APPLICATION OF SPECIALIZED SURFACE GEOCHEMICAL TESTING TO DEFINE PRODUCTIVE AND FAULTED AREAS RELATED TO HYDROTHERMAL DOLOMITE GAS PRODUCTION IN THE APPALACHIAN BASIN OF NEW YORK

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Abstract and Key Words

Hydrocarbon microseepage from commercial Black River reservoirs helps to pre-screen large areas to focus leasing, seismic and drilling activities. Variables that distinguish gas and dry reservoirs are ethene, isobutane, isopentane, methane and propane. The lack of dryness ratio (C1/C2) and %propane anomalies in soils over some fields might reflect the presence of deep faults that carry heavier hydrocarbons and metals to surface and/or drops in reservoir pressure related to production and breaching by deep faults.

Major faults that extend into the basement may intersect and possibly hinder production from dolomite reservoirs by altering the quality of the reservoir seal. Indications of these faults are anomalous ethane/ethene ratios relative to methane, Ca, Mg, Sr, Pb, Zn and Tl in soils.

Key Words: Surface geochemistry, hydrothermal dolomites, exploration geochemistry, trace metals, hydrocarbons

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TABLE OF CONTENTS

Section	Page
SUMMARY	vii
INTRODUCTION	1
OBJECTIVES	2
DESIGN PRINCIPLES	4
DATA ACQUISITION	7
RESULTS OF THE GEOCHEMICAL SURVEY	8
CONCLUSIONS	10
APPLICATION OF RESULTS TO EXPLORATION IN NEW YORK	15
TECHNOLOGY TRANSFER	15
BIBLIOGRAPHY	17

LIST OF FIGURES

Figure 1	Model of hydrocarbon microseepage	5
Figure 2	Map of study area	5
Figure 3	Example Soil Profile	6
Figure 4	Quackenbush Probability with C1/C2 Ratio	12
Figure 5	Ethene and iC4-iC5 Factor Scores	12
Figure 6	Percent Propane	13
Figure 7	Ethane/Ethene Ratio and Lead	13
Figure 8	Ethane/Ethene Ratio and Calcium	14
Figure 9	Ethane/Ethene Ratio and Magnesium	14

LIST OF TABLES

Table 1	Produced gas composition from Wilson Hollow Field	6
Table 2	Hydrocarbon and elemental anomalies identified in the study area	9

SUMMARY

Hydrocarbon gas anomaly signatures are associated with all of the known producing areas in the study area, however, the signature appears to vary from weak production to strong production. Strong production exhibits a recognizable signature that can be used for reconnaissance and development exploration purposes. All of the hydrocarbons present in the soils over Black River gas reservoirs are also in the produced gas. The ethane-iC4-iC5 association is noted in soils above all gas fields, but the dryness ratio (C1/C2) and percent propane are more anomalous over Quackenbush, Cutler Creek and the new SRA3 #1 discovery.

Linear metal-hydrocarbon anomalies are clearly associated with recognized deep faults that cross portions of the study area. There are additional linear metal-hydrocarbon anomalies that could be associated with un-mapped deep faults that intersect Black River reservoirs. Evidence that supports the occurrence of these anomalies along deep faults are:

(1) Anomalous ethane/ethene ratios relative to methane suggests rapid ascent of a heavier hydrocarbon to surface along faults such that there is insufficient time for oxidation to ethene. In unfaulted areas, where microseepage of ethane is slower, there is abundant ethene in the soils (i.e. over Quackenbush).

(2) The MVT element association (Ca, Mg, Sr, Pb, Zn, Tl) suggests that the Black River hydrothermal dolomite reservoir has been tapped by a deep fault. There are no dolomites or apparent metalliferous assemblages at surface or in the overlying stratigraphic section to derive such a mineral assemblage.

None of the most productive fields in the area (e.g., Quackenbush) appear to be dissected by these types of deep faults, possibly implying that the best reservoirs have not been breached by leaky faults (based on surface lineaments and geochemical data). Wilson Hollow, Terry Hill South, and County Line have been breached by deep faults along which heavier hydrocarbons can ascend rapidly. This would explain the heavier hydrocarbons and metals over these fields as opposed to Quackenbush, Cutler Creek and the new discovery that have not been breached by deep faults.

