

Chapter 5

LIGHT HYDROCARBONS FOR PETROLEUM AND GAS PROSPECTING

V.T. JONES, M.D. MATTHEWS and D.M. RICHERS

INTRODUCTION

Surface geochemical prospecting for hydrocarbons includes a myriad of techniques ranging from the direct detection of hydrocarbons escaping from subsurface accumulations and source beds to identifying secondary responses in the soils, rocks and biota in proximity to such accumulations or source beds. In the historical sense, the observation of visible seepage of hydrocarbons is the oldest method of prospecting for petroleum. Drake's historic well near Titusville, Pennsylvania, was drilled on the basis of a seep in the adjacent creek bed. The relationship of such "macroseeps" to reservoirs was well established by Link (1952), who stated: "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". In this respect, few would argue that the presence of a macroseep indicates the presence of petroleum migration or surface source beds. Microseeps, or smaller scale macroseeps, also occur because of the physical continuity necessarily imposed by nature. These are invisible seeps, usually detectable only by sensitive instruments or by the visible result of their effect on the near-surface environment. These microseeps, although perhaps not as obvious or dramatic as macroseeps, are just as valid for the exploration of undiscovered reserves. This chapter presents the conceptual and practical application of microseepage detection and interpretation in the evaluation of areas for their subsurface hydrocarbon potential.

Five factors are necessary to form a hydrocarbon reservoir. These are: (1) a source; (2) a reservoir in which the hydrocarbons can collect or concentrate; (3) a means of trapping these fluids in this reservoir (a seal); (4) a pathway to the reservoir (migration); and (5) the proper timing such that the source, reservoir, seal and migration pathway are present when required. Near-surface seepage of thermogenic hydrocarbons indicates the subsurface presence of a mature source and migration pathway. It also suggests that, if the hydrocarbons are reservoired, the seal is imperfect. This is true of both macroseepage and microseepage. Patton and Manwaring (1984) found that even in an area of extensive evaporites (Hugoton Field, Kansas), the seal was not perfect, and that microseepage could be detected in the vicinity of the Syracuse Fault.

Basically, surface geochemical prospecting is a source-rock tool applied at the surface. The magnitude of a microseep from a reservoir is related to the permeability of the migration pathway (and not to the economic worth of the reservoir). A surface geochemical survey is not currently, and perhaps never will be, a stand-alone prospect tool. However, with judicious use, this technology can provide information on the maturity of source beds in a basin and the composition of subsurface hydrocarbons. In addition, detection of surface microseepage allows mapping the surface expression of the migration patterns created by the expulsion of fluids as a basin compacts and matures. When used in conjunction with geophysical and geological information, geochemical data can refine subsurface models of hydrocarbon trapping and migration configurations. It is only through careful analysis and integration with other exploration tools that one can achieve the optimum benefits from this technology.

Near-surface hydrocarbon detection techniques have been shown in both the former USSR and the United States to be capable of distinguishing basins (or large portions of basins) that are unproductive from those that are productive, and of distinguishing the type of production (oil, gas, or mixed oil and gas). This ability has been independently recognised by Jones and Drozd (1979), Mousseau and Williams (1979), Janezic (1979), Weismann (1980), Drozd et al. (1981), Jones and Drozd (1983), Richers (1984), McCrossan et al. (1971), Richers et al. (1982, 1986), Horvitz (1985) and Klusman and Voorhees (1983). Surface geochemical techniques can select which of several frontier basins has the greatest chance of containing reservoired hydrocarbons, and the expected composition (gas, oil, mixed), in addition to high-grading portions of these basins that have the highest potential. The premise that microseeps occur and that they provide useful information for exploration is no longer questionable.

ORIGINS OF LIGHT HYDROCARBON GASES

Origin of petroleum

The formation of petroleum and natural gas from organic matter through increasing depth of burial and temperature has been very well established by many geochemical studies (Tissot and Welte, 1978; Hunt, 1979). As shown in Fig. 5-1, the generation of the light hydrocarbon gases, methane (C_1), ethane (C_2), propane (C_3) and the butanes (C_4), occurs in three main stages: diagenesis ($<50^\circ C$); catagenesis ($50-200^\circ C$); and metamorphism ($>200^\circ C$), in which only dry gas and ultimately graphite are formed. During the first stage bacteria acting under reducing conditions on organic substrates in sediments form predominantly methane. According to Hunt (1979), about 82% of the methane and practically all the heavier hydrocarbon gases are formed in the next, catagenic stage. Ethane, propane and the butanes are formed in the temperature range from $70 - 150^\circ C$ with peak generation occurring around $120^\circ C$. As shown in Fig. 5-1, a very large thermal methane peak occurs near $150^\circ C$.

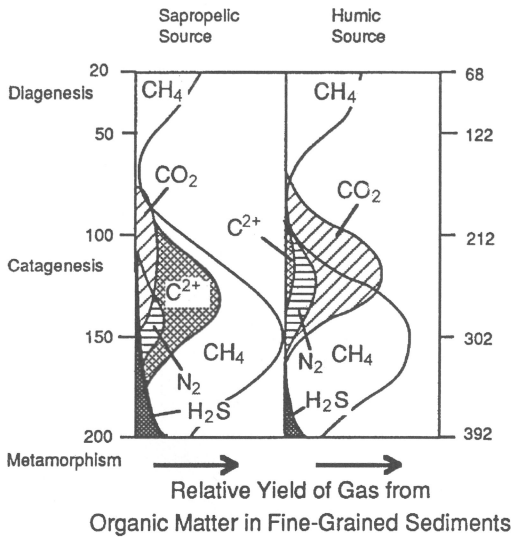


Fig. 5-1. Generation of gases with depth: C₂₊ represents hydrocarbons heavier than CH₄; N₂ is generated initially as NH₃.

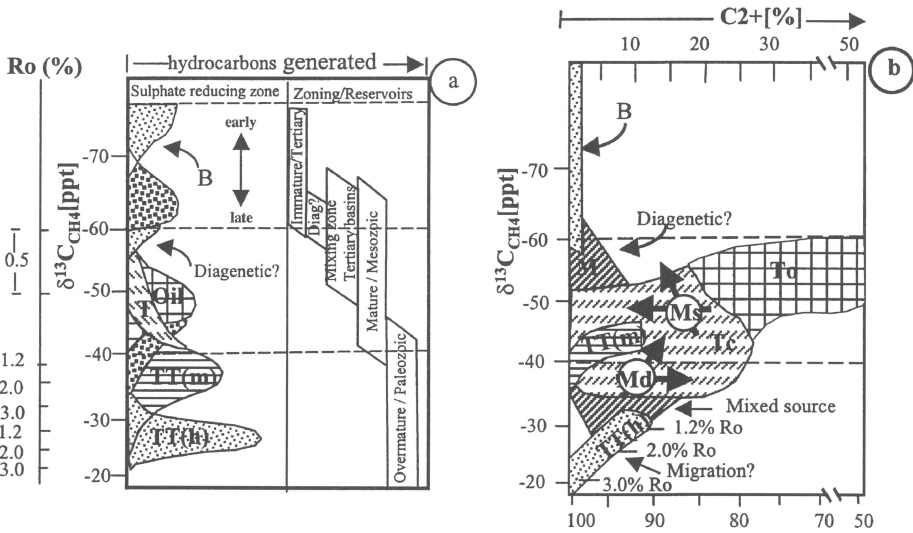


Fig. 5-2. Genetic characterisation of natural gases by compositional and isotopic variation: (a) formation of natural gas and petroleum in relation to maturity of organic matter; (b) relative concentration of C₂₊ hydrocarbons in relation to ¹³C in CH₄, with arrows indicating compositional changes due to shallow migration (Ms) and deep migration (Md) (reproduced with permission of the American Association of Petroleum Geologists, whose permission is required for future use, from Schoell, 1983, AAPG Bull., vol. 67, no. 12, Fig. 1, pp. 2226-2227, AAPG©1983).

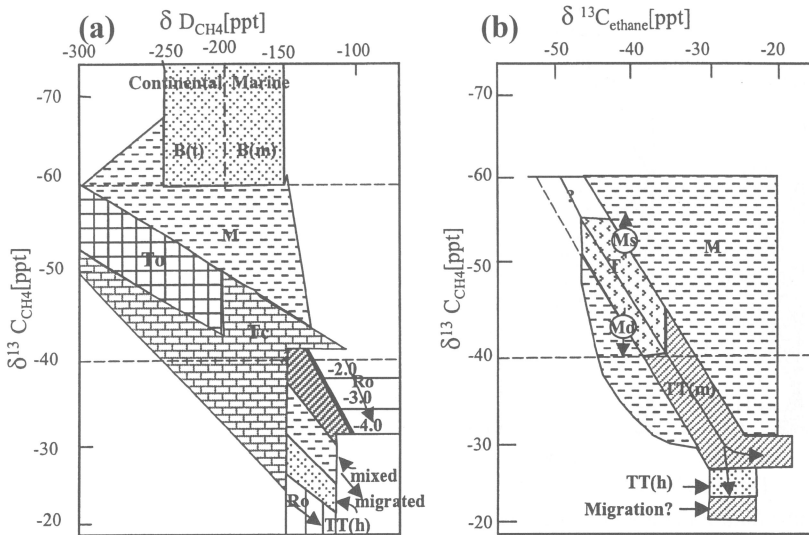


Fig. 5-3. Genetic characterisation of natural gases by isotopic variation: (a) relative concentration of deuterium and ¹³C in CH₄; (b) relative concentration of ¹³C in CH₄ and in C₂H₆, with arrow Md indicating the result of mixing with isotopically-positive CH₄ from depth, and arrow Ms indicating the result of shallow mixing with isotopically-negative CH₄ of biogenic origin (reproduced with permission of the American Association of Petroleum Geologists, whose permission is required for future use, from Schoell, 1983, AAPG Bull., vol. 67, no. 12, Fig. 1, pp. 2226-2227, AAPG©1983).

In addition to time, the quantity of gaseous hydrocarbons formed varies with the type of organic source material, which can be broadly classified as sapropelic (marine) or humic (terrestrial). As shown in Fig. 5-1, considerably more C₂-C₄ and other oil-type hydrocarbons are generated from sapropelic sources than from humic sources. In addition to the different volumes and types of petroleum (oil *versus* gas) produced from the two source materials, their carbon isotope compositions are different; terrestrial organic matter is reported to have lower ¹³C concentrations than marine organisms (Galimov, 1968; Silverman and Epstein, 1958).

The carbon isotope concentration of ¹³C, as compared to ¹²C, is also very useful for classifying natural gases as to their source type and/or maturity. Maturity is generally proportional to the depth of generation. Schematic diagrams published by Schoell (1983a, 1983b) distinguish the major natural gas types into three end members, as shown in Fig. 5-2. Schoell suggests that most natural gases are admixtures of these three basic end members. As shown in Fig. 5-3, further classification of reservoir gas types can be made from data for deuterium in methane and ¹³C in methane and ethane.

TABLE 5-I

Literature review of biogenic light hydrocarbon production (C₁-C₄)

Reference	Study
Coleman, 1979	Methane in glacial till gases: $\delta^{13}\text{C}_1$; C ₁ /C ₂ > 1000
Davis and Squires, 1954	Cellulose, ethanol and sewage fermentation: C ₂ -C ₄ < 2 x 10 ⁻⁵ %; C ₁ /C ₂ > 10 ⁵
Voytov et al., 1975	Swamp gases, glacial till gases, subsoil bacterial gases: C ₁ > 99%; C ₂ -C ₄ < 10 ⁻⁴ %; C ₁ /C ₂ > 10 ⁶
Kim and Douglas, 1972	Cellulose fermentation: C ₁ > 99%; C ₁ /C ₂ > 500; C ₂ -C ₄ < 10 ⁻² %
Stahl, 1974	Bacterial gases: C ₁ > 99%; $\delta^{13}\text{C}_1$ < -60‰
Bukova, 1959	Anaerobic bacterial decomposition, soil gases, sewage, silt: C ₁ > 99%; C ₁ /C ₂ > 1000

Origin of light hydrocarbon gases in the near-surface

The near-surface occurrence of ethane through butanes is of fundamental importance to the purpose of this chapter and to the usefulness of these gases as prospective indicators of buried natural gas and petroleum deposits. An extensive review of the literature suggests that C₂-C₄ hydrocarbons can be generated biogenically; however, solid proof exists only for methane and ethylene as major products of bacteria (McKenna and Kallio, 1965). A review of the literature shown in Table 5-I provides conflicting evidence for the biogenic occurrence of the C₂-C₄ hydrocarbons, although most of the literature suggests an abiogenic, thermocatalytic origin for these gases. Compositionally, however, these gases display large variations and do not resemble compositions characteristic of petroleum gases. All these studies are further characterised by methane:ethane ratios in excess of 1000 and a percent methane composition >99%, and are quite uncharacteristic of petrogenic gases. Some of the results reported before the invention of the gas chromatograph must be regarded with suspicion due to limitations of the analytical methods employed and possible sampling collection at locations contaminated by mixed biogenic and petrogenic gases. Russian researchers have illustrated that some of the earlier analytical methods, such as the combustion technique of Kartsev et al. (1959), can measure gases that are mistaken for hydrocarbons.

