9	0.4	1.9
Dolomite	1.2	1.5	1.0	0.9	0.9		
Disordered Kaolinite	2.7	4.0	2.3	0.7	1.5	3.5	3.1
2M1 illite (SG4)	30.5	30.2	26.6	33.5	32.5	35.8	32.7
Chlorite Tusc	7.3	7.9	9.0	11.9	12.0	17.2	14.9
Pyrite	8.0	5.2	3.2	2.1	2.1	1.4	1.5
Marcasite	0.9						
TOTAL	89.57	91.8	87.80	87.26	88.53	90.07	90.06

Table 2: The mineral composition of the Marcellus and Geneseo shale samples as determined by the RockJock® software.

Mineral present	D1	D2	D3	D4	D5	D6	D7	D8	D9
Quartz	25.2	45.6	45.7	43.4	42.8	45.6	42.9	45.2	37.3
Intermediate Microcline feldspar	1.9	2.9	2.8	2.3	2.8	2.1	2.6	2.9	3.1
Orthoclase feldspar			0.2						
Albite feldspar (Cleavelandite)	1.9	4.4	4.1	3.9	3.7	3.3	3.5	4.0	2.8
Calcite				0.3					0.1
Dolomite		0.6	0.5	1.0	0.3				0.2
Disordered Kaolinite	4.8	2.8	2.5	3.0	2.4	2.8	2.5	3.0	2.3
2M1 illite (SG4)	44.8	22.7	23.9	24.5	25.9	28.9	26.3	25.3	27.3
Chlorite CCa-1				1.5	0.9		1.7	1.0	
Chlorite CCM					2.3			3.0	
Chlorite CO			8.1						
Chlorite Tusc	13.2		5.7	6.5	4.5	7.2	5.0	2.5	9.7
Mg-Chlorite (Cinocllore)		1.2	4.3		0.9	5.2	1.3		
Pyrite	3.5	2.3	1.9	1.8	3.7	2.5	4.7	1.7	2.7
Marcasite			1.2	1.1	1.1	1.0	1.0	1.0	1.0
TOTAL	95.36	82.38	100.97	89.33	91.35	98.42	91.66	89.68	86.6

Table 2 cont.: The mineral composition of the Dunkirk samples as determined by the RockJock® software.

Mineral present	D10	D11	D12	D13	D14	D15	PC1	D16	D17
Quartz	41.2	39.8	47.1	42.6	41.4	39.1	26.5	47.9	40.5
Intermediate Microcline feldspar	2.1	3.3	1.9	2.8	2.8	2.5	1.9	3.9	2.6
Orthoclase feldspar							1.5		
Albite feldspar (Cleavelandite)	3.1	3.1	3.9	3.6	3.4	4.0	1.8	4.5	5.2
Calcite	0.1			0.2	0.1				
Dolomite	0.1				0.1				
Disordered Kaolinite	2.7	2.1	2.9	2.0	3.0	3.5	3.2	3.8	4.8
2M1 illite (SG4)	31.0	28.6	26.6	31.7	30.7	30.0	29.5	30.3	32.6
Chlorite CCa-1						2.2			1.6
Chlorite CCM						2.5	3.1	0.8	4.0
Chlorite Tusc	10.1	9.0	9.9	10.7	10.3	4.0	3.7	6.9	5.2
Mg-Chlorite (Clinochlore)							4.2	3.5	0.6
Pyrite	2.8	2.1	1.8	1.9	2.0	1.8	2.6	1.3	2.2
Marcasite	1.0	1.1	0.6	0.7	1.0	1.1	0.9	0.7	0.8
TOTAL	94.2	89.1	94.8	96.3	94.9	90.74	78.99	103.60	100.0

Table 2 cont.: The mineral composition of Dunkirk shale samples (cont.).

Mineral present	D18	D19	D20	D21	D22	H1	H2	H3	H4	A1
Quartz	50.1	42.1	28.8	39.3	43.7	50.4	53.6	35.4	41.0	36.1
Intermediate Microcline feldspar	2.4	1.7	2.3	2.1	2.2	1.2	2.0	2.1	2.4	1.9
Albite feldspar (Cleavelandite)	5.3	3.3	2.9	4.6	5.0	7.8	7.8	4.4	5.2	4.4
Disordered Kaolinite	3.5	3.1	1.2	2.1	3.9	7.2	3.3	4.0	3.7	5.0
2M1 illite (SG4)	22.9	34.6	31.1	29.5	27.2	21.0	19.7	36.3	26.4	44.9
Chlorite CCa-1									3.0	
Chlorite CCM						4.2		5.4		8.4
Chlorite CO										
Chlorite Tusc	9.5	13.0	13.3	13.0	11.7	5.1	11.7	6.7	6.9	7.7
Mg-Chlorite (Clinochlore)						3.1	1.8	2.1		
Pyrite	2.1	2.6	4.9	2.7	1.7	1.7	0.7	2.3	2.0	0.6
Marcasite			0.4	0.6	0.6			0.9	0.4	
Halite										0.9
Jarosite										1.6
TOTAL	95.7	100.3	84.9	94.0	96.0	101.9	100.5	99.57	91.0	111.49

Table 2 cont.: Mineral composition of Dunkirk shale samples (cont.) along with samples from the Hume formation.

<u>Sample</u>	<u>KI</u>	<u>Low Metamorphic Zone</u>
Clarksburg	0.290	Anchizone/Epizone
Point Gratiot	0.116	Epizone
Point Gratiot	0.297	Anchizone/Epizone
Point Gratiot	0.295	Anchizone/Epizone
Point Gratiot	0.286	Anchizone/Epizone
Point Gratiot	0.176	Epizone
Point Gratiot	0.296	Anchizone/Epizone
Point Gratiot	0.253	Anchizone/Epizone
Point Gratiot	0.265	Anchizone/Epizone
Point Gratiot	0.295	Anchizone/Epizone
Point Gratiot	0.261	Anchizone/Epizone
Point Gratiot	0.282	Anchizone/Epizone
Point Gratiot	0.251	Anchizone/Epizone
Point Gratiot	0.267	Anchizone/Epizone
Beil Property	0.263	Anchizone/Epizone
219 S	0.281	Anchizone/Epizone
219 N	0.301	Anchizone/Epizone
Lake Erie State Park	0.260	Anchizone/Epizone
Walnut creek	0.318	Anchizone/Epizone
Varisburg	0.236	Anchizone/Epizone
Varisburg	0.258	Anchizone/Epizone
Beaver/Meadow creek	0.245	Anchizone/Epizone
Silver creek	0.303	Anchizone/Epizone
Finger Lakes trail ash layer	0.239	Anchizone/Epizone
Finger Lakes trail	0.309	Anchizone/Epizone
Mills Mills	0.269	Anchizone/Epizone
Zoar Valley	0.290	Anchizone/Epizone

Table 3: Kübler Index values for samples from the Dunkirk and Hume formations. The Silver Creek sample is from the Pipe Creek Formation.