Section 1

INTRODUCTION

The deep Black River gas play in central New York is fast becoming a significant exploration and production trend, particularly for operators like Fortuna Energy, Inc., which is now producing over 100 million cubic feet of gas per day from several new Black River fields. Direct Geochemical has conducted a number of surface geochemical studies around North America in areas of hydrothermal dolomite development and has observed geochemical trends and characteristics that suggest that its use as an exploration tool would be successful. Direct Geochemical had completed successful reconnaissance demonstration projects during 1998-99 and 2000-2001 under NYSERDA's sponsorship, using the Stagecoach Field (1998-99) and Glodes Corner (Trenton) and Genegantslet (Devonian) in 2000 & 2001. The Stagecoach project focused on a single field and play type but experimented with three independent sampling and analytical combinations of light hydrocarbons for the geochemistry. As a result, there was a great deal of data for evaluation, and a preferred suite of light hydrocarbons and sampling method were identified, but the resulting product was not particularly user friendly, nor were a variety of technical issues firmly addressed for future users with other, unrelated prospects and plays in mind. The results of the Stagecoach study have been well received at conferences, and through our subsequent article in the Oil and Gas Journal in September 2000.

The Glodes Corner/Genegantslet study had a different objective: take the preferred sampling and light hydrocarbon analytical technique and apply it to two different gas objectives, in an effort to demonstrate the wider applicability of the method to different geologic and geochemical play types. The results of these studies also have received wide acceptance, including two articles in the Oil and Gas Journal during 2002. Following the completion of the Glodes Corner/Genegantslet study, Direct Geochemical applied some additional testing to stored samples collected during the project and retained after meeting the obligations to NYSERDA, including the trace metals analysis. Profile data showed strong hydrocarbon anomaly data near the fault boundaries of the graben, along with trace metal anomalies. In addition, redox and other metals data supported the hydrocarbon anomaly showing the distribution of subsurface gas deposition.

Subsequently, Direct also conducted a fairly detailed survey over the Grant Canyon/Bacon Flat fields in south central Nevada. Grant Canyon exhibits strong HTD characteristics, as the reservoir is a Devonian carbonate. This survey showed strong MVT mineral assemblages, a magnesium anomaly over the most strongly dolomitized portion of the field and some spikes of metals in the vicinity of major faults. In addition, it showed a relatively strong heavy (oil) hydrocarbon anomaly over the field, even though it is very much depleted and operating under reduced pressures.

The data on these hydrothermal-related oil and gas fields suggest that at least two types of anomalies are present:

- An apical hydrocarbon anomaly that overlies the subsurface accumulation of gas or oil
- Anomalies of hydrocarbons, trace metals, and other parameters that reflect the existence of subsurface structural features, e.g., faults and fractures, that connect to deep-seated reservoirs, mineralization processes and fluid flows

The exact ramifications of the latter anomalies are still not well understood, but give hope that with additional testing at higher densities, may reveal more about geologic processes that are intrinsic to hydrocarbon emplacement and trapping. These findings formed a basis for designing the survey that is the subject of this report.

OBJECTIVES

The objectives of this present investigation fall into two categories:

- 1. Technological: understand better the hydrocarbon and trace metal relationships to the subsurface accumulations of hydrocarbons and geological process that affect such accumulations
- Regional: develop a detailed model/analog for Black River exploration and development in central New York and identify or high-grade prospective areas for drilling, and make the information available to industry on a user-friendly basis

Achieving these objectives will demonstrate the practical utility of surface geochemical methods in identifying key hydrocarbon location and structural geologic features that allow companies to minimize risk and maximize the use of exploration resources.

