HANSON-WADE WORKSHOP ON UNDERSTANDING SURFACE GEOCHEMICAL EXPLORATION TECHNOLOGY

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LIGHT HYDROCARBONS FOR PETROLEUM AND GAS PROSPECTING

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Workshop Summary

Surface and Marine Geochemical Methods of Petroleum Exploration

An overview of all surface and marine geochemical prospecting techniques is provided, including both direct and indirect methods. Major emphasis will be placed on surface and marine geochemical prospecting techniques using free or dissolved gases; however, the topics covered are wide ranging and include fluorescence, microbiological and hydrogeochemical methods as they apply to reservoir proximity studies. Topics include general and historical background on macroseepage relationships to reservoirs, methods of microseepage detection in both onshore and offshore environments (including sampling techniques for surface sediments, bottom muds, seawater and seismic shotholes), microbiological methods, fluorescence of imaging. bitumens. radiometric concepts. space benzene and iodine hydrogeochemical methods, application of carbon isotopes, generation of biogenic gases and their implications to exploration and environmental surveys. Hydrocarbon pattern recognition and dating will be discussed along with methods for identifying refined petroleum products, crude oils, and their weathered residues. Deep earth gases, such as helium, hydrogen and carbon dioxide, and mercury, associated with earth tectonics (earthquakes) and their relationship to subsurface reservoirs will be discussed. Geochemical data handling, mapping and statistical methods will be covered, including a focus on the philosophy of anomaly selection and recognition.

Emphasis will include comparison of free, adsorbed and integrative gas measurement techniques for mapping migrated hydrocarbons. The course will involve theory of the basic science, case studies, laboratory procedures and field studies as outlined below.

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INTRODUCTION

ORIGINS OF LIGHT HYDROCARBON GASES Origin of petroleum Origin of light hydrocarbon gases in the near-surface Laboratory and field evidence of biogenic C₂-C₄ hydrocarbons Distinguishing petrogenic and biogenic hydrocarbons

HISTORY

Basic concepts Methods of geochemical prospecting

PHYSICAL BASIS FOR MIGRATION OF HYDROCARBONS TO THE SURFACE Basic assumptions Physical transportation by effusion Physical transportation by diffusion

HYDROCARBON RESIDENCE SITES AT SURFACE Free gas Bound gas Choice of free or bound gas

FACTORS INFLUENCING NEAR- SURFACE HYDROCARBON FLUX Microbial activity Barometric pumping Earthquakes

SAMPLING AND MEASUREMENT METHODS

Atmospheric techniques Soil gas Dissolved gas Headspace gas Disaggregation Acid extraction Integrative Adsorption Fluorescence Microbiological

SAMPLING STRATEGY

- DATA INTERPRETATION Preferential pathway model Geochemical populations
- ENVIRONMENTAL APPLICATIONS High Resolution Capillary GC Forensic Geochemical Methods

CASE HISTORIES AND DISCUSSION

PREFACE

Present day exploration for oil and gas requires a coordinated effort based on all useful techniques of geophysics, geology, and geochemistry. This overview of geochemical prospecting contains a brief outline of all current geochemical prospecting techniques which are considered useful by the author. It is intended for the use of the exploration geologist or geophysicist who wishes to enhance his exploration activities through the use of geochemistry. Despite the tendency for each new technological advance to be hailed a panacea, we must avoid doing so, since there is no direct method for finding oil and gas. Each exploration tool has its positive and negative points, and it is up to the explorationist to use these tools properly. The basic problem is one of economics in an era of rising exploration, developing, and marketing costs. The function of an exploration geologist is to increase the odds of drilling a producing well by every economic means at his command. Within these limitations, geochemical prospecting techniques can aid a rational exploration program.

INTRODUCTION

To set the stage for a better understanding of unconventional methods, it is helpful to very briefly consider the development of conventional exploration technology.