Laboratory and field evidence of biogenic C₂-C₄ hydrocarbons

Studies were conducted at Gulf Research & Development Company by Janezic (1979) to investigate the anaerobic microbial evolution of C₁-C₄ hydrocarbons upon decomposition of various organic substrates including green plant branches, grass

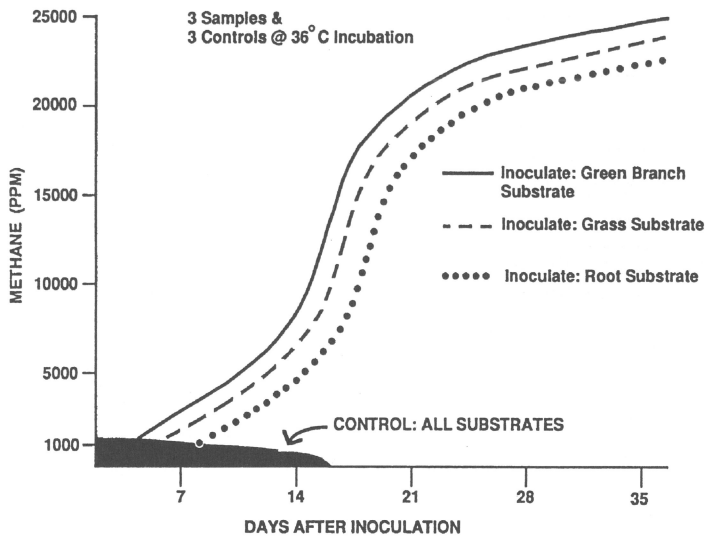


Fig. 5-5. Anaerobic microbial evolution of CH₄ upon decomposition of various organic substrates.

Another approach was that taken by Coleman (1979), who studied both the chemical and isotopic composition of glacial till gases in Illinois. Coleman obtained the same result, finding that C₂-C₄ gases are not present in the glacial till gases in Illinois. Coleman also determined ¹⁴C age dates on the gases and showed that the biogenic methane varied from about 10,000 years to as much as 40,000 years in age. This is particularly significant since it suggests that no bacterial generation of C₂-C₄ hydrocarbons occurs, either initially in test tubes or even within the first 40,000 years in glacial till.

TABLE 5-II

Generation of C₁-C₄ hydrocarbons *in vitro* (average concentrations, ppm)

Gas	36°C		25°C	
	Inoculate	Control	Inoculate	Control
Methane	14,862.000	3.416	4,814.000	2.003
Propane	0.081	0.073	0.051	0.050
i-butane	0.022	0.022	0.014	0.009
n-butane	0.055	0.060	0.038	0.033
Ethylene	5.101	1.670	2.310	0.434
Propylene	0.086	0.089	0.057	0.045

Distinguishing petrogenic and biogenic hydrocarbons

The results of the studies by Janezic (1979) and Coleman (1979) strongly suggest that C₂-C₄ hydrocarbons are not generated biogenically. Most of the previous studies cited appear to be compromised because they were conducted in natural environments in which migrated petrogenic gases might have also been present.

Even assuming that small quantities of C₂-C₄ gases are generated in biological environments, a methane:ethane ratio greater than 500 appears sufficient to delineate anaerobic gas production from thermocatalytic gases, since such ratios do not occur in petrogenic natural-gas deposits. As shown in the test-tube experiments (Table 5-II and Fig. 5-5), this value is achieved within two to three days for all substrates studied and exceeds 100,000 after seven days of incubation. Similar values are cited in the literature (Frank et al., 1970; Swinnerton and Lamontagne, 1974; Bernard et al., 1976; Sackett, 1977; Reitsema et al., 1978) as the biogenic threshold in marine geochemical prospecting (Table 5-III).

HISTORY

The first attempt to relate soil-gas hydrocarbon concentrations to oil and gas deposits was made in 1929 in Germany by Laubmeyer (1933). Surveying a known oil deposit, he collected samples of soil gas from systematically-located boreholes 1-2 m deep, after sealing them from the atmosphere for 24-48 hour periods. Using portable analytical equipment, he demonstrated that the samples over the deposits were enriched in methane. Soil-gas investigations were initiated shortly after this time in the then Soviet Union by Sokolov (1933), who verified Laubmeyer's results (Kartsev et al., 1959), but measured both methane and heavier hydrocarbons.

Research in the area of surface prospecting was also carried out in the United States during the 1930s beginning with Teplitz and Rodgers (1935), Rosaire (1938) and Horvitz (1939). These investigations entailed the collection and analysis of the soils

TABLE 5-III

Literature review of methane/ethane ratios diagnostic of biogenic origin

Reference	Diagnostic of biogenic origin
Davis and Squires, 1954	$C_1/C_2 > 500$
Reitsema et al., 1978	$C_1/C_2 > 500$
Frank et al., 1970	$C_1/(C_2+C_3) > 1000$
Bernard et al., 1976	$C_1/(C_2+C_3) > 1000; \delta C^{13} -50\%$
Sackett, 1977	$C_1/(C_2+C_3) > 1000; \delta C^{13} -50\%$

themselves for hydrocarbon gases. The use of adsorbed gas on soils was regarded as an important improvement upon soil gas, as short-term diurnal variations in soil-gas flux could be avoided by the assumption that soil would have a tendency to establish over time a metastable equilibrium with the regional flux.

Basic concepts

In the years following these early studies, the basic concepts have remained largely the same, except that detection limits have been improved with technological advances. Recent work has focused on compositional ratios or signatures of the light hydrocarbon gases and their relationship to known hydrocarbon products in the investigated area (Weismann 1980; Jones and Drozd, 1983).

Emphasis has also been placed on the fundamental principles of surface seepage, and the interpretation of the data. It is the opinion of the authors that the overall acceptance of microseep technology in the West has been hindered not only by the emphasis and success of seismic methods but also because of the lack of a comprehensive and public surface geochemistry database. There are, by comparison, more publications on geochemical survey data and basic concepts in the Soviet and Russian literature. As a consequence, many of our discussions rely on experience gained in the private sector in the West, supplemented by literature published in the East.

Although the Soviet/Russian literature is clearly positive about surface microseep technology, the Western literature is strongly divided. Debnam (1969) has reviewed several cases crediting geochemical prospecting with petroleum discoveries. Overall success rates are in the range 25-75%. Duchscherer (1980) reports a success rate of 25%, slightly over the industry average, of which 58% are stratigraphic traps. Sealey (1974a, 1974b) reported a success rate of 80% in Texas using a microbiological technique.

Methods of geochemical prospecting

Geochemical methods of prospecting are classified as direct or indirect. The direct methods involve detecting the presence of dispersed oil components in the form of hydrocarbon gases or bitumens in the soils, waters or rocks in the vicinity of oil and gas accumulations. The indirect methods involve detecting any chemical, physical, or microbiological changes in the soils, waters, rocks or vegetation spatially associated with the oil and gas deposits. Figure 5-6 is a schematic diagram outlining most of the direct and indirect methods currently in use (Kartsev et al., 1959).

Identifying secondary responses generated by leakage of hydrocarbons at the surface has merit and has been reported by many investigators. These include the use of (1) soil microbes (Soli, 1954, 1957; Kartsev et al., 1959; Sealey, 1974a; Sealey, 1974b); (2) reduction effects (Pirson et al., 1969; Donovan, 1974; Ferguson, 1975); (3) carbon and

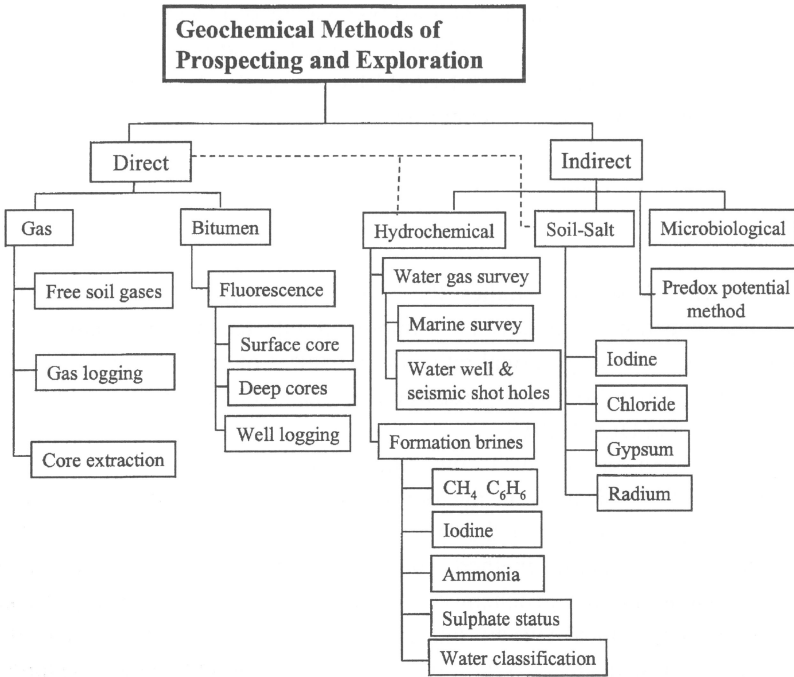


Fig. 5-6. Geochemical methods of prospecting for petroleum and natural gas (reproduced with permission from Kartsev et al., 1959, *Geochemical Methods of Prospecting and Exploration for Petroleum and Natural Gas*, copyright by the University of California Press).

oxygen isotopes (Donovan et al., 1974); and many other effects as reviewed by Matthews (1985).

As an exploration tool, the identification of hydrocarbon seeps is particularly useful when coupled with remotely-sensed images and photographs. Case studies by researchers in the West have shown that secondary indicators of microseepage are often present in the near-surface environment. Examples noted by Horvitz (1972), Donovan (1974), Donovan and Dalziel (1977), Matthews (1985) and Ferguson (1975) have indicated the presence of diagenetic alteration of soils above or adjacent to hydrocarbon accumulations. Work by Rock (1985), Matthews et al. (1984) and Patton and Manwaring (1984) has shown that these effects may often be reflected in the health and type of vegetation over the seep, which also alters the spectral response detected by satellite and airborne sensors. These methods of geochemical prospecting for oil and gas are reviewed in more detail in Chapter 7.

Others have noted changes in resistivity or radioactive signatures above accumulations due to the seepage and possible interaction of ascending fluids and solutions with the encapsulating medium. In some cases the actual removal or addition of soluble chemical species has been noted.

It appears therefore that the direct detection of hydrocarbon gases is not the only means of identifying areas of active microseepage, but that a myriad of other possible secondary techniques can be used either as adjuncts, or as solitary techniques in themselves, to infer the presence of hydrocarbons in the subsurface environment. Most of these utilise the detection and subsequent analysis of gaseous hydrocarbons, while other methods employ the detection and analysis of liquid hydrocarbons, non-hydrocarbon gases, the presence and relative concentration of bacteria, and even the presence (or absence) of inorganic compounds and elements. For the most part, however, methods that directly measure the hydrocarbon content of soils or soil atmospheres have met with the most acceptance.

PHYSICAL BASIS FOR MIGRATION OF HYDROCARBONS TO THE SURFACE

Basic assumptions

The fundamental assumption of near-surface hydrocarbon prospecting techniques is that thermogenic hydrocarbons generated and trapped at depth leak in varying quantities towards the surface of the Earth. That these hydrocarbons present in the near-surface environment represent the products of generation and migration from subsurface points of origin is a necessary conclusion that is universally accepted with respect to hydrocarbon macroseepage. Examples abound, such as the Santa Barbara Channel seeps, the La Brea Tar pits of Los Angeles, the Athabasca Tar Sands, etc. The same relationship has been equally well established, although less commonly accepted, for microseepage.

A further assumption is that the pattern and intensity of this leakage also provides information on preferential pathways that the leakage follows, and as such can be combined with additional geologic information to predict broad subsurface hydrocarbon fairways. In fact, in some instances it has been claimed that such data can identify areas of reservoired hydrocarbons. This last claim is often the subject of heated debate, however, commonly depending in which camp (for or against geochemistry) the explorationist resides.

The physical state of the hydrocarbons during transport is not well known; see Matthews (1996a) and Matthews (1996b) for a full discussion. Nevertheless, most of the models proposed for the transport of these fluids from source to reservoir (aqueous transport, micellar, discrete oil-phase transport, gaseous transport, etc.) are applicable to the continued transport of hydrocarbons from these source beds and/or reservoirs to the near-surface environment. An additional constraint on land is that the last stage of transport is generally above the water table. The physics of transport can be subdivided into two categories, effusion and diffusion.

Physical transportation by effusion

Effusion transport is believed to be the dominant mode of moving hydrocarbons to the reservoir and to the near-surface environment. The sharp localised nature of many anomalies associated with microseepage and macroseepage is more consistent with an effusion model rather than a diffusion model. The experience of the authors in monitoring leakage from gas storage reservoirs and controlled experiments where subsurface gas pressures were typical of true reservoirs suggests vertical transport rates of several metres (tens of feet) per day, clearly greater than the distances of migration dictated by the diffusion mechanism alone (Jones and Thune, 1982).

The sharp and often linear nature of anomalies suggests that faults and fractures play an important part in the movement of these gases. Major linear features discernible on satellite images, as well as other remotely-sensed media, from Patrick Draw, Wyoming, show such a relationship (Richers et al., 1982). The Lost River, West Virginia, Geosat study (Matthews et al., 1984) shows anomalously-high soil-gas values in relation to linear features on imagery. There are anomalously-high gas values along faults in the San Joaquin Basin and in the Wyoming-Utah Overthrust Belt (Jones and Drozd, 1983).