Background Behind Geochemical Exploration For Petroleum

The premise behind surface geochemical exploration for petroleum is that light hydrocarbons (i.e. C1-C5) ascend rapidly to the surface from a pressured reservoir as buoyant colloidal-size "microbubbles" along water-filled fractures, joints and bedding planes (Saunders et al., 1999; Price, 1986). Studies over gasstorage reservoirs support the rapid development of soil-gas hydrocarbon anomalies over a charged reservoir, and the rapid depletion of such anomalies once the reservoir has been depleted (Coleman et al., 1977). Partial aerobic and anaerobic bacterial consumption of the ascending hydrocarbons produces carbon dioxide and hydrogen sulphide, which can significantly alter the chemical and mineralogical composition of overlying sediments (Schumacher, 1996). Changes to overlying sediments can include (1) adsorption of light hydrocarbons on clay particles or inclusion of hydrocarbons in secondary carbonate cements, (2)

development of soil bacteria anomalies and the development of "paraffin dirt", (2) precipitation of isotopically light calcite, pyrite, pyrrhotite, uranium, sulfur, and magnetic iron oxides, (3) bleaching of redbeds through the removal of Fe^{3+} by reduced groundwater, (4) conversion of illitic clays and feldspars to kaolinite by acidic, reduced groundwater, and (5) variations in the major and trace element chemistry of soil and vegetation. Chemical reactions that produce the various minerals found in "reduced chimneys" above petroleum reservoirs are shown in Figure 1.

Geochemical exploration for oil and gas reservoirs has been ongoing for over 70 years. The first soil gas survey was conducted in Germany in 1929 (Laubmeyer, 1933). In this study, Laubmeyer observed more total hydrocarbons (methane) in soil air over productive areas than over non-productive areas. The first reported soil gas work in the United States was by Rosaire (1938) and Horvitz (1939). Their research showed that there is a higher concentration of hydrocarbons adsorbed on soil particles than in soil air. Since these pioneering studies, geochemical exploration for petroleum has evolved into a very diversified science.

Direct methods, which involve the determination of hydrocarbon concentrations in near-surface soil and soil-air at parts per million (ppm) to parts per billion (ppb) levels have been used by many workers (Seneshen et al., 2004; Horvitz and Ma, 1988). Several case studies have documented either apical or halo hydrocarbon anomalies over existing oil and gas reservoirs.

Indirect methods involve the use of non-hydrocarbon pathfinders for exploration. There are several empirical studies that document changes in the near-surface environment related to hydrocarbon microseepage:

- (1) Variation of major and trace element levels in soil (Duchscherer, 1984),
- (2) Isotopically light calcite in rocks overlying petroleum reservoirs that form a shallow resistive zone over the Ashland gas field in southeastern Oklahoma (Oehler and Sternberg, 1984),
- (3) The formation of pyrite and other sulphides that have been observed in drill cuttings and indirectly by Controlled-source Audiofrequency Magnetotellurics and Induced Polarization surveys (Oehler and Sternberg, 1984),
- (4) The presence of magnetic iron oxides (high magnetic susceptibility) in rocks and sediments over petroleum reservoirs (McCabe et al., 1987),
- (5) Variation of major and trace element levels in vegetation (Klusman et al., 1992),

- (6) Soil bacteria anomalies (Riese and Michaels, 1991),
- (7) Non-hydrocarbon soil gas anomalies including CO₂, O₂, He and sulphur-species (Barianaga and Farwell, 1988),
- (8) Radiometric anomalies (Curry, 1984), and
- (9) Spectral anomalies that reflect the hydrocarbon-induced alteration zone (Peters, 1983).

DESIGN PRINCIPLES

Design principles are vital to the success of any field investigation in the exploration for natural resources. The design of the survey was based on experience in testing Black River and other HTD targets, geologic information, production information on fields in the vicinity, topography, and land ownership patterns.

Geology and Gas Production in the Study Area

Black River hydrothermal dolomite reservoirs in the study area range in depth from 9,000 to 10,000 feet. These narrow, east-northeast trending reservoirs reflect the channeling of hydrothermal fluids along zones of extension in Late Paleozoic time. Extension and dolomitization could have occurred along pre-existing faults during early Paleozoic rifting. The hydrocarbons were probably derived from interbedded Ordovician source rocks.