Oil seeps were reported in the earliest recorded history. Drilling in the U.S.A. is said to have started with the Drake well in Titusville, PA in 1859. The first wells drilled were based on creekology and it is truly amazing that 22 years were required for the anticlinal theory to be proposed in 1861, and finally accepted in 1883. The first well to be drilled using this new technology resulted in the discovery of the Mannington field in West Virginia. To quote from a summary written by F.A. Thurman (R.M.A.G., Oil and Gas Volume, Colorado-Nebraska, 1961):

"Other geologically located discoveries followed. Despite the preponderance of amassed arguments in favor of the theory and despite its demonstrated practical results, the oil companies continued to ignore geologic aid and continued to make locations on the basis of topography, witch hazel twigs, advice of the driller, advice of spiritualists and chance drilling.

Structural contouring was introduced into the United States in the late 1850's by J.P. Lesley and was used in the mapping of coal lands. The first published structurally contoured map of an oil area was contained in a report by Benjamin Smith Lyman on the Punjab Oil lands of India, published in Lahore in 1870. Critics have claimed, not without some justification, that the anticlinal theory of accumulation and structural maps have impeded the progress of geological exploration for 75 years.

Contrast the willingness to drill an anticlinal prospect against the lethargy, or even hostility, directed against a stratigraphic trap prospect. For decades the industry has been cursed with the closed contour concept and only the fact that so few undrilled closed contour prospects remain, drives exploration back to the basic and fundamental geology outside the sphere of the closed structure. In actuality, exploration trends have been based on economics - it has been less costly to find structural traps than stratigraphic.

In the course of development many significant geologic facts pertaining to the oil and gas origin, migration and accumulation were learned and finally, by 1908, a few companies were cautiously following geologic advice, or at least surreptitiously putting it into the files as a hedge against remote possibilities. The improved success ratio of the few companies

known to be, or suspected of using geological information was soon apparent, and by 1915 the field geologist was in his heyday. Hundreds of field parties were mapping structure in almost every sedimentary basin in the nation.

In areas of surface cover and subsurface complexity, surface mapping alone failed to provide the necessary answers and various forms of geophysical investigations began to be used as exploration tools. They too stemmed from long and honorable backgrounds, even though adaption to oil and gas finding was new.

Magnetic surveys, the oldest known geophysical method of prospecting, date back to the use of the magnetic compass to locate iron ore deposits ... use of magnetics in oil exploration gained favor in the early 1920's, concurrently with the development of other geophysical methods. World War II saw the development of the airborne magnetometer to spot submarines from low flying aircraft. It requires but a little ingenuity and a few changes in the instruments to adapt this type of survey to one suitable for structural exploration, and today the airborne magnetometer is widely used for rapid, broad, regional studies. This popularity has been due, in large part, to the ease of covering otherwise inaccessible areas, low cost per unit covered and the speed with which a survey can be made. Since the principal effect measured by a magnetometer emanates from igneous basement rocks, magnetic surveys have been found most effective when used in conjunction with gravitational studies to provide supporting or supplementary data.

Knowledge of gravity began when Galileo discovered the natural laws of free fall and pendular motion in 1589. Richter, in 1672, noticed that pendulum clock rates varied as the clocks were moved from place to place and the realization of gravity variation was born. Bouquer (1698-1759) was possibly the first to make pendulum observations for the purpose of determining gravitational differential. Late in the 1880's van Eoetvoes began his work on the torsion balances, an instrument for determining the horizontal gradient of gravity. The first recorded use of gravity mapping in oil exploration was conducted in 1915 and 1916 over the Egbell oil field of Czechoslovakia. The survey was successful. In 1917 the first gravity survey over a salt dome was completed in North Germany. In 1922 De Golver and Roxana Petroleum Corporation (Shell) each imported torsion balances to the United States. Discovery of the Nash salt dome in the Gulf Coast region of Texas resulted in 1924 and within the next two years several gravity discoveries followed. The torsion balance was off to a good start in its new environment and as rapidly as the instruments could be made they were put into service in all potential producing areas. By 1926 torsion balance use had spread to the Rocky Mountains region and in that year the Midwest Refining Company did some experimental work in the Wellington area of Colorado.

Pendulum and torsion balance surveying declined rapidly after the development of the modern type gravimeter in 1930. As is the case with all exploration tools and techniques, the major usefulness declines as new tools and new thoughts are developed. A new and more exact tool was being readied contemporaneously with the gravimeter and soon the seismograph was occupying the exploration spotlight.