The Russians have shown that the magnitude of soil-gas values on faults increases dramatically shortly after an earthquake in which fault movement is involved (Zorkin et al., 1977). An extensive study, involving 105 observation wells, 3-5 m deep, was set up over the Mulcto oilfield in northeastern Salchalin. A total of 3,700 samples was collected and analysed over a four-month period with the most active wells sampled daily (Table 5-IV). The results from this study provide impressive evidence for the tectonic relationship of this leakage gas flux (Fig. 5-7). This study leaves no doubt that faults and fractures provide the main control on the effusion of gases from the subsurface.

Physical transportation by diffusion

Diffusion, on the other hand, is a slow and widely-dispersive process. Antonov et al. (1971) measured hydrocarbon diffusion coefficients for a variety of rock types from several hydrocarbon provinces in the former USSR. They discovered that the coefficients of diffusion vary over a wide range (10^{-3} - 10^{-8} cm²/s) depending on the particular lithology and geologic conditions.

The time required for diffusion to occur can sometimes be restrictive. Indeed the time required not only often exceeds the age of the hydrocarbon accumulation but also quite often exceeds the age of the host rock. If this were the dominant process for migration, then the appearance of soil-gas anomalies in the near subsurface would indicate only very shallow accumulations. If a non-steady state exists, where the hydrocarbon signal observed represents only 0.001 times the steady-state signal, then diffusion times could be reduced by a factor of 25 compared to that of the steady-state model. Table 5-V

TABLE 5-IV

Gas concentrations in the near-surface rocks before earthquake and (in italics) after earthquake

Date	Strength of shock	Distance from CPI center to deposit (km)	Well No.	Time of sampling days*	10 ⁻⁴ Vol percent (ppm)	10 ⁻⁴ Vol percent (ppm)	Vol percent	Percentage of hydrocarbon fraction of gas
09.09.1974	K=9	100	8	6	135.40	1.90	0.00	98.56
				3	<i>283.70</i>	<i>4.20</i>	<i>0.00</i>	<i>98.50</i>
08.04.1975	M=4	12	8	2	73.60	0.81	0.53	98.35
				4	<i>213.50</i>	<i>2.34</i>	<i>1.22</i>	<i>98.96</i>
24.05.1975	K=6.2	25	8	2	188.50	3.18	3.10	98.50
				1	<i>525.00</i>	<i>2.52</i>	<i>7.10</i>	<i>99.50</i>
04.07.1975	K=7.2	9	8	1	152.00	7.36	17.80	95.50
				2	<i>852.00</i>	<i>8.85</i>	<i>15.70</i>	<i>98.97</i>
08.07.1975	K=7.5	25	11	5	935000.00	11908.70	0.09	98.70
				2	<i>954000.00</i>	<i>12465.00</i>	<i>0.26</i>	<i>98.70</i>
05.10.1975	K=9.5	100	8	6	58.80	3.80	26.80	93.90
				1	<i>396.00</i>	<i>5.80</i>	<i>33.60</i>	<i>98.60</i>
		100	61	5	256000.00	1273.00	3.60	99.54
				1	<i>273000.00</i>	<i>1399.00</i>	<i>4.20</i>	<i>99.54</i>

* From the onset of shock

shows some of the times that this scenario would require. However, diffusion can still be considered as a potential secondary process in microseepage.

Sokolov (1965) calculated diffusion to be sufficient to have resulted in the dissipation of oil fields formed in the Palaeozoic, although to what extent, if any, this has occurred is not known. Furthermore, if any such fields had leakage along faults and fractures or due to erosion of the seal, diffusion might not be able to bring about accumulation before much faster effusive loss caused depletion. Diffusion of benzene into brines adjacent to accumulations has been demonstrated and used as an exploration tool by Zarella et al. (1967).

In productive basins the process of diffusion from both source rocks and reservoirs may be responsible for observed elevated background concentrations that have no apparent relationship to the known accumulations. Alternatively, the presence of free hydrocarbons effusing outward and upward in areas of microfractures and dispersed by groundwater flow could similarly account for this background. If diffusion were the

TABLE 5-V

Hydrocarbon diffusion times (minimum years) through sediments of different thickness (Antonov, 1971)

Diffusion coefficient (cm/sec)	Steady state			Non-steady state		
	1000 m	2000 m	3000 m	1000 m	2000 m	3000 m
5×10^{-5}	4.9	20	44	0.2	0.7	1.6
1×10^{-5}	24	98	220	0.9	3.6	8.1
5×10^{-6}	49	195	440	1.8	7.2	16
1×10^{-6}	244	976	2200	9.8	36	81
5×10^{-7}	488	1950	4400	18	72	162
1×10^{-7}	2440	9760	22000	90	360	810
5×10^{-8}	4880	19500	44000	180	720	1620
1×10^{-8}	24400	97600	224000	900	3600	8100

responsible mechanism, then one might expect broad anomalous zones, with localised effusive "spikes" superimposed on the background. Starobinetz (1983) listed as typical examples of diffusion the studies of Driepro-Douetsk and Anuddria grabens.

Aside from the potential of diffusion for producing a broad dispersive background, it would also be expected to alter the composition of the gases detected in surface methods. Starobinetz (1983) notes that not only can diffusion affect composition, but two additional processes have a similar effect. These are chromatographic separation and selective adsorption.

An example of such chromatographic separation is shown in Fig. 5-8 (Sokolov, 1971b), which shows the results of a mixture of methane and benzene injected into the bottom of a hand-bored 6-metre deep well. Samples of subsoil air were taken periodically from observation wells 1-2 m deep, resulting in the obvious separation shown in Fig. 5-8. Indeed these processes have been cited by detractors of surface prospecting as evidence that the technique is not a valid means of searching for subsurface hydrocarbon deposits, arguing that pulses (non-steady state) of gases will have a different composition from their source because of the chromatographic separation. The example shown in Fig. 5-9, taken from an artificial underground coal gasification experiment near Rawlins, Wyoming (Jones and Thune, 1982), shows that such effects are only temporary. In this experiment, a pulse of gas travels from a retort at a depth of 180 m (600 feet) and migrates vertically and laterally to a series of observation wells 5.5 m (18 feet) deep. As shown in Fig. 5-9, although the first gas to be seen in high concentrations is methane, the compositional separation does not last more than a few days before equilibrium is achieved, when all the migrating gases have ultimately reached the surface.

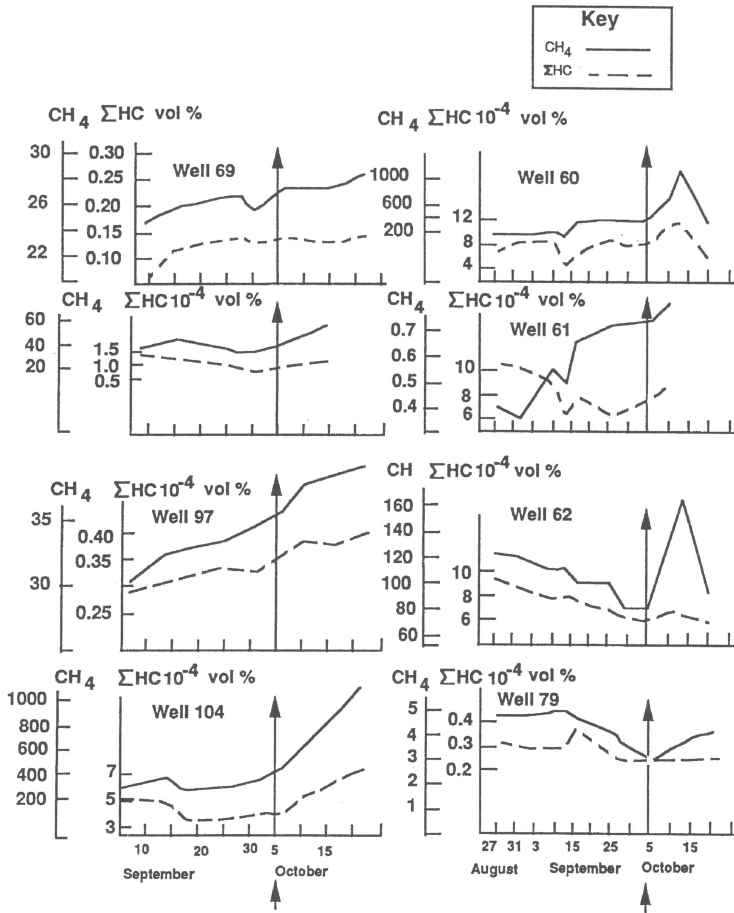


Fig. 5-7. Methane and total hydrocarbon gases in subsoil before and after an earthquake (reproduced with permission from Zorkin et al., 1977).

As to the second point, if selective adsorption is occurring, the volumes of material escaping over geologic time should ultimately saturate (poison) the adsorber such that no additional material can be adsorbed, or at best, material is exchanged in a steady-state. The result will be a gradual return of the signal to the original composition. This is clearly shown in a study by Zorkin (1977a).

There is, however, one important area where diffusion may be responsible for compositional changes; near the soil-air interface. Methane should, due to its lightness and zero net dipole moment, be preferentially lost (followed perhaps by ethane). This would possibly result in an oilier gas signal at the surface. This could be countered by the production of biogenic methane, which might partially compensate for this loss.

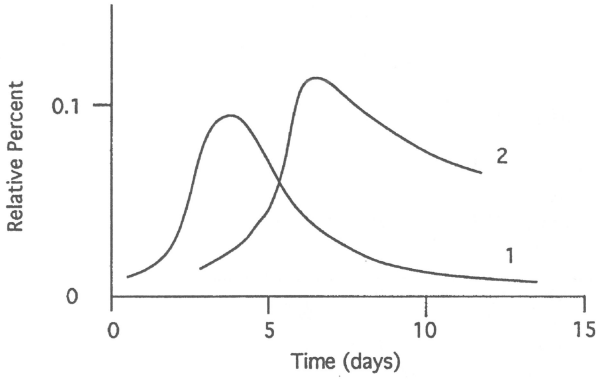


Fig. 5-8. Differentiation of methane (1) and heavy hydrocarbons (2) during migration from an artificial source (from Sokolov, 1971b).

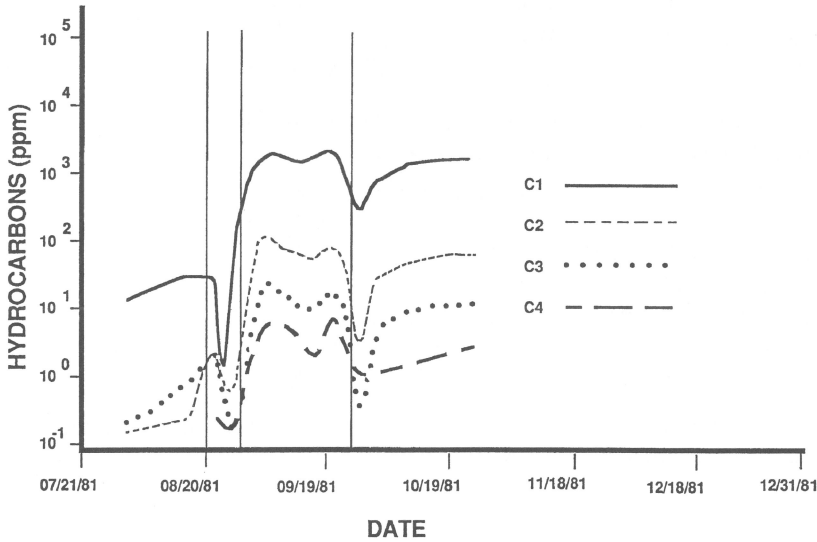


Fig. 5-9. Arrival at a surface well of hydrocarbon gases following a subsurface coal-burn experiment at Rawlins, Wyoming (reproduced with permission of the Society of Petroleum Engineers from Jones and Thune, 1982, Surface detection of retort gases from an underground coal gasification reactor in steeply dipping beds near Rawlins, Wyoming, SPE 11050).

HYDROCARBON RESIDENCE SITES AT SURFACE

The most important of the direct techniques shown in Fig. 5-6 involve the measurement of light hydrocarbons, methane through butane. Because of their volatility, these light hydrocarbons are generally found in the free pore space. The seepage of

hydrocarbons into the near-surface environment above the water table must involve transport through both water-filled and air-filled pores. Sampling these pore gases is obviously one of the most fundamental concepts. However, gases can be bound in the sediment matrix. This latter possibility leads to the development of some disaggregation and desorption extraction techniques.

Discussion of sampling techniques must involve both "free" and "bound" gases. To facilitate this discussion the collection, measurement and analysis of light (C_1 - C_4) hydrocarbons will be broken into two main categories each with two subcategories: (1) free gas, which can be vapour or dissolved gas; and (2) bound gas, which can be adsorbed gas or chemi-adsorbed gas.

Free gas

Gases in the free pore space can be found either in the vapour state or dissolved in water. Extensive research at Gulf Research and Development Company has demonstrated that the "free" and "dissolved" gas seeps yield comparable compositional results, both to one another and to their associated reservoirs when they are properly collected and analysed (Teplitz and Rodgers, 1935; Jones, 1979; Janezic, 1979; Mousseau and Williams, 1979; Weismann, 1980; Drozd et al., 1981; Williams et al., 1981; Jones and Drozd, 1983; Richers, 1984; Price and Heatherington, 1984; Matthews et al., 1984; Jones et al., 1984). This documentation even extends to numerous observations over artificial underground gas generation and storage reservoirs (Jones and Thune, 1982; Jones, 1983; Pirkle and Drozd, 1984).