The reservoirs in the study area produce significant amounts of gas on an annual basis and production rates for individual wells vary from 0.4 to 19 mmcf/d (Figs. 2 and 3). As of 2002, the most productive fields were Wilson Hollow, Quackenbush Hill, Terry Hill South and Cutler Creek (Figure 1). Recent production data are unavailable, but apparently Quackenbush Hill is now outperforming the older Wilson Hollow and Terry Hill South Fields. The dry gas produced is uniform in composition between fields, and it consists mainly of methane with minor C_2 - C_5 hydrocarbons, CO_2 and N_2 (Table 1). The productive portions of the fields appear to be spatially limited, particularly in the north-south direction.



Figure 1. Possible model of hydrocarbon microseepage-related alteration over petroleum deposits (modified after Saunders et al., 1999)



<u>Figure 2</u>. Map which shows location of the study area and distribution of gas fields, wells, lineaments and soil sample locations. Production data for each field represents annual production for the year 2002. These data were obtained from the New York State Museum website.

Component	Mol%
Methane	97.97
Ethane	0.45
Propane	0.05
-Butane	0.15
N-Butane	0.13
-Pentane	0.02
N-Pentane	< 0.01
Hexanes+	< 0.02
Nitrogen	1.07
002	0.16

Table 1. Produced gas composition from the Rice 1301 well in the Wilson Hollow Field (Courtesy of

Sampling Medium

Soils were chosen as the preferred sample medium in the NYSERDA study because of uniform parent material in the area (99% basal till), ease of collection, ability to evaluate both alteration and hydrocarbon sorption over in soils over Black River gas fields, and minimal impact on landowners (Fig. 1). Samplers were careful to collect soils that are consistent in terms of color and texture. Suntan lotion was washed off hands prior to sampling to avoid zinc contamination in the samples. Zinc is an important pathfinder element associated with Mississippi Valley Type mineralization that is commonly associated with hydrothermal dolomite reservoirs. The soils were collected from 8 to 12"-depth with a tree-planting shovel and stored in teflon-sealed glass jars for transport to the laboratory. Sample site locations were recorded on a Garmin eTrex GPS and field notes were taken at each site.



<u>Figure 3</u>. Example of soil profile developed on basal till that overlies Upper Devonian shale along a creek bed in the new exploration area.

Sampling Density

One of the difficulties commonly encountered in geochemical surveys is that sample intervals are inadequate to resolve anomalies. The sample interval chosen is based on the size of the target such that two consecutive anomalies can be realized over the area of interest. For this study, a total of 1265 soils were collected over an area of approximately 500 km² at intervals of 100 to 500 m (Figure 2). Of the 1265 samples collected, 669 (53%) were along public roads that cross gas fields, 394 (31%) were from the new exploration area (blind test), 130 (10%) were samples around productive gas wells, and 72 (6%) were samples around dry wells.

Hundreds of landowners inhabit the region. Except for the blind test area, it was impossible to economically grid the area. Therefore, a modified grid based on the road network, was established. The sample lines ranged up to a couple of miles apart, but the samples were densely acquired along the lines. Roads mainly were north-south in orientation, however, several generally east-west roads were also sampled to provide additional contouring support.

Modeling/Orientation Sampling

The variation in current production led to an opportunity to evaluate the effects of productivity on geochemical signature. The initial thought was to focus on the variation in hydrocarbon signature—either compositionally or quantity—in order to determine if strongly pressured fields exhibited a different signature than more depleted, reduced pressure fields. One the data became available, the intent was to evaluate how apparent faulting and fracturing and mineralization at the surface reflected the variations in productivity. In addition, it was essential to sample extensively in areas of dry holes in order to establish what background signatures are apparent.

DATA ACQUISITION

Analytical Methods

Soils were dried at low temperature in a temperature-controlled oven to avoid altering mineralogy, which can increase variability in hydrocarbon and elemental concentrations. The samples were sieved to a finegrain size fraction through stainless steel screens and aliquots of sample were then weighed out for hydrocarbon, elemental, pH and conductivity analyses.