The earliest work in the field of artificial seismology is credited to Robert Mallet, who as early as 1846 had expressed the idea of differential and diagnostic velocities. His early experiments were carried out with small charges of gunpowder. A bowl of mercury, placed some distance from the shot, acted as a seismoscope and the appearance of ripples on the surface of the mercury indicated to the observer the arrival of the seismic wave. The shot was electrically fired when the observer started the chronograph. He stopped the clock when the ripples were observed and the time interval was measured. It is natural that instruments, methods and accuracy improved over the years when great strides were made in theoretical seismology by men as Abbot, Milne, Gray, Hecker, Zoeppritz and Geiger.

Minthrop applied for a patent in Germany covering the use of refraction profiling for location of the depth and type of subsurface formations. He organized refraction work in Mexico for the Mexican Eagle Oil Company in 1923. The same year Marland Oil Company was using another Seismos crew along the Mexia fault zone in Texas. Probably the first seismograph work done in Colorado was the experimental refraction work done in the Wellington area in April of 1930 by a Prospektion G.M.B.H. crew out of Goettingen, Germany. Following this assignment the crew moved to Wyoming. The survey was beginning which was to result in the discovery of the Beaver Creek field in 1938.

Despite the fact that the seismograph was developed in Germany, credit for development of the reflection method belongs to the United States. As this method was developed it rapidly replaced refraction surveying and did a better job at less cost with greater mobility at far greater speed. Tremendous strides have been made in instrumentation and interpretation during the last fifteen years. To seismic surveys must go the credit for discovery of more oil than the remainder of geophysical methods combined. As the amount of unexplored territory grows less and the problems of interpretation of new ideas grow greater the inexorable law of diminishing returns will become operative even as it is in other exploration methods.

It must be noted that originally, surface mapping, magnetometer, gravimeter and seismograph, were all developed as tools to locate structural anomalies. It is axiomatic that with each structure drilled, there remains one less to be drilled. Geological exploration methods and aims have, therefore, been undergoing constant and gradual change to explore new ideas and develop techniques of finding oil independent of the anticlinal theory of accumulation. Exploration techniques have been cyclical, each new concept or tool extending over a period of relatively few years. Today, for lack of better tools, physical exploration continues on course with an attempted super-refinement of existing tools. Such programs eventually nudge at the margin of economic returns.

There are actually scores of tools available to the geologist today which were undreamed of a few years ago - and each tool, under proper conditions, will provide a bit of information in the struggle to interpret the third dimension."

Today, the main effort in the search for oil and gas follows the geophysical approach. Initially, the geophysical method could only indicate the presence of favorable conditions for petroleum accumulation. The recent introduction of sophisticated recording equipment has provided the geophysical approach with the ability to determine seismic amplitudes with a fair degree of confidence. These new Bright Spot techniques have allowed the detection of lithologic changes, and in some instances, the actual detection of oil and gas sands. However, a Bright Spot effect can be obtained from many stratigraphic situations other than reservoir fluids. In particular, thin beds can show dramatic amplitude changes due to constructive interference. Changes in lithology cause velocity changes which produce effects similar to gas and oil sands. Pinchouts, erosional surfaces and laminar sections are all poor places to use Bright Spot analysis. The main success of direct detection geophysical methods thus far has been in offshore areas. The geophysical approach has been less successful on onshore areas such as the Northern Sacramento Valley. This is primarily because the gas accumulations in this province are generally discovered in lenticular sands which are often limited by pinchouts and unconformities.

SURFACE GEOCHEMICAL TECHNIQUES

Surface geochemical prospecting is analogous to the oldest geological method of prospecting for petroleum. It is a search for oil and gas seeps. The difference, as applied today, is that the geochemical approach is concerned with micro-concentrations of petroleum substances which are invisible to the eye, while the geological approach seeks macro-concentrations which are visible to the eye. Unfortunately, the importance of seeps has been minimized in the thinking of many of the explorationists today. The best remedy for this is to require everyone to re-read Walter Link's classic 1952 paper on the "Significance of Oil and Gas Seeps in World Exploration." Link's abstract follows:

"A look at the exploration history of the important oil areas of the world proves conclusively that oil and gas seeps gave the first clues to most oil-producing regions. Many great oil fields are the direct result of seepage drilling.