Sampling of vapour can be extended to any depth above the water table by analysing the exhaust air from an air-drilled well. Complications occur because of dilution effects by the air injected for drilling and by the additional fact that the drill bit disaggregates and liberates rock or matrix gas in the process of drilling the hole.

Dissolved gases must be extracted from the aqueous system before analysis. This is usually accomplished by a simple gas-water partition into a vapour phase followed by standard headspace measurement techniques (McAuliffe, 1966). Alternatively a so-called "stripper" continuously partitions the dissolved gases into a carrier gas which is then sent to a gas chromatograph for analysis (Mousseau and Williams, 1979; Aldridge and Jones, 1987). These separations are aided by the very low solubility of the light hydrocarbon gases.

Standard mud gas logging is one variant of dissolved gas analysis conducted on deeper drill holes. A gas trap is deployed in the return mud system for extracting the dissolved and free gases. Compositional information obtained from mud logging gas is useful for predicting the composition of a potential reservoir (Pixler, 1969). These same ratios have been found to be indicative of oil *versus* gas potential from surface seeps observed from 4 m (12 feet) deep soil-gas measurements or from analysis of gases dissolved in the shallow groundwater (Jones and Drozd, 1983).

Bound gas

Bound gas, which is adsorbed on both the organic and inorganic matter contained in the sediment by means of physicochemical binding, introduces new complexities into defining the appropriate sample for analysis. The difficulty with defining this bound gas is forced by the reality that rocks and/or sediments contain gases of multiple origins. By their very nature, sediments contain both migratory (epigenetic) and indigenous (syngenetic) gases. Migratory gases (biogenic and thermogenic) have migrated to the surface from a deeper, more concentrated source.

Indigenous gas is related to biogenic, diagenetic and thermogenic generation within the rock sampled at the surface and to recycled materials which may contain some physically-transported hydrocarbons tightly bound in inclusions or other interstitial sites within the sediment matrix. The nature of the bonding of the hydrocarbons to the grain surfaces leads to two categories, adsorbed and chemi-adsorbed. These form an important part of this discussion because of misnomers involved with the use of the word "adsorbed".

True adsorbed gases are by definition bound to the surfaces of sediment or rock particles. As defined by Greenland (1981) adsorption is the process by which a chemical species passes from one bulk phase to the surface of another, where it accumulates without penetrating the structure of the second phase. Because the light hydrocarbons are so labile, they do not strongly adhere to surfaces and are easily desorbed if the source of these gases is removed. The gas must be replenished by continuous migration in order to maintain the presence of adsorbed gases on the available surfaces.

Bound within the rock matrix, or within certain minerals (calcite, oxide coatings, etc.) gases are chemi-adsorbed. They can be removed only by a chemical attack that completely dissolves the rock or sediment matrix. Sometimes these more tightly-bound gases not only include indigenous gases, but also might integrate the signal over time, mixing the products of "dead" or "non-active" seepage with those gases actively migrating today. The non-active seeps are often coupled to the lithologies of transported, non-residual sediments (Richers et al., 1986). These last considerations provide two of the main reasons why "free" and "chemi-adsorbed" gases are often found to have no obvious spatial correlation.

Choice of free gas or bound gas

Any prospector would generally agree that it is desirable to measure only the gas which has migrated from depth, since this is clearly the gas signal which is related to buried reservoirs. The difficulty in doing this begins with choosing the method of sample collection, because there are few sample-collection techniques that do not mix the syngenetic and epigenetic gases. Both "free" and "adsorbed" hydrocarbons can often be related to a migratory source, and thus can yield useful exploration information. The free

gases appear to be dominated by the migratory gases, unless samples are taken within an outcropping source rock. In addition, the free gases also contain any biological gases which, because of their recent generation, also occur in the free state. If source rocks or recycled source-rock materials are present near surface, then the "adsorbed" gases can obtain a major contribution from these sources. Exclusions are often provided by sampling in areas where calcite concretions have been deposited from carbon dioxide generated by biological oxidation of seepage hydrocarbons. This is one reason why adsorbed gas has been successful in marine offshore environments. A good example is provided by studies of the Green Canyon macroseeps (Anderson et al., 1983; Pirkle, 1985).

If one can assure that only migratory gas is measured, then the type of gas measured is unimportant. Including indigenous (syngenetic) gas results in misleading measurements. This is believed by the authors to be one of the primary causes of failure in the application of surface geochemical prospecting. Failure to collect a properly-distributed data set can be equally misleading and result in an incorrect interpretation, since interpretations will always be the educated guesses of an explorationist.

Any measurement on a real-world sample is always a combination of the free and bound gas sample types. This is because the process of taking the gas sample generally requires that the sediment or rock system is disturbed by some mechanical means which creates the mixing of these sample types. Because of this unavoidable interaction, we have recognised the need to consider an intermediate sample-collection technique that measures the more loosely-bound gases liberated into a container containing the core sample.

Sampling gases that accumulate within the gas-filled "headspace" of a core-sample container is potentially flawed because of the obvious losses encountered in transferring a sample to a container. This is further compounded by the difficulty in achieving a rapid and total equilibration of the core gases into the headspace. An alternative technique for measuring the loosely-sorbed gas has been proposed by Hunt and Whelan (1979), in which the headspace equilibrium is obtained mainly by mechanical disaggregation and heat. In our opinion, this disaggregated gas should more properly be called "adsorbed" gas. The truly "free" gas is always lost (or at least greatly diminished in volume) from any sample of core that is brought to the surface for collection and handled before being put into a sample container (Sokolov, 1971b). Typical losses are shown in Table 5-VI.

This mechanically-disaggregated gas has been usefully applied as a bridge to relating the free and bound gas (Richers et al., 1986). Simple mechanical disaggregation always liberates a considerable volume of gas which, if handled properly, has a predictably oilier composition than the associated free gas. This change in composition, created by fractionation of the lighter components, is demonstrated later in examples under case studies.

TABLE 5-VI

Generation of C₁-C₄ hydrocarbons *in vitro* (average concentrations, ppm)

Rock type	Depth (m)	Hydrocarbon concentration, C (10 ⁻⁴ cm ³ /kg)		Relative loss, C _{kc} / C _{open}
		Sealed kc sampler	Open-hole sampler	
Sandstone	385	106243	119	893
Shale	575	2431	52	47
Shale	620	1610	35	46
Sandstone	640	36473	69	529

FACTORS INFLUENCING NEAR- SURFACE HYDROCARBON FLUX

The hydrocarbon flux near to the surface varies according to the supply of hydrocarbons and whether local chemical and biological conditions favour their preservation or breakdown. In addition, hydrocarbon magnitudes at any given location vary with time because of displacement by wind, rain and barometric pumping (Wyatt et al., 1995).

Microbial activity

In a very extensive review, Price (1985) suggested that surface bacterial activity can totally obliterate the gases in a microseep. That this is not typically the case has been demonstrated by extensive research over both macroseeps and microseeps (Jones, 1984). However, bacterial activity does probably contribute to the noisy appearance of soil-gas seepage.

Barometric pumping

An example of gas flux related to barometric pumping has been demonstrated over an underground propane-storage reservoir. This mined cavern is about 60 metres (200 feet) deep. In order to observe the gas flux related to atmospheric phenomena, plastic ground sheets about 1.5 x 1.5 m (5 x 5 feet) were buried along their edges to contain any gas flux. The variation with rainfall is shown as vertical bars in Fig. 5-10. A very large seepage anomaly is shown by the dashed line at the right edge of the first bar. The rain probably displaced the gas in the ground and caused it to come up underneath the ground sheet. However, the same effect is not repeated every time it rains. Around the 19th, 20th, 21st and 22nd days of the month very small barometric changes were observed. Nevertheless, small barometric lows have clearly-expressed gas-flux increases. Thus falls in barometric pressure lead to a gas flux that escapes into the atmosphere. This

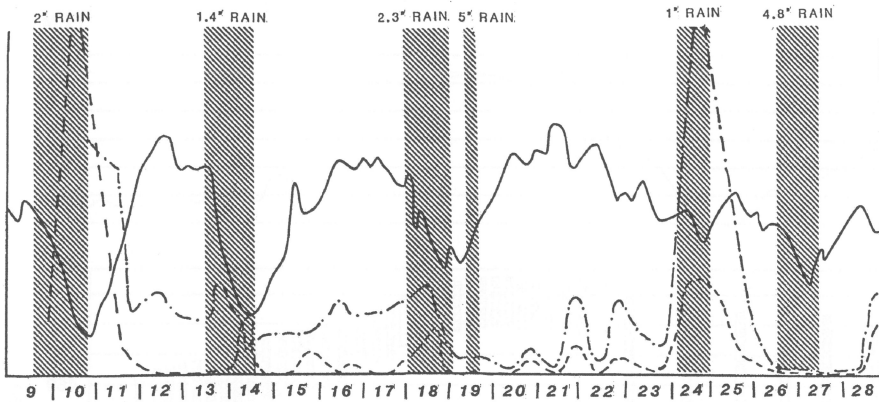


Fig. 5-10. Changes in flux of propane concentration (dashed lines) with barometric pressure (solid line) and rainfall (shaded bars) at two surface sample sites over an underground propane-storage reservoir; horizontal scale shows days of month.

escape occurs despite the extensive microbiological activity that has developed over this cavern.

As shown in Fig. 5-11, a propane profile collected over the top of the cavern requires a log scale to illustrate the enormous range in gas leakage flux. An interesting secondary observation taken from this example is the obvious colour changes noted on the soil cores. These chemical changes are related to hydrocarbon seepage and might be used as an additional exploration tool to provide evidence of where the gas leakage has occurred around any type of storage cavern. The soil changes from red-brown to green-black directly over the top of the cavern, where the largest seepage anomalies occur.

Thus the main difficulty with atmospheric sampling is created by meteorological changes which can greatly displace and dilute the seepage emissions. In addition, it is clear that the stress fields in the Earth can also influence this gas flux significantly.

Earthquakes

The fact that earthquakes may sometimes be preceded by geochemical anomalies was discovered at about the same time in Japan (Okabe, 1956) and the then USSR (Fursov, 1968). Earthquake prediction studies in Russia, Japan and China include extensive geochemical measurements. Chinese geochemical data are reported to have contributed, at least partly, to the successful prediction of several strong earthquakes (Allen et al., 1975). In contrast, the Earthquake Hazards Reduction Program in the United States emphasises mainly geophysical data.



Fig. 5-11. Propane concentrations and soil colour of augered samples along a traverse of sample sites over an underground propane storage reservoir.

Limited programmes using radon for earthquake prediction began in the United States about 1975, at about the same time as Gulf Research and Development Company first made measurements on light hydrocarbons, helium and hydrogen on the San Andreas Fault in the Cholame Valley in California (Jones and Drozd, 1983). This study confirmed that helium is a deep-basement or tectonic indicator which is commonly independent of oil and gas deposits. This is clearly illustrated in Fig. 5-12, in which helium anomalies appear to be associated with the San Andreas fault and with two other deep-basement faults. The proposed deep fault on the west flank of the Lost Hills oil field also acts as a common migration pathway for hydrocarbon gases (Fig. 5-13). This initial study, and the joint research programme subsequently initiated by Gulf Research and Development Co. with the Cal-Tech earthquake radon programme, was designed to obtain data concerning the rates of change of gas flux associated with tectonic stress in the Earth.

Numerous other examples of gas flux related to earthquakes have been reported, for example, by Kartsev et al. (1959), Fursov et al. (1968), Elinson et al. (1970), Sokolov (1971b), Ereemeev (1972) Ovchinnikov et al. (1972), Zorkin (1977b), Melvin et al. (1978), Wakita et al. (1978, 1980), Barsukov et al. (1979), Borodzich et al. (1979),

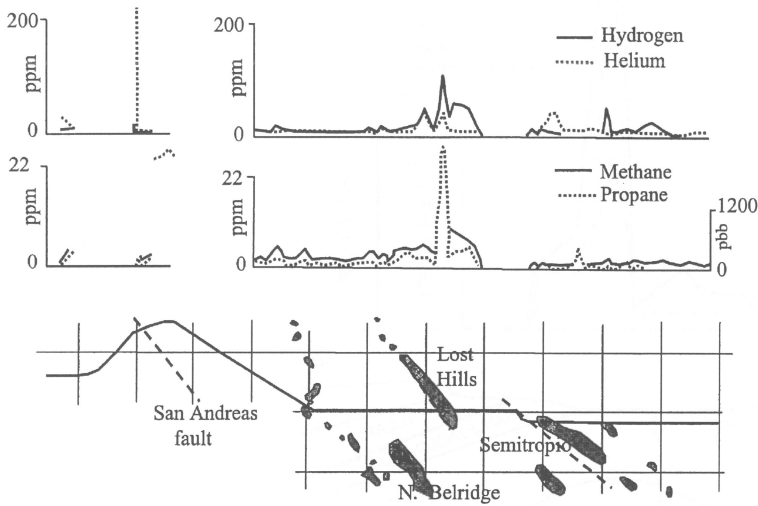


Fig. 5-12. Relation of near-surface gases to deep faults and oil fields along a traverse in the Cholame Valley, California (reproduced with permission of the American Association of Petroleum Geologists, whose permission is required for future use, from Jones and Drozd, 1983, AAPG Bull., vol. 67, no. 6, Fig. 12, p. 942, AAPG©1983).