For hydrocarbon data, soils are thermally desorbed using a proprietary technique developed by Direct Geochemical. The desorbed gases are injected into a gas chromatograph with a flame ionization detector (GC-FID) for analysis of C_1 - C_6 hydrocarbons. Detection limits are at low parts per billion levels.

For the elemental analysis, the sieved soil is digested in concentrated nitric acid and the supernatant is then filtered and analyzed for 26 major and trace elements by Inductively Coupled Plasma Emission

Spectroscopy (ICP-ES). The pH and conductivity of a 1:1 soil slurry was estimated with probes and pH and conductivity meters. Internal standards, duplicates and blanks are analyzed within batches as quality control checks. The precision of the hydrocarbon, elemental, pH and conductivity analyses is better than +/-10% at the 95% confidence level.

Interpretation and Mapping

Multivariate statistical techniques were applied to attempt to discriminate between productive and nonproductive areas using samples collected around gas and dry wells as a training set. These techniques measure the covariance of several variables in multidimensional space simultaneously. For example, several hydrocarbons may correlate over productive areas as opposed to dry areas allowing for the distinction between favorable and unfavorable exploration targets. Development of a discriminant model allows the classification of samples from an unknown area into "productive or non-productive" categories based on the probability of a sample belonging to either category. In addition to multivariate analysis, several hydrocarbon ratios were examined to evaluate the "dryness and wetness" of the seeping gases. Both the hydrocarbon and elemental data were converted to "Z-scores" to better assess anomaly contrast. These scores are calculated by subtraction of the sample mean from individual values and division by the sample standard deviation. The data are then reduced to a mean of zero, and anomalies are represented as standard deviations (1, 2, ...etc.) above the mean. The hydrocarbon, elemental, pH and conductivity data are displayed using unbiased computer contour and proportional symbol mapping techniques.

RESULTS OF THE GEOCHEMICAL SURVEY

The results of the study are very encouraging in that the shallow surface geochemical methods tested are capable of:

- (1) Outlining areas with high Black River gas potential.
- (2) Mapping faults that intersect and possibly breach gas reservoirs.

Four anomaly types have been recognized in the study area (Table 2). In general, there is more methane relative to ethane (C1/C2 ratio is a measure of gas dryness) in soils over Quackenbush Hill, Cutler Creek, and sporadic parts of Wilson Hollow, County Line, and Terry Hill South (Fig. 3). When Quackenbush gas probabilities are superimposed on the C1/C2 ratio there is significant correspondence (Fig. 3). A post-survey well (SRA3 #1) intersected significant gas production (19 mmcf/d) where anomalous gas probabilities are correlated with the dry gas ratio in the new exploration area (Fig. 3). In addition to the dryness ratio, other variables that contribute to the discrimination of gas and dry reservoirs are ethene, isobutane, isopentane and, to a lesser degree, propane. Factor scores show the spatial distribution of samples with a strong correlation between ethene, isobutane and isopentane in the study area. This hydrocarbon association is anomalous over all or parts of all gas fields in the study area (Fig. 4). Propane is particularly anomalous over the highly charged Quackenbush Field and around the new SRA3 #1 discovery

well (Fig. 5). Anomalously low dryness ratios are evident over mapped and inferred lineaments, particularly in the eastern half of the study area (Fig. 3).

Lead in soils, which can be an indicator of Mississippi Valley Type (MVT) mineralization, is antithetic with the C1/C2 ratio, but sympathetic with the ethane/ethene ratio (cf Figs. 5 and 6). Calcium and magnesium show similar anomaly patterns to that of lead, but they are not as widely dispersed (Figs. 7 and 8). Other variables that correlate with the Pb, Ca, Mg association are Sr, Zn, and Tl. This element association shows linear anomaly trends which, in some cases, are aligned with mapped lineaments.