Seepages are most numerous in the youngest sediments, especially where they have been folded, faulted, and eroded, and on the margins of basins. Exceptions are easily explained by a comparatively calm geological history as depicted by the Gulf Coast region, West Texas, the Mid-Continent, and areas bordering stable masses.

Many seepages are the result of destruction of major accumulations of oil reservoirs. By studying seeps and the reason for their location, geologists can see exposed on the face of the earth a great many "type oil accumulations."

Recent illustrations of the value of seeps in geologic thinking are the developments in Western Canada, the Uinta Basin of Utah, and Cuyama Valley in California."

In 1981, Dr. John Hunt gave an invited paper at the annual AAPG meeting in San Francisco in which he stated that "70% of the world's known oil reserves can be related to seeps." Dr. Hollis D. Hedberg concluded the discussion following Dr. Hunt's paper by stating that, "There seems to me to be no question of the innate value of the geochemical information. A geochemical survey should not be thought of as a black magic means of spotting the location of oil or gas pools, but only as a simple common-sense method of gathering data on hydrocarbon occurrences to dilute to make visible seeps or impregnations data which if collected reliably, interpreted wisely, and used intelligently along with all other lines of evidence will always be useful in the petroleum exploration of any area."

On land, most visible seepages have already been recorded and the nature of their relationship to subsurface petroleum accumulation has been studied, if not always successfully concluded in an economic deposit. Link's models showing macroseeps are very instructive for understanding microseeps. Offshore, the situation is somewhat different. There, visual observation of seepages has been impeded by water cover and reliance must be placed very largely on chemical analysis of dissolved gases in the water column and the interstitial waters filling the pores of the blanket of young sediment covering much of the sea floor. The main task now for surface geochemical prospecting is the identification of the micro, or less clearly manifested "seepages," which can be determined only by detailed chemical analysis of fluids in surface and near-surface rocks. The problems are not whether there is any value to the data, but rather, are the techniques of identification and the geological interpretation useful enough to justify the cost?

The main advantage of geochemistry over geophysics and geology is that it is not limited by the type of trap in which the hydrocarbons have accumulated. Geochemistry is especially useful in prospecting for stratigraphic and lithologic pools which are not associated with easily discernable structural features. It is also useful in deciding whether a previously discovered structural trap contains petroleum, however the absence of measurable seepage must be used very cautiously in making negative conclusions. Geochemical prospecting can only verify the existence of petroleum hydrocarbons, which may be present either in a concentrated or dispersed form. None of the geochemical methods can predict whether an oil or gas anomaly is of economic proportions.

Geochemical methods of prospecting for petroleum should be used only in conjunction with all available geological and geophysical data. The authenticity of an anomaly, and the likelihood of finding petroleum within the area of the anomaly, may be ascertained only by strict correlation with the geological structure of the region.

GEOCHEMICAL INDICES OF PETROLEUM

Geochemical methods of prospecting are classified as direct or indirect. The direct methods involve the establishment of the presence of dispersed oil components in the form of hydrocarbon gases or bitumens in the soils, waters, and rocks in the vicinity of oil and gas accumulations. The indirect methods are based on the detection of any chemical, physical, or microbiological changes in the soils, waters, or rocks associated with the oil and gas deposits. Figure 1 is a schematic diagram outlining most of the direct and indirect methods currently in use (A.A. Kartsev, et al., 1959). The most important of these is the gas survey which is discussed in detail in the attached papers. Note the designations, route and area surveys. A route survey is a reconnaissance survey to determine the regional background and trends, and especially to locate anomalous regions. An area survey is a detailed survey of an anomalous region used for selecting and evaluating particular anomalies.

Second in rank to the gas survey is the bitumen survey. This direct method is based on the detection of oil bitumens in the soil using their ability to fluoresce when excited by ultraviolet light. The geochemical definition of bitumen is a natural organic substance soluble in neutral organic liquids under normal conditions of temperature and pressure. Typical solvents of bitumens are petroleum ether, benzene, chloroform, carbon tetrachloride, carbon disulfide, and ethyl ether. The great majority of organic compounds which exhibit intense fluorescence possess cyclic, conjugated structures. Since most bitumens fall into this class of compounds, nearly all of them fluoresce.