Mamyrin (1979), King (1980b), Reimer (1980), Shapiro et al. (1981, 1982), Mooney (1982) and Pirkle and Jones (1983). Particularly intriguing examples have been published by Antropov (1981) of atmospheric methane flux related to petroleum deposits (Fig.5-14) and seismic shock (Figs. 5-15 and 5-16). These measurements were made with adsorption-type gas lasers: one type makes point measurements of the sample in an adsorption tube (Iskatel-2); the other (Luch) measures the specific gas adsorption along a path length (1-100 m).

SAMPLING AND MEASUREMENT METHODS

There are a variety of sample collection and hydrocarbon analysis methods use in geochemical surveys for oil and gas deposits. In the case of free gas, samples are collected either in the atmosphere or, more usually, within the soil. For bound gas soil or rock is collected and the gas is liberated by one of several methods. In practice, however, it is rarely possible to determine solely free gas or solely bound gas.

Atmospheric techniques

The detection of hydrocarbons above the ground surface offers obvious advantages: continuous sampling, no permit requirements, access over rough and hostile

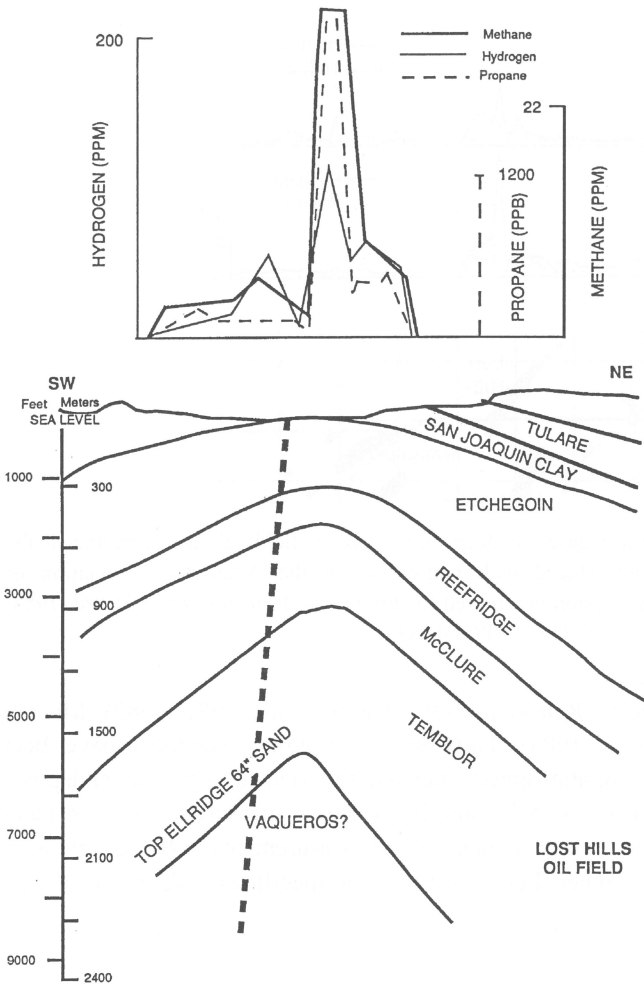


Fig. 5-13. Relation of near-surface gases to proposed deep fault adjacent to Lost Hills oil field, San Joaquin Basin, California (reproduced with permission of the American Association of Petroleum Geologists, whose permission is required for future use, from Jones and Drozd, 1983, AAPG Bull., vol. 67, no. 6, Fig. 13, p. 943, AAPG©1983).

environments, large areas covered rapidly. A drawback is that diffusive and convecting mixing in the atmosphere decreases the signal strength with distance from the sediment or soil surface. Nevertheless, the capability of detecting gases in the atmosphere has seen significant developments over the past 10-15 years. Research has resulted in the development of approaches based on microwave energy, infrared lasers and adsorbed hydrocarbons on aerosols carried into the atmosphere by thermals.

The microwave approach has been developed by Owen (1972), Gournay (1979) and Thompson (1981). Although Thompson (1981) has stated that "conclusive proof does

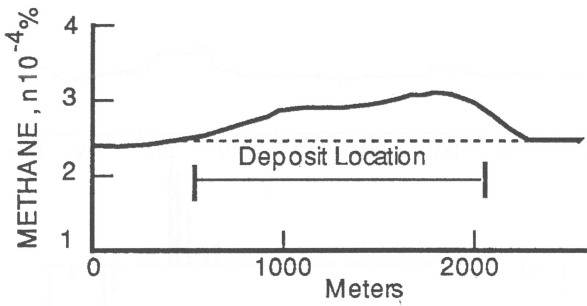


Fig. 5-14. Variations in methane concentration in air above a petroleum reservoir (from Antropov, 1981).

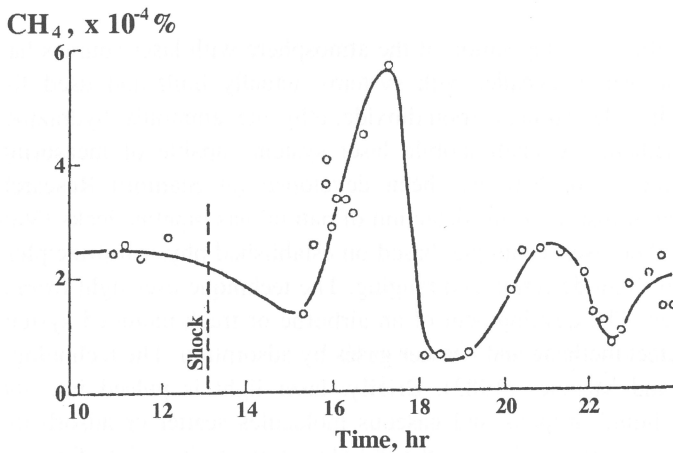


Fig. 5-15. Variations in methane concentration in air as a result of seismic shock to the ground (from Antropov, 1981).

not exist that the gases being detected by the sensor are low molecular-weight hydrocarbons and nothing else", he has published numerous positive case studies relating the response of one of these instruments to soil gas probe anomalies (Burson and Thompson, 1985). Additional technical difficulties result from the fact that microwave adsorption energy levels represent rotational energy in the molecule. Deactivation of rotational energy by collisions can occur rapidly at atmospheric pressure, causing the molecule excited by the microwave energy to lose its adsorbed energy in a non-emission mode, thus reducing the signal-to-noise ratio. This coupled with the low concentrations of hydrocarbons in the atmosphere has meant that the technique has not been extensively tested as an exploration tool.

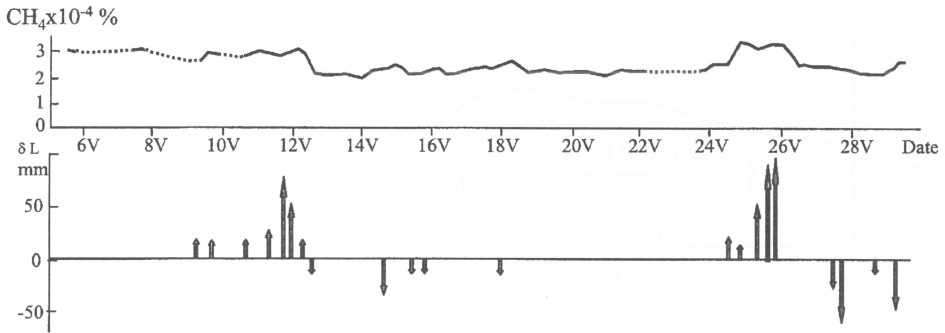


Fig. 5-16. Variations in methane concentration in air with crustal displacement in a seismically-active region (from Antropov et al., 1981).

Remote monitoring of the gas composition of the atmosphere with laser sources has been actively pursued for over a decade, with systems actually built and used for nitrogen dioxide, sulphur dioxide, ozone, carbon dioxide, ethylene, ammonia, hydrazine, hydrogen fluoride and methane. A small mobile laser system capable of measuring methane and ethane in the atmosphere has been developed (at Stanford Research Institute for the Gas Research Institute) for detection of natural gas pipeline leaks (Van de Laan et al., 1985). Another laser technique, based on established physical principles, is LIDAR, which stands for light detection and ranging. The technique uses light from a tuneable infrared monitored. The development of an airborne or truck-mounted system CO_2 laser to selectively detect methane and heavier gases by adsorption. The technology was reviewed by Grant and Menzies (1983). Briefly, laser light is pulsed into the atmosphere and aerosols, liquid droplets and gaseous molecules scatter or adsorb the light in different ways. Some portion of the scattered light returns to its point of origin, where a telescope-like receiver channels it to a photodetector, which produces an electrical signal proportional to the optical radiation received by the telescope. The length of time between transmission and reception indicates from what distance the light was scattered and the intensity of the electrical signal indicates the concentration of the particles or molecules being capable of range resolving the location and concentrations of an atmospheric gas cloud will provide an extremely efficient and cost-effective exploration tool for detecting both macroseeps and microseeps in frontier regions.

The third atmospheric technique analyses the residual liquid and/or condensate hydrocarbon traces on aerosols carried into the atmosphere by thermals (Barringer, 1981). The aerosols are created by gas bubbles which exsolve into the atmosphere from the sea in areas where microseeps create gas bubbles which reach the sea surface. The aerosols are concentrated from large volumes of air and collected by an airborne cyclone sampler carried aboard an aircraft which is flown at 30 m (100 feet) above the sea surface. Hydrocarbons adsorbed on the aerosols are measured by a flame ionisation detector which yields a total hydrocarbon signal. This system is claimed to produce

detector which yields a total hydrocarbon signal. This system is claimed to produce direct vertical anomalies over reservoirs at depth. This technology appears reasonable for detection of seepage which is large enough to produce free gas bubbles, but for feeble seepage (i.e., below water solubility levels) the effectiveness would seem to be reduced by dispersion due to underwater currents.

Soil gas

The hydrocarbon gases migrating through soil pore spaces are not dissipated and diluted to the same extent as those in the atmosphere. There are, however, problems posed by the very low levels of hydrocarbon gases and by the diurnal "breathing" of many near-surface soils. In order to overcome these problems, soil-gas techniques which integrate the hydrocarbon signal were introduced by Pirson (1946), Horvitz (1950), Kartsev et al. (1959), Karim (1964), Heemstra et al. (1979), Hickey (1983), Hickey et al. (1983) and Klusman and Voorhees (1983).

Karim (1964) published data on laboratory adsorption studies for light hydrocarbons using activated charcoal, molecular sieve (diatomaceous earth) and silica gel. As shown in Table 5-VII, these substrates greatly increase the concentrations available for analysis, but selective adsorption severely affects the relative compositions of the individual gases. The lightest gases are obviously not as effectively trapped by adsorption techniques as are the heavier, less volatile components. This is particularly true for methane and ethane. The adsorption capacities of the substrates are also strongly reduced by moisture content, which may vary from site to site, particularly since the sampling is conducted in the ground where moisture content varies more rapidly than in the atmosphere.

Klusman and Voorhees (1983) introduced a variation of this technique which uses sample collection on charcoal wire over extended collection times, followed by analysis using a quadrupole mass spectrometer. The advantages cited are lower field expenses, increased field mobility, improved signal-to-noise ratio and negation of barometric and other meteorological factors. Major drawbacks are that the most mobile light gases are not collected by the charcoal wire, so that the samples comprise mainly the intermediate to heavier molecular-weight components, which include butane through gasoline and diesel. Multivariate statistical techniques are required to interpret the large number of mass peaks recorded, which includes both parent and multiple daughters. In some cases qualitative information based on fragment patterns of the adsorbed compounds is possible (Fig. 5-17). However, different molecular species and their fragment patterns overlap; for example, propane and carbon dioxide have identical masses (44) and thus cannot be separated. The exploration value of these data lies in the demonstrated presence of reservoir-type hydrocarbons at the surface and the composition noted in the lighter to heavier fragment patterns.

TABLE 5-VII

Concentrations of hydrocarbons adsorbed by different adsorbents

Tube Length	Hydrocarbon concentration (ppm)						Total	Ratio to source*
	Methane	Ethane	Propane	i-butane	n-butane	Pentane		
<u>Activated carbon Columbia G</u>								
3 in	5	10	21	30	33	35	134	22.3
8 in	11	21	43	59	64	71	269	44.9
12 in	19	36	72	99	108	120	454	75.7
18 in	29	53	109	143	160	178	672	112.0
<u>Molecular sieve 4A</u>								
3 in	8	40	52	3	67	73	243	40.5
8 in	12	60	80	5	100	110	367	61.2
12 in	13	67	89	6	110	130	415	69.2
18 in	14	71	93	7	129	152	466	77.7
<u>Molecular sieve 5A-13X</u>								
3 in	8	44	62	78	82	97	371	61.9
8 in	12	67	100	120	125	122	546	91.0
12 in	15	81	127	143	149	146	661	110.2
18 in	16	83	129	151	150	153	682	113.7
<u>Silica Gel</u>								
3 in	8	4	14	11	13	12	62	10.3
8 in	33	17	60	43	61	50	264	40.4
12 in	61	32	110	81	109	94	487	81.2
18 in	109	65	193	141	190	163	861	143.5

* Total adsorbed hydrocarbon concentration / hydrocarbon concentration in source gas

The difficulty in interpreting this particular type of data is further compounded by its application in the upper soil zone where the most active plant and microbiological activity takes place. Many organic and inorganic compounds (humic acids CO₂, N₂O, NO₂, etc.) are produced in this zone, all of which are rapidly adsorbed by activated charcoal. These compounds are present in macro concentrations (parts per thousand to percent) and produce fragment patterns which overlap the much lower concentrations of hydrocarbons, which are generally in the ppm range.