	2002 Production	Ethene-	Dryness	%Propane	Ethane/ethene,
	(bcf)	iC4-iC5	Ratio	1	Ca, Mg, Sr, Pb,
			(C1/C2)		Zn, Tl
Quackenbush Hill	6.8	\checkmark	\checkmark	\checkmark	None
New Discovery	Not producing	\checkmark	\checkmark	\checkmark	None
(SRA3 #1)	yet				
Cutler Creek	1.1	\checkmark	\checkmark	\checkmark	None
Wilson Hollow	10.5	\checkmark	Sporadic	None	\checkmark
Terry Hill South	3.2	\checkmark	Sporadic	Sporadic	\checkmark
County Line	0.4	\checkmark	Sporadic	Sporadic	\checkmark

Table 2. Hydrocarbon and Elemental Anomalies Identified in the Study Area

Discussion of Results

Any discussion of the results of this study must take into account:

The linear heavier hydrocarbon/metal anomalies, which are aligned with known lineaments in places.

The variable hydrocarbon signature over fields that produce dry gas of identical composition.

The linear metal-hydrocarbon anomalies could be explained by deep faults that intersect Black River reservoirs. Evidence that supports the occurrence of these anomalies along deep faults are:

(1) Anomalous ethane/ethene ratios relative to methane suggests rapid ascent of a heavier hydrocarbon to surface along faults such that there is insufficient time for oxidation to ethene. In unfaulted areas, where microseepage of ethane is slower, there is abundant ethene in the soils (i.e. over Quackenbush).

(2) The MVT element association (Ca, Mg, Sr, Pb, Zn, Tl) suggests that the Black River hydrothermal dolomite reservoir has been tapped by a deep fault. There are no dolomites at surface or in overlying stratigraphic section to derive such a mineral assemblage.

An interesting observation to note is that the most productive fields in the area (i.e. Quackenbush) do not appear (based on surface lineaments) to be dissected by these types of deep faults, possibly implying that the best reservoirs have not been breached by leaky faults.

All of the hydrocarbons present in the soils over Black River gas reservoirs are also in the produced gas (Table 1). The ethane-iC4-iC5 association is noted in soils above all gas fields, but the dryness ratio (C1/C2) and percent propane are more anomalous over Quackenbush, Cutler Creek and the new SRA3 #1 discovery (Figs. 4 and 5).

Ethene can be produced through biological or chemical oxidation of ethane and other hydrocarbons as it gradually ascends to surface. Isobutane and isopentane, which are present in the produced gas, are also part of this "slow" microseepage association. The dryness ratio (C1/C2) and percent propane anomalies over Quackenbush, Cutler Creek and new gas discovery (SRA3 #1) relative to Wilson Hollow, Terry Hill South and County Line is puzzling considering that produced gas composition from all fields is nearly identical. Possible reasons for the different hydrocarbon signatures observed in soils over the fields are:

Wilson Hollow, Terry Hill South, and County Line have been breached by deep faults along which heavier hydrocarbons can ascend rapidly. This would explain the heavier hydrocarbons and metals over these fields as opposed to Quackenbush, Cutler Creek and the new discovery that have not been breached by deep faults.

Pressure in the older Wilson Hollow, Terry Hill South and County Line reservoirs may have declined more than Quackenbush, Cutler Creek, and the new discovery because of more production and/or breaching by deep faults. The drop in reservoir pressure may have slowed or curtailed microseepage to surface such that the dryness ratio and percent propane anomalies have disappeared. The ethane-iC4-iC5 association in soils over all gas fields suggests that this assemblage of hydrocarbons is more stable in soils and can exist for sometime after microseepage ceases because of pressure drops related to production and/or breaching by faults.

The explanation for the change in the hydrocarbon signature in soils over compositionally identical reservoirs can be further refined once current production pressures for all gas fields are obtained.