The hydrochemical techniques are considered as both direct and indirect. The determination of petroleum hydrocarbons in water is direct. The marine hydrocarbon program is an excellent example of the use of the direct gas survey to water-covered regions. It is also possible to conduct a survey of the hydrocarbon gas content of ground water; for example, surveys have been conducted in the Snake River Downwrap using the water from all available wells (Sidle and Jones, 1982).

Beginning in 1955, W.M. Zarrella and other Gulf Research and Development Corporation scientists developed a technique for using the benzene content of subsurface brines recovered from drill stem tests to predict the presence of petroleum accumulations (W.M. Zarrella, et al, 1967, Coggeshall and Hanson, 1956, Mousseau and Zarrella, 1962, and A. Gene Collins, 1974). This geochemical technique is very useful and should be applied in the drilling of both development and wildcat wells.

In addition to benzene, there are several other hydrochemical indicators of petroleum which will not be discussed in detail. Of these indicators, the three most important are: (1) soluble bitumens (naphthenates), (2) iodine, and (3) ammonia. Indirect hydrochemical indicators are the dissolved salts and ions which indicate favorable conditions for the presence of oil

reservoirs. These indirect indicators are (1) hydrosulfides and other reduced compounds of sulfur, (2) absence of sulfates, (3) soda (HCO3), (4) bromine, and (5) the classification of subsurface waters.

Motojiama has reported a definite relation between natural gas and its associated waters in Japan. Figure 2 lists the ionic species that the Japanese have found to be important in natural gas prospecting. The water samples are collected from boreholes of about 10 meters depth, and from wells and springs when available. The Geological Survey of Japan has reported success in prospecting for natural gas in oil fields, coal fields, and related gas fields since 1948 using geochemical water analysis. A summary slide developed and published by A. Gene Collins (1975) that compares hydrogeochemical indicators associated with oil and gas reservoirs is shown in Figure 3.

Soil-salt methods of prospecting are based on the determination of the content and composition of salts and other mineral components in soils. The following types of soil-salt methods have been applied: (1) chloride, (2) iodine, (3) gypsum, (4) radium. The only one of these which is direct is iodine, and we shall confine our discussion to this indicator.

The significance of iodine in soils results from its presence in underground waters associated with petroleum. A.R. Barringer has reported lodine in the air over the Gables Oil Field in southwest Ontario (A.R. Barringer, 1970) and in the air in the vicinity of the Midway-Sunset Oil Field in California (Barringer and Moffat, 1971). It is reported by Cosgrove (1970) that the iodine content correlates with the organic carbon in some shales and sedimentary rocks. S.N. Maksimova (1964) has claimed that iodosubstituted hydrocarbons are actually involved in the genesis of oil. The existence of this possibility was proven by Kuhlman and Drickamer (1972), who showed that iodine acts as a catalyst at high pressures and allows the synthesis of new hydrocarbons.

The oxidation and reduction potential methods (Eh or redox potential) are a measure of the relative concentrations of oxidized or reduced species in a chemical system. It is known that a reducing atmosphere is necessary for the production of hydrocarbons. The redox potential of petroleum-associated waters is influenced by many reduced species such as sulfur compounds. When the water is brought to the surface, the change in pressure and temperatures will affect the Eh, and if the sample is allowed to come into contact with the atmosphere, the equilibrium of the sample will change immediately. This conceptual method is difficult to apply and has never been proven to work.

Microbiological prospecting for petroleum involves obtaining suitable samples of soils and waters, analyzing these for hydrocarbon oxidizing microbes, and plotting the results on an areal basis (Kartsev, et al., 1959 and S.N. Maksimova, 1964). Methods have been developed which utilize the hydrocarbon-oxidation activity of microbes as an indirect index of petroleum hydrocarbons in soils and waters (Kartsev, et al., 1959 and J.B. Davis, 1969). This is an indirect method that adds considerable variability and noise to the data. Magnitudes are related to the number of bacteria present and this is affected by lithology (nutrients) and soil moisture, in addition to the presence or absence of a seep. Any type of organic contamination interferes with the process. There is no compositional information regarding oil versus gas available, as with free soil gases.