Another consideration in using adsorbents is the residence time required for the collector in the soil medium. Care must be taken to ensure that the entire survey area is sampled for the same time interval. Also, each region has its own unique flux rate which will affect the results. In a region with a low flux, the collectors should be left buried in the soil for a longer period of time than collectors in a region of higher flux. An orientation survey should always be designed to establish the proper length of time required to obtain valid data prior to conducting a large scale survey.

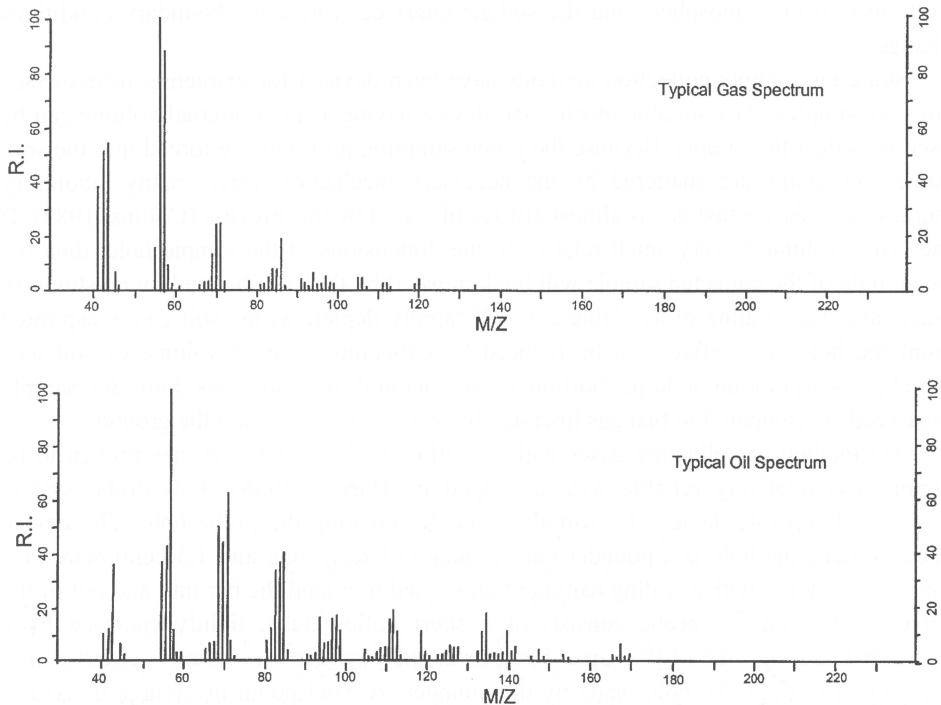


Fig. 5-17. Typical mass spectra of gas and oil.

Although the concept and approach of this technique are excellent, it does not integrate the flux of hydrocarbons heavier than butanes during the one to two weeks for which the collectors are left in the soil. Hydrocarbons heavier than butanes are liquids, and do not migrate more than a few centimetres during the short collection period. It may be equally effective to place a soil sample in a jar with the collection wire; the collection efficiency could probably even be increased by heating the sample jar.

Direct sampling of free soil gas requires that a sampling probe be inserted into the ground to collect a soil gas sample. The deeper the penetration, the more difficult and expensive the procedure becomes, eventually requiring that analysis be conducted on drilling fluids or rock samples recovered from a hole. Deeper holes almost always encounter water, which also influences the collection of free gases, forcing one to analyse the gas content of some type of recycled water or mud system which is used to drill the hole.

Although sampling from holes of any depth is possible, for simplicity two free soil-gas techniques will be discussed and compared (as case studies): shallow probes (Matthews et al., 1984) which penetrate to 1.2 m (4 feet); and auger holes (Jones and Drozd, 1983) which are 3.5 m (12 feet) deep. These methods differ mainly in terms of the resulting soil-gas sample. The shallow-probe samples are influenced more by closer

proximity to the atmosphere and the soil/air interface, where the boundary conditions change.

Numerous sample collection methods have been devised for extracting near-surface soil-gas samples. Any suitable mechanical device having a small internal volume can be used to collect the sample. Because the probe sampling port must be forced into the soil, some soil grains are shattered by the necessary mechanical force; many laboratory studies have shown that gas is almost always liberated by this process (Collins, 1983). If the probe volume is very small relative to the dimensions of the sample hole, then the magnitude of the collected sample will be dominated by the gas liberated by crushing. In such cases the volume of available gas will rapidly deplete as the soil gas is aspirated from the hole. This effect can be reduced by collecting a larger volume of soil gas, thereby incorporating a large portion of the natural free soil gas into the sample measured, as compared to that gas liberated by forcing the probe into the ground.

One method of collecting gases with a shallow-probe system that has proven to be simple and relatively reliable was developed by Burtell (1988). This probe system consists of separate devices for sampling and for creating the probe hole. The device used to make the hole is a pounder bar 1.2 metre (4 feet) long and 1.3 centimetre (1/2 inch) in diameter, with a sliding hammer that is used to pound the bar into and out of the ground. The soil gas probe consists of a short hollow tube, tightly enclosed by a concentric sealing tube of the same diameter as the pounder bar, which is inserted into the ground through the hole made by the pounder. A hand pump or syringe is used to evacuate the residual atmospheric gases from the hollow probe before the soil-gas sample is collected. The soil-gas sample is collected in a 125 ml glass serum bottle with an aluminium crimp top securing a butyl-rubber stopper. The sample bottle is evacuated just before the sample is collected in order to reduce the possibility of contamination and to eliminate atmospheric dilution effects. A sample of the soil gas is drawn into the evacuated bottle. Additional soil gas is then pumped under pressure into the sample container.

Probe sampling using this or any similar portable design can be used in a variety of geologic terrains within the limits of surface geologic features. Since an effective soil gas survey measures gas concentrations which have migrated into the soils, it is important that sample locations be placed in areas with at least one metre of residual soil. Alluvial and glacial deposits can also be sampled in most areas, provided there is not active, high-volume sediment deposition (which would require a deeper sampling method). Water-saturated soils and mud should be avoided because the wet sediments clog the sampler and if the open pore spaces normally present in the soil are reduced by water, then the amounts of free soil gas are much lower than in non-saturated soils.

Shallow probe techniques are prone to near-surface lithologic, meteorological and barometric effects. This means that one must be careful in interpreting background values since the absence of an anomaly in a prospective or producing area may be related to lithology, rainfall, meltwater or barometric pumping. Areas containing

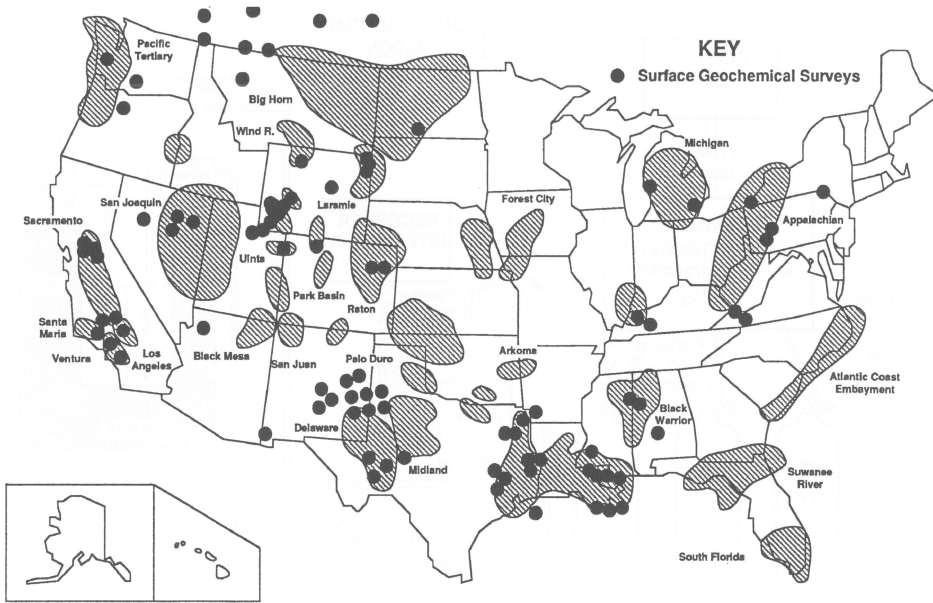


Fig. 5-18. Location of major basins in the USA (shaded) and surface geochemical surveys (black dots) carried out by Gulf Research and Development Company.

anomalously high gas contents, on the other hand, are almost always real seeps, since active flux is necessary to overcome these dilution effects.

Shallow probes have been used successfully at Lost River in Hardy County, West Virginia, Patrick Draw in Sweetwater County, Wyoming (Matthews et al., 1984; Richers et al., 1982), Arrowhead Hot Springs in San Bernardino County, California (Burtell, 1988) and on a large number of surveys conducted throughout the industry. Limited tests by Williams (1985) in the west Texas Permian Basin suggest that shallow probes are difficult to use in this area because of impermeable deposits of caliche and thick salt and anhydrite beds at a depth of about 300 m. An example of a halo-type anomaly reported by Williams (1985) is included in his thesis.

Despite these limitations, shallow-probe sampling is still worthy of consideration because of the low sampling cost and ease of access in rugged areas with limited roads. With this method, small crews of only one or two persons can obtain large numbers of samples at minimal expense. In addition obtaining a permit (if required) is usually relatively simple because permitting authorities tend to classify such surveys as causing minimal environmental impact. The mobility of the soil gas probe sampling technique opens up large areas to geochemical exploration that are otherwise difficult to explore.

Another means of obtaining free soil gas data is from auger holes drilled to 3.5 m (12 feet). These holes generally yield higher hydrocarbon concentrations than shallow probes. A fairly extensive research programme at Gulf Research and Development

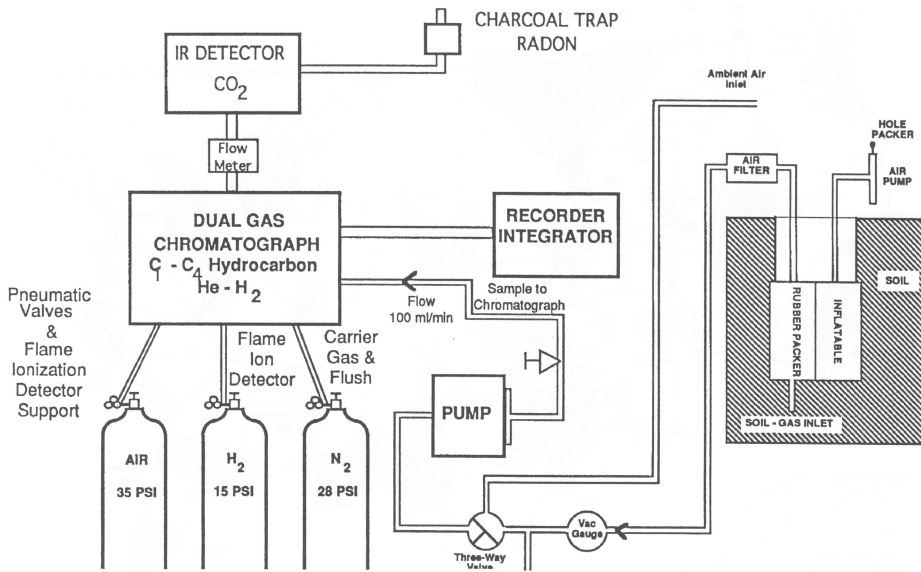


Fig. 5-19. Soil gas sampling procedure used by Gulf Research and Development Company.

Company established a database for geochemical exploration using auger holes comprising more than 21,000 analyses covering 16,000 line km (10,000 line miles) (Jones and Drozd, 1983). The locations of some of the research surveys are shown by black dots on a map of the major US basins (Fig. 5-18).

An important aspect of this technique is that the data contain compositional information that not only can be tied to known fields but also are capable of predicting the oil *versus* gas potential of an unknown area before drilling. This predictive capability has proven to be applicable to several other techniques as well.

A diagrammatic representation of the soil-gas sampling procedure used by Gulf Research and Development Company is shown in Fig. 5-19. Soil gas measurements are made in an auger hole, at least 4 m (13 feet) deep and typically 8.9 cm (3.5 inches) in diameter. A probe jacketed with an inflatable rubber packer is placed in the hole. When inflated, the packer effectively isolates the bottom of the hole from the atmosphere, so that the sealed base of the hole effectively serves as the sample container for the liberated gases. Soil gases are then either pumped into evacuated steel bombs or glass bottles for later analysis, or pumped directly into an on-site dual-column gas chromatograph for determination of the light hydrocarbons, helium and hydrogen. A 1 metre alumina-packed column coupled to a flame ionisation detector (FID) is used to determine the hydrocarbon content and a 3 metre molecular sieve column coupled to a thermal conductivity detector is used for the hydrogen and helium determinations. Carbon dioxide is analysed continuously using infrared adsorption techniques.