CONCLUSIONS

The following conclusions are drawn from this test of surface geochemical methods over deep Black River gas targets in central New York:

The surface geochemical methods tested are effective in terms of:

(i) Detection of unique microseepage from commercial Black River reservoirs, which will help to prescreen large areas to focus leasing, seismic and drilling activities. Variables that distinguish gas and dry reservoirs are ethene, isobutane, isopentane, methane and propane. The lack of dryness ratio (C1/C2) and %propane anomalies in soils over some fields might reflect the presence of deep faults that carry heavier hydrocarbons and metals to surface and/or drops in reservoir pressure related to production and breaching by deep faults.

(ii) Mapping of faults that intersect and possibly hinder production from dolomite reservoirs. Indications of these faults are anomalous ethane/ethene ratios relative to methane, Ca, Mg, Sr, Pb, Zn and Tl in soils.

(iii) Minimal impact to landowners because of the rapid, non-invasive nature of the sample collection method.



Figure 4. Quackenbush gas probability superimposed on the C1/C2 ratio Z-score. The gas probability was derived through discriminant analysis of C1-C6 hydrocarbon data using the samples collected around Quackenbush gas wells and dry wells. Note that the recent well (SRA 3 #1) drilled by Fortuna Energy, Inc in the new exploration area is correctly predicted by the discriminant model and high C1/C2 ratio. Production rates for wells outside of the new exploration area are for the year 2002, and these were obtained from the New York State Museum website.







Figure 7. Ethane/ethene ratio Z-score superimposed on the lead Z-score. High ethane/ethene ratios are thought to be indicative of faults because rapid ascent of ethane does not allow adequate time for oxidation to ethene. The correlation of ethane/ethene ratios with lead could reflect the presence of Mississippi Valley Type mineralization along the faults.



Figure 9. Ethane/ethene ratio Z-score superimposed on the magnesium Z-score.

APPLICATION OF RESULTS TO EXPLORATION IN NEW YORK

This investigation, particularly in the context of earlier projects done by Direct Geochemical with NYSERDA sponsorship, and of other Trenton/Black River projects elsewhere in the Northeast U.S.A., suggests that a surface geochemical study has powerful application to exploration in New York. The method should be integrated into exploration programs for the following applications:

- Reconnaissance. Conducting sampling at moderate to high frequency along existing road and trail networks can quickly and inexpensively outline areas of gas potential, and can at very low risk, firmly exclude broad regions. This approach will use primarily light hydrocarbon analysis, with metals analysis on a selective basis following initial interpretation. The metals will be used to identify major faults that could be responsible for breaching of reservoir seals.
- Drilling Locations. When samples are taken in a tight, quasi-rectangular grid, focused in areas previously selected using geochemistry, seismic, and other methods, geochemistry can identify the areas most likely for gas accumulations and can help avoid major faults. The method uses light hydrocarbon testing, followed up by selected analysis of trace metals.
- Structure. Analysis of metals, and of the ethene/ethane ratio (and combined with total hydrocarbon flux) can reveal the existence of major fault and fracture networks. This can play powerfully into the siting of seismic and other studies.

TECHNOLOGY TRANSFER

The results of this geochemical study in New York have been disseminated to the public by:

- (1) Oral presentations at:
 - a. IOGANY summer meeting in Clymer, New York (July 7, 2004).
 - b. Strategic Research Institute Shale Gas Conference in Denver, Colorado (July 30, 2004).
 - c. Strategic Research Institute Unconventional Gas Revolution Conference in Denver, Colorado (December 13, 2004).
- (2) Poster presentations at:
 - a. IOGANY/OPI meeting in Niagara Falls, Ontario (November 8-9, 2004).
 - b. Rocky Mountain Association of Geologists Hydrothermal Dolomite Symposium in Denver, Colorado (November 15, 2004).

- (3) Publication in:
 - a. American Oil & Gas Reporter (September, 2004)
 - b. Explore newsletter for Association of Applied Geochemists (January, 2005).
- (4) Trade booth display at:
 - a. Annual AAPG Meeting in Dallas, Texas (April 18-21, 2004).
 - b. Annual CSPG Meeting in Calgary, Alberta (May 31-June 4, 2004).
 - c. Western Section-AAPG meeting in Denver, Colorado (August 9-11, 2004).
 - d. Eastern Section-AAPG meeting in Columbus, Ohio (October 3-6, 2004).
 - e. Denver Technofest (November 1, 2004).
 - f. IOGANY/OPI meeting in Niagara Falls, Ontario (November 8-9, 2004).