In addition, striking mineralogic and chemical changes have been reported by T.J. Donovan in outcrops of a Permian redbed sequence overlying the oil-productive parts of the Cement anticline in Oklahoma. Gypsum beds along the flanks are altered abruptly to erosionresistant carbonate rocks at the crest of the fold in the Keechi Hills. Associated sandstones, typically red and friable in the surrounding region, are altered to pink, yellow, and white on the flanks of the anticline and to hard carbonate-cemented gray sandstone at the crest. The zone of concentration is reported to extend to at least 2500 feet. Color changes in the sandstone are related to reduction and dissolution of iron in the presence of hydrocarbons. In addition, calcitized gypsum is reported to be exceptionally deficient in C13 and light carbon/heavy oxygen cements directly overlie petroleum producing zones where fluids have superior vertical avenues of communication (faults, etc.). Away from these avenues of leakage, the influence of hydrocarbons on the isotopic composition of the carbonate cements decreases systematically. This paper by Donovan offers exceptionally strong proof of the vertical migration of hydrocarbons, however, such macro effects appear to be mainly associated with macro seeps rather than micro seeps.

GEOCHEMICAL APPLICATIONS

Most of this course will deal with surface geochemical prospecting, which is the most direct and widespread application of geochemistry to petroleum exploration. Several papers along with an extensive bibliography describing surface geochemical applications to exploration, production and environmental problems are included with this summary overview in the CD's provided as handouts.

Surface geochemical detection of hydrocarbons is a logical extension of the use of macroseeps which have obviously had a major impact on oil and natural gas exploration from the earliest days of the industry. As noted in the paper by <u>Jones and Drozd (1983)</u>, Gulf Research and Development Corporation (<u>GR&DC</u>) played a significant role in extending this technology to the benefit of the explorationist for a period in excess of 45 years. The period of 1932 to 1940 saw the work of A.J. Teplitz at Gulf recognize the difference between petroleum gases and marsh gases in the near surface. The exploration significance of these findings was not fully realized at that time because of the paucity of survey data and the limited number of chemical indices available with the cumbersome, relatively insensitve analytical methods available. A period of 20 years elapsed before breakthroughs in analytical technology (high sensitivity gas chromatography) made possible the new surface geochemical exploration methods. Gulf Research and Development pioneered in development of the instrumentation required to achieve the analytical precision and sensitivity and the quantitative development necessary for exploration implementation.

In 1975, regional surveys involving both oil and gas fields were carried out, resulting in the establishment of compositional indicators for prediction of reservoir type. With the implementation of the first full-time surface geochemical data acquisition program in 1976, evidence for migration of gases from ultra-deep reservoirs and the significance of fracture systems as conduits for migration from reservoir to surface was obtained. Continued field work and laboratory studies led to refinements in developing criteria to recognize gas, condensate and oil signatures and distinguishing reservoir characteristics through overlying glacial till. Work in 1978 and 1979 succeeded in adding to fundamental predictive knowledge as well as practical exploration techniques (Jones and Drozd, 1983, Jones et al. 2000). Relationship of compositional parameters of marine seeps in the Gulf of Mexico with production and establishment of isotopic and chemical agreement of reservoir and surface gases were additional accomplishments (Williams and Mousseau, 1981).

The attached abstracts and papers represent a significant contribution to the development of this emerging technology as we understand it today.

The surface geochemical technology developed over the past several years has also found increasing use in secondary applications to problems associated to petroleum product storage and distribution, secondary recovery operations, underground coal gasification, and

petroleum production. These applications are in addition to its primary function in petroleum exploration.

In the area of petroleum product storage, the technology has been used in several remedial efforts which aided the delineation and cleanup of surface contamination following the loss of product from underground storage wells (Jones and Burtell, 1996). The results were most useful in identifying the type of gases as well as their distribution and concentrations throughout the area.