TABLE 5-VIII

Composition range of soil-gas hydrocarbons over different reservoir types

	C_1/C_n	C_1/C_2	$(C_3/C_1) \times 1000$
Dry gas	95-100	20-100	2-20
Gas condensate or oil and gas	75-95	10-20	20-60
Oil	5-50	4-10	60-500

TABLE 5-IX

Average composition ratios of soil-gas hydrocarbons over different reservoirs

Reservoir type	Location	Date	C_1/C_n	C_1/C_2	$(C_3/C_1) \times 1000$
Dry gas	Sacramento Basin	1972	95	55	6
		1974	95	49	8
		1975	94	55	11
Oil and gas	San Joaquin Basin	1972	82	8	46
		1974	84	7	61
		1975	82	8	56
Gas condensate	Southwest Texas	1975	89	12	33
		1976	90	11	30
Oil	Western Overthrust	1978	88	12	30
	Uvalde, Texas	1975	77	5	77
	Permian Basin	1976	75	5	64
	Utah Overthrust, Pineview	1976	77	5	83
	Appalachians, Rosehill	1978	73	4	141
	Uinta Basin, Duchesne	1976	68	4	171

The auger hole technique yields excellent compositional information, even though the magnitudes are influenced slightly by the mechanical disaggregation associated with the drilling process. Compositional results for auger holes are sufficiently important to warrant further discussion here. An empirically-determined range of soil-gas data is shown in Table 5-VIII and a small selection of auger hole survey results is shown in Table 5-IX. The geochemical distinction between gas-type basins and oil-type basins was first noted from surveys in the Sacramento and San Joaquin Basins in California. Initial compositional data were gathered in these two basins in three separate years with excellent repeatability (Table 5-IX). Additional surveys conducted in southwest Texas supported the differences noted in California. Final confirmation on the oil *versus* gas predictions was obtained when numerous surveys were carried out in all three types of productive areas: gas, gas-condensate and oil. Soil-gas data from the Sacramento dry-gas, Alberta gas-condensate, and Permian Basin oil areas were used to establish statistically-valid populations based on histograms that demonstrate a close association with reservoir gases and gas shows in drilling fluids.

TABLE 5-X

Composition (mole fractions of C₁-C₄) of typical reservoir types (Katz and Williams, 1952)

Reservoir type	Methane	Ethane	Propane	Butanes
Dry gas	0.91	0.05	0.03	0.01
High pressure gas	0.81	0.07	0.07	0.05
High pressure oil	0.77	0.08	0.08	0.07
Low pressure oil	0.37	0.21	0.21	0.21

Some typical percentages of methane and relative amounts of ethane through butanes in different types of deposits are given in Table 5-X. These data, taken from Katz and Williams (1952), show clearly that methane decreases in the trend from a dry-gas deposit to a typical low-pressure undersaturated oil deposit containing only dissolved gas but no gas cap. A better demonstration of this relationship comes from the study by Nikonov (1971), who compiled gas-analysis data from 3,500 different reservoirs in the United States, Europe and the then USSR, and grouped them into the populations shown in Fig. 5-20a. Gases from basins containing only dry gas (designated NG) contain less than 5% heavy homologs, whereas gases dissolved in oil pools (designated P) contain an average of 12.5% - 15% heavy homologs. The heavy homologs include ethane, propane, butane and pentane.

Three of the near-surface data sets from Table 5-VIII are particularly convincing because the soil-gas measurements were made in basins that contained only one type of production. As shown by Fig. 5-20b, they are the dry-gas production of the Sacramento Basin (more than 450 sites), the gas-condensate production in the Alberta foothills (more than 650 sites), and the oil production of the Permian basin (more than 450 sites). Figures 5-20c, 5-20d and 5-20e show methane content (%C₁), the methane:ethane ratio (C₁/C₂), and the propane:methane ratio (1000 x C₃/C₁) from the soil-gas populations over these three basins. These data clearly demonstrate that the chemical compositions of the soil gases from these three different areas form separate populations that appear to reflect the differences which exist in the subsurface reservoirs in these three basins. This correlation is particularly striking when compared with the data of Nikonov (1971), shown in Fig. 5-20a.

The use of hydrocarbon compositions in soil gas prospecting requires enough data to allow statistically-valid and separate populations to be defined, so that a particular geochemical anomaly can be related to a geologic or geophysical objective or province. A percentage composition based on only two or three sites having 85% or 95% methane is not sufficient to define a population. As shown in Fig. 5-20a, considerable overlap exists among the intermediate gas-condensate and oil-type and gas-type deposits. In basins having mixed production, prediction of a reservoir gas-to-oil ratio (GOR) is clearly impossible.

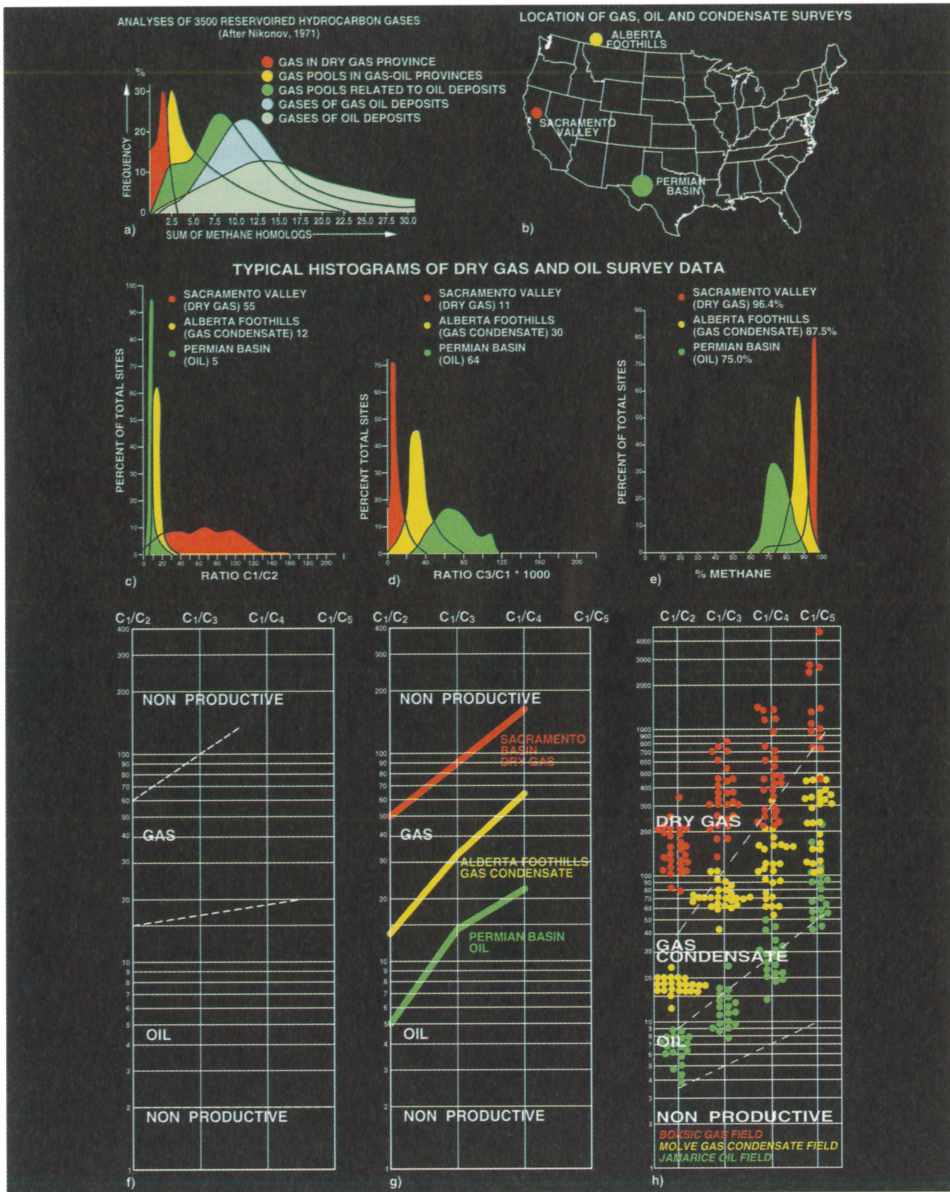


Fig. 5-20. (a) Frequency distribution of the sum of methane homologs in 3,500 samples from different types of reservoirs (from Nikonov, 1971). Gas, oil and condensate surveys: (b) location; frequency distributions of hydrocarbons in soil gas over different basins, (c) methane:ethane ratio, (d) propane:methane ratio, (e) methane content, (f) Pixler ratio diagram (Pixler, 1969), (g) soil-gas data plotted on Pixler diagram. (h) Reservoir gas analyses of Verbanac and Dunia (1982) plotted on Pixler diagram.

Where seeps contain gases from more than one reservoir, their compositions may not match those of any of the underlying reservoirs. Mixing of a shallow oil and a deep gas will generally yield an oily but intermediate-type composition. Without some knowledge of the reservoir possibilities, this type of signature cannot be recognised. Nevertheless, the intermediate nature of the seep will indicate some liquid potential at depth. Thus, dry-gas basins can be distinguished from basins that have at least some liquid oil or condensate potential. As suggested by Bernard (1982), the presence of fairly large ethane-propane-butane anomalies strongly suggests an oil-related source.

Pixler (1969) found that the gases observed during drilling could distinguish the type of production associated with the hydrocarbon show during mud logging and published the graph shown in fig. 20f. Pixler's data were obtained by monitoring the C_1 - C_5 hydrocarbons collected by steam-still reflux gas sampling during routine mud logging. Individual ratios of the C_2 - C_5 light hydrocarbons with respect to methane provided discrete distributions that reflect the true natural variations of formation hydrocarbons from oil and gas deposits. Ratios below approximately 2 or above 200 indicated to Pixler that the deposits were non-commercial. The upper range for these ratios for dry-gas deposits has been enlarged by Verbanac and Dunia (1982), who studied more than 250 wells from 10 oil and gas fields. Their data, shown in fig. 5-20h, suggest the following upper limits for dry-gas reservoir ratios: $C_1/C_2 < 350$, $C_1/C_3 < 900$, $C_1/C_4 < 1,500$, $C_1/C_5 < 4,500$. These ratios clearly aid in defining transition between thermogenic and biogenic gases. Another empirical rule suggested by Pixler is that the slope of the lines defined by these ratios must increase to the right; if they do not, the reservoir will be water-wet and therefore non-productive. Verbanac and Dunia (1982) suggested that a negative slope connecting individual ratios may result from fractured reservoir zones of limited permeability.

Auger-hole soil-gas data for the surveys over the three basins described above are plotted on a Pixler-type diagram of reservoir gases in Fig. 5-20g. Direct comparison of these two independent data sets is very striking and proves the concept of migration of reservoir hydrocarbons to the surface. It is important to note that amounts of migrated gases almost always decrease in the following order: methane > ethane > propane > butane. Thus, in a Pixler-type diagram, soil gas-data, like reservoir data, generally plot as line segments of positive slope for the soil gases to represent a typical migrated seep gas. Exceptions to this order have been noted where surface source rocks were drilled, which thus far have yielded ratios with lighter gases depleted in relation to heavier gases. According to Leythaeuser et al. (1980), this would be expected if gases in the boundary layer very near the surface followed a diffusion model. Thus, compositional changes related to diffusion might be expected at or very near a boundary layer where the hydrocarbon gas concentration approaches zero. This behaviour has been observed when comparing soil gas probe data measured at very shallow depths (0.3-0.6 m, 1-2 feet) with the corresponding data from 4 metre (13 feet) auger holes. The shallow probe data are always "oilier", indicating preferential loss of methane and implying diffusion from the 4-m (13-foot) level to the surface. If diffusion were the dominant migration mechanism,

TABLE 5-XI

Composition ratios of soil-gas hydrocarbons over Pleasant Creek gas storage area

Date	C_1/C_n	C_1/C_2	$(C_3/C_1) \times 1000$
May 1975	90	20	19
July 1975	89	18	24
July 1976	89	16	20

a chromatographic effect would be expected for gas that migrated through the Earth. The fact that the compositions of the soil-gas data from auger holes match the underlying reservoirs confirms that the major migration mechanism to the near-surface must be via faults and fractures, rather than by diffusion.

The percent-methane compositions from the auger hole surveys conducted over the Sacramento and San Joaquin Basins are plotted in Fig. 5-21. There is a decrease from 98% methane in the north of the Sacramento basin to 90% in the south part, whilst the soil gas over the San Joaquin Basin has 82% methane. These data imply that a soil-gas grid would have defined local differences regionally. Furthermore these geochemical data are repeatable (Table 5-XI); the percent-methane values on Fig. 5-21 were all determined at least two or three times over a three-year period and found to be repeatable. Compositional data have remained repeatable throughout our experience with soil-gas surveys.

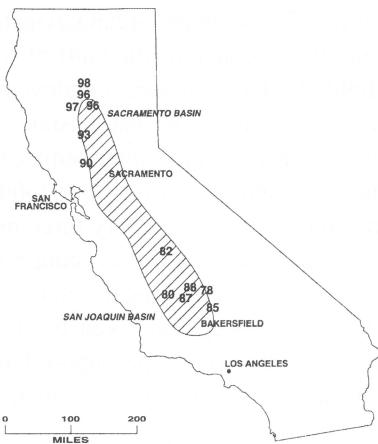


Fig. 5-21. Percent-methane in soil gas over the Sacramento and San Joaquin Basins, California.