Bibliography

Barinaga, C.J. and Farwell, S.O., 1988. Soil-sorbed, sulfur-containing gases: analytical methodology and preliminary application to geochemical petroleum prospecting, *Applied Geochemistry*, Pergamon Press, Oxford, Vol. 3, pp. 165-172.

Coleman, D.D., Meents W.F., Liu Chao-Li, and Keough R.A., 1977. Isotopic identification of leakage gas from underground storage reservoirs – a progress report: Illinois State Geological Survey, Illinois Petroleum No. 111, 10 p.

Curry, W.H., 1984. Evaluation of surface gamma-radiation surveys for petroleum exploration in the deep Powder River Basin, Wyoming, in M.J. Davidson and B.M. Gottlieb (eds.), *Unconventional Methods in Exploration for Petroleum and Natural Gas III*, Southern Methodist University, Dallas, TX, pp. 25-39.

Duchscherer, W., 1984. Geochemical hydrocarbon prospecting, with case histories: Tulsa, Oklahoma, Penn Well Publishing, 196 p.

Horvitz, L., 1939. On geochemical prospecting, Geophysics, Vol. 4, pp. 210-225.

Horvitz, E.P. and Ma, S., 1988. Hydrocarbons in near-surface sand, a geochemical survey of the Dolphin Field in North Dakota, *Association of Petroleum Geochemical Explorationists Bulletin*, Vol. 4, No. 1, pp. 30-61.

Klusman, Ronald W., Saeed, Mahyoub A., and Abu-Ali, Mahdi A., 1992. The potential use of biogeochemistry in the detection of petroleum microseepage, *American Association of Petroleum Geologists Bulletin*, Vol. 76, No. 6, pp. 851-863.

Laubmeyer, G., 1933. A new geophysical prospecting method, especially for deposits of hydrocarbons, *Petroleum*, Vol. 29, No. 18, pp. 1-4.

McCabe, C., Sassen, R., and Saffer, B., 1987. Occurrence of secondary magnetite within biodegraded oil, *Geology*, Vol. 15, pp. 1351-1370.

Oehler, D.Z. and Sternberg, B.K., 1984. Seepage-induced anomalies, "false" anomalies, and implications for electrical prospecting, *American Association of Petroleum Geologists Bulletin*, Vol. 68, pp. 1121-1145.

Peters, E.R., 1983. The use of multispectral satellite imagery in the exploration for petroleum and minerals, *Philosophical Transactions of the Royal Society of London, Series A: Mathematical and physical sciences*, Vol. 309, No. 1508, pp. 245-255.

Price, L.C., 1986. A critical review and proposed working model of surface geochemical exploration, in M.J. Davidson (ed.), Unconventional methods in exploration for petroleum and natural gas IV: Dallas, Southern Methodist University Press, p. 245-304.

Riese, W.C. and Michaels, G.B., 1991. Microbiological indicators of subsurface hydrocarbon accumulations, *American Association of Petroleum Geologists Bulletin Association Round Table* (Abstract), Vol. 75, No. 3, p. 660.

Rosaire, E.E., 1938. Shallow stratigraphic variations over shallow Gulf Cost structures, *Geophysics*, Vol. 3, pp. 96-115.

Saunders, D.F., Burson, K.R. and Thompson, C.K., 1999. Model for Hydrocarbon Microseepage and Related Near-Surface Alterations, *American Association of Petroleum Geologists Bulletin*, Vol. 83, No. 1, pp. 170-185.

Schumacher, D., 1996. Hydrocarbon-induced alteration of soils and sediments, in *D. Schumacher and M.A. Abrams (eds.), Hydrocarbon migration and its near-surface expression: American Association Petroleum Geologists Memoir 66*, pp. 71-89.