A near-surface soil-gas geochemical survey was also conducted in conjunction with the Phase II underground coal gasification experiment at the North Knobs GR&DC-DOE UCG facility (Jones and Thune, 1982, Jones, 1983, Jones and Burtell, 1996). Soil gases were measured in 122 eighteen foot deep permanent sites over a time period extending from July 1981 to July 1982. Baseline values were established one month before the 600 foot deep report was pressured and fired. Monitoring of leakage gases continued daily throughout the three months during the burn and for one month after in order to follow the relaxation of surface leakage. A published report containing contour maps which illustrate the surface leakage patterns over four time windows is included in these course notes. These maps indicate that a recognizable surface response occurred within two to six days after changes in the subsurface report pressures. Both vertical and lateral leakage occurred. This data set could be used to determine the effects of earth filtration to gas migration.

The Geosat oil and gas test site program stimulated interest in the interaction between surface hydrocarbon concentrations and interpretation of remote sensing data. The test case results suggested that lineaments correspond to avenues of preferential hydrocarbon seepage and that this seepage affects vegetation health and populations at Patrick Draw field in Wyoming and potentially at Lost River field, West Virginia.

The <u>Patrick Draw</u> study shows that a zone of stressed vegetation, visible on thematic mapper data, definitely coincides with an area of marked leakage of hydrocarbons and that the composition of these gases would predict an intermediate type oil and gas reservoir such as exists in the area. The study further indicates that the leakage is in large part controlled by the presence of fractures/faults recognized as lineaments on the remote sensing image.

The Lost River study specifically investigated the possible existence of hydrocarbon leakage causing anomalous populations of maple trees in a Climax Oak forest. These maples were first recognized by study of thematic mapper simulator data. The soil gas hydrocarbon concentrations are above average in several of the maple anomalies over the field. This supports the inference that the maples are present because they are more tolerant of soil conditions where hydrocarbon seepage is active. The crest of the field has low soil gas magnitudes, but high values occur to the updip eastern edge of the field along a fault/fracture that was detected in the seismic data.

The conclusion that preferential pathways of hydrocarbon leakage are recognized in spectral and textural analysis of remote sensing data is supported by other studies and integrated into a suggested exploration/hydrocarbon migration model. A paper by Matthews, Jones, and Richers (1984) which discusses these results in detail is attached.

Experience to date reveals that the surface gas survey yields noisy, but compositionally recognizable anomalies in regions known to contain oil and gas fields. These anomalies are noisy because they are strongly influenced by the location of major faults and fractures. They are more reproducible in composition than magnitude and have been demonstrated to change in response to change in source type, or reservoir.

Most of the advances cited above are substantiated in the published literature included on the CD handouts. In spite of these advancements, we must recognize the limitations of the current state of development of this "direct detection" technique. Modeling of basin development, integrating source and depositional parameters with basin subsidence, deformation, timing of fracturing, fluid migration from source-to-reservoir and reservoir-tosurface, is needed and should be part of the future research in geochemistry. These geochemical techniques can also be used to quantify and map reservoir parameters, providing information on unproduced reservoir compartments within existing and/or abandoned oil and gas fields. Continued exchange of ideas and information with scientists in related fields such as geophysics, geology, botany, microbiology, earthquake prediction and geochemistry of surfaces will also pay large dividends in our basic understanding of this very complex process.

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Hanson-Wade Workshop Understanding Surface Exploration Geochemistry Technology

Petroleum Exploration Geochemistry

Discussion of Key Points

Surface and Marine Geochemical Surveys

Overview/Facts/Limitations

There is no doubt that Macroseeps have highlighted productive areas <u>Walter Link's classic paper AAPG 1952</u> <u>Seep Models Middle East</u> <u>Offshore GOM</u> Onshore Texas/La Gulf Coast

John Hunt AAPG 1981 70% of Known Reserves Related to Visible Seeps

Classic Examples

This has proved successful in the offshore Gulf of Mexico <u>Green Canyon</u>, Complex Salt Tectonics <u>Seismic Geochem</u> examples

Direct Vertical Detection Macro Economic

Macroseeps: Oil dripping from sediment cores! Migration through vertical fault conduits

Contrast with Microseep Example <u>Kansas Morrow Sand Channel</u> Examples Direct Vertical Detection Micro Economic