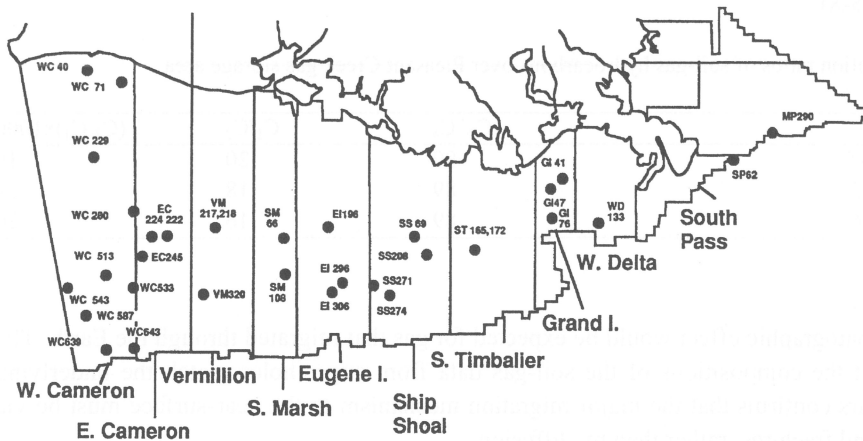


Fig. 5-22. Well locations offshore Louisiana for which gas compositions are published (from Rice, 1980).

Dissolved gas

In offshore prospecting, “sniffers” have been used to detect anomalous hydrocarbon concentrations in bottom waters. An extensive review of the literature was published by Philp and Crisp (1982). Some of the most significant results reported by Williams et al. (1981) are highlighted here.

Gulf Research and Development Company designed and operated several marine seep detectors that were employed aboard various research vessels, such as the RV Hollis Hedberg and its predecessor the RV Gulfrex. These ships circumnavigated the globe and conducted extensive detailed surveying in areas such as the Gulf of Mexico (Mousseau and Williams, 1979). The RV Hollis Hedberg system employed three separate water inlets which, whilst the ship was underway at normal seismic survey speeds, continuously supplied sample streams from the near surface, intermediate depths to 135 m (450 feet) and a deep-towed sample inlet at a depth of nearly 180 m (600 feet). Each sample stream is analysed for seven hydrocarbon gases once every three minutes with a sensitivity that depends upon the hydrocarbon and, for example, is about 5×10^{-11} litres of propane at STP per litre of seawater. By using multiple depth inlets, surface contamination can be demonstrated to have no effect on seeps observed by the deep inlet. At sea, sniffer geochemical data from a deep tow inlet were superimposed to scale on a seismic section to aid the explorationist in making real-time evaluations of hydrocarbon potential of structurally-significant areas.

As for surface soil gases, a powerful confirmation of the validity of marine geochemical data can be shown by the very close agreement between the composition of component hydrocarbons in production gases and the composition of seep anomaly gases in the same areas. Figure 5-22 shows the well database used for this confirmation

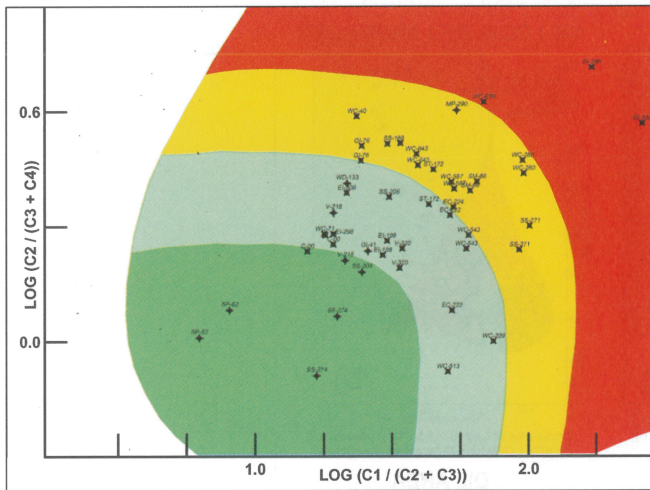


Fig. 5-23. Compositional crossplots of Rice's reservoir gas analysis. The underlying color code was chosen to distinguish oil, oil-condensate, gas condensate and gas within Rice's Gulf of Mexico production data.

in the Gulf of Mexico (Rice, 1980). For each of the 32 fields shown on this figure, the USGS has published the composition of gases produced from predominantly gas fields, oil fields and combined oil and gas fields or condensate fields.

A crossplot of the compositions of gases from all field types is shown in Fig. 5-23 (Williams et al., 1981). The underlying colour code on this figure was chosen to distinguish oil, oil-condensate, gas-condensate and gas production using the Rice well analysis data as a standard. The log of the ratio of ethane to propane-plus-butane is plotted against the log of the ratio of methane to ethane-plus-propane. A distinctive compositional clustering of gas anomalies signifies different kinds of production: oil anomalies occur near the origin and become gassier as the points move up and to the right in Fig. 5-23. A crossplot of 146 sniffer geochemical anomalies from the same part of the Gulf of Mexico is plotted in Fig. 5-24b for direct comparison with the Rice well data shown in Figures 5-23 and 5-24a. As shown, the overall distribution is similar to the well data. Figures 5-24c and 5-24d illustrate the contrast in composition of dissolved hydrocarbon anomalies from a gas area and an oil area in the Gulf of Mexico. This type of regional separation was found to be typical of surveys conducted throughout the world.

The fact that production and surface anomaly gases correspond both onshore and offshore is significant. It proves that the observational techniques are valid despite the great variation in these surface environments.

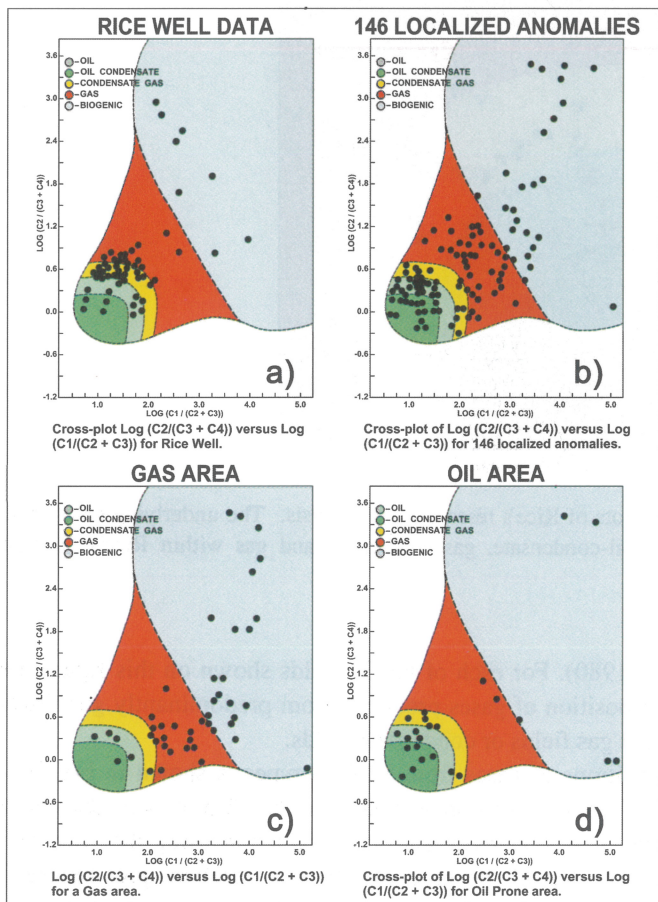


Fig. 5-24. Crossplots of the compositions of gases from offshore Louisiana: (a) well gases throughout the area; (b) marine sniffer gases throughout the area; (c) marine sniffer gases from a gas area; (d) marine sniffer gases from an oil area.

Headspace gas

A headspace sampling technique is commonly employed for the analysis of canned samples from drilling returns and from shallow sediments. In this technique a controlled volume of sediment is placed in a can or jar filled with a measured volume of degassed brine. The can is sealed and a measured volume of brine is displaced with nitrogen to create a known volume headspace. The can is then allowed to come to equilibrium. The concentration of light gases can then be measured by syringe injection of a headspace sample into a gas chromatograph equipped with a flame ionisation detector.

In order to maintain reproducibility it is important to measure all volumes accurately. In a typical operation using 500 ml (one pint) cans, the procedure is to place 300 ml of degassed salt-water brine into the 500 ml can and add sediment until the can is filled to the brim, giving 200 ml of sediment and 300 ml of brine. The can is sealed and then zero-grade nitrogen is injected through a prepared septum to displace 100 ml of brine and leaving the can with a 2:2:1 mixture of 200 ml brine, 200 ml sediment, and 100 ml headspace.

Experiments have shown that a fairly long time is required for the adsorbed sediment gases to completely equilibrate with the headspace. This equilibrium time is shortened by heating and shaking the cans before analysis. A generally accepted procedure is to heat the cans for about 12 hours at 60-70°C, followed by shaking in a paint mixer for five minutes. After heating and shaking, the cans are allowed to stand for at least five further minutes to ensure that dissolved gases return to the headspace.

One of the drawbacks of using this technique is the need to freeze the canned samples if they cannot be analysed within one or two weeks of their collection. Failure to follow this procedure can create problems because of the generation of biogenic gas in the cans or the bacterial oxidation of the hydrocarbon gases to carbon dioxide.

Hydrocarbon concentration values are reported in terms of ppm by volume in the nitrogen headspace or as ppm or ppb by weight, normalised to the weight of sediment. Gases concentrations reported by weight are not truly representative of the actual gas migrating from depth because some of the free gas has been allowed to escape during collection and sample preparation. Furthermore, the sorbed gas is never completely extracted into the headspace, and may not always reflect the true gas content of the soil.

The headspace sampling technique can yield useful results if sufficient numbers of samples can be collected to use statistical populations to suggest anomalous areas. One should always exercise caution, however, with respect to characterisation of gas composition, since evaporation during the collection stage always occurs, resulting in the relative depletion of the lighter gases.

Disaggregation

Extensive soil gas sampling programmes carried out by the petroleum exploration industry have demonstrated that the crushing and/or disaggregation of soils (including the action performed in drilling auger holes) is an important component part of the extraction of gas from the soil. This suggests that it would be advantageous to employ a soil core disaggregation technique which would closely mirror the effect of auger hole drilling. A device developed at Citco and commonly used in both industry and academia for analysing well cuttings appears suitable for accomplishing this objective (Whelan, 1979; Hunt and Whelan, 1979; Whelan et al., 1980). In fact, Richers (1984) has demonstrated successfully that in some instances, such as at Rose Hill, Virginia, and in

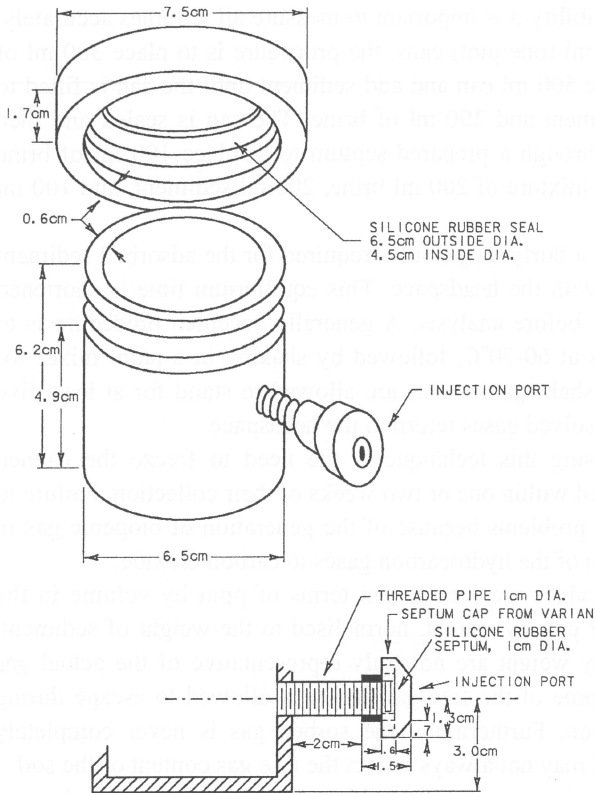


Fig. 5-25. Stainless steel disaggregation mill used in headspace analysis

the Western Overthrust Belt, the results obtained by this technique are in very good agreement with data from auger holes.

The device used in this technique is a small stainless steel ball-mill containing two stainless steel or ceramic balls which crush and disaggregate the sample when the ball-mill is shaken (Fig. 5-25). This approach concentrates the loosely-bound adsorbed gases into the headspace of the ball-mill. Because of the equilibrium problem mentioned above under headspace techniques, this sampler was adapted by Whelan (1979) and Whelan et al. (1980) to ensure that lithified sediments and cuttings are completely broken up during analysis.

Basically, the technique is as follows. A small (but constant) volume of sediment, soil or cuttings is placed into the mixer cell along with two ceramic or stainless steel ball-bearings, and water is added to bring the remaining headspace to 10 cc. The mill is sealed and placed in a SPEX/Mixer-Mill and agitated for about five minutes. The cell is then immersed into a hot-water bath at 90°C for three minutes. A 1 ml aliquot of gas-free water is injected into the cell through a septum-sealed side arm on the cell, and then a 1

ml aliquot of the headspace is sampled using a locking gas-tight syringe. The sample is then hand injected into a gas chromatograph equipped with a flame ionisation detector for analysis of the disaggregated gases. It is assumed that these gases represent micropore gas, some free gas and lightly adsorbed gas on the sample-medium surface.

This technique (or modifications of it) has been used in the analysis of well cuttings and deep sea cores (Hunt and Whelan, 1979), in addition to surface geochemical prospecting (Richers et al., 1986; Richers and Weatherby, 1985).

Initial tests of this method were conducted at Gulf