Obviously Magnitude not related to economics <u>Green Canyon</u>, Trinidad <u>Pleasant Creek</u> <u>Marquez, East Texas</u> <u>East Canyon</u>, <u>Jasper</u> General Levalle

Magnitudes Related To <u>Pressure-Permeability</u> <u>Pineview</u> <u>Ryckman Creek</u> <u>Infantias Field</u> Link Macroseeps

There are obvious fault and bedding plane relationships

Underground Coal Gasification

Seepage Represents Focused Migration From Depth Snake Valley Driven By Source Rocks and Basin Dewatering Obviously Macroseeps and Microseeps Seeps Are Not Necessarily Vertical

Up Gradient, Direct, <u>No "Halos"</u>, Spotty Gas Anomalies <u>Link models</u> explains seep migration

Numerous examples suggest a pressure-permeability pathway similar to macroseeps: <u>Actual studies verify migration model</u>

Origins C1-C4, C5+, <u>C15+</u> BTEX, <u>Fluorescence</u> CO2, <u>H2S</u>

Composition most important Source rock tool applied at the surface

<u>Katz and Williams Reservoir Compositions</u> <u>US Basins Map</u> <u>Soil Gas Compositions</u> Venezuela <u>Pixler Plots</u>, <u>Nikonov C2/C3</u>, Verbanic <u>Reservoir Pixlers</u> <u>Ternary Plots</u> <u>ECI Ratios</u>

> Probe examples Snake Valley, Nevada Argentina Filo Morado Loma de La Lata Kenai Península, Venezuela, Ethiopia

OBVIOUSLY SEEPS DO NOT OCCUR ONLY OVER FIELDS

THE MOST IMPORTANT ADVANCMENTS CONDUCTING SOIL GAS SURVEYS REGIONALLY OVER ENTIRE BASINS

ENVIRONMENTAL CONTAMINATION

BIOGENIC GASES

<u>Green Canyon Data Table</u> <u>National Geographic</u> Note biogenic methane mixed with thermal methane

ENVIRONMENTAL EXAMPLES

Biogenic gases (CH4, CO2) play very important role

Very special environment

Anaerobic Methane Generation

These anaerobic gases are generated in essentially every contaminated environment

Methane occurs very close to free product

USGS Oil Spill in Bemidji, Minnesota

Austin Tank Farm,

Cardon Refinery Plume scale 10's to 100's of feet

Petroleum Fingerprints Identify Contamination Products

In particular Presence of ethane, propane, and butanes are the most significant gases: <u>Ethane, propane are not generated biogenically</u> (test tube generation of biogenic gases) (Coleman age dates glacial till gases) <u>Salt Dome, no Ethane in Biogenic Gases</u>

Biogenic methane is not always bad, GreenCanyon Table Ethane enrichment

REGIONAL SOIL GAS SURVEYS CLEARLY DEMONSTRATE COMPOSITIONAL COHERENCE THAT CAN ONLY COME FROM DEEP SOURCE ROCKS <u>Raining Hydrocarbons</u> COLLECTION OF THOUSANDS OF SAMPLES OVER <u>ENTIRE BASINS</u> HAS SHOWN ITS NEARLY IMPOSSIBLE TO FIND CONTAMINATION WHEN SAMPLING ON A <u>REGIONAL GRID</u> CONTAMINATION PODS ARE VERY SMALL AND ALWAYS COMPOSITIONALLY UNIQUE

SOIL GAS IS SPECIAL CASE OF MUD LOGGING APPLICATION SEISMIC SHOTHOLE EXAMPLES

GREAT BASIN COMPOSITIONAL EXAMPLES

LAKE MARACAIBO SOIL GAS SURVEY

PLAYA VISTA EXAMPLE

Onshore/offshore Applications Examples/Pictures

Sampling and Analysis Techniques Basinwide Petroleum Systems Defined Compositional Correlations Prediction of Oil vs. Gas Thermal Maturity Variations Source Rock Variations

INDIRECT METHODS

Remote Sensing, PhotoGeology, Landsat, Hyperspectral Imaging <u>Microbiological Prospecting</u> Radiometrics, Micromagnetics, Iodine

METHODS THAT DON'T MAP MIGRATED GASES

Adsorbed Gases Petrex, <u>Gore</u>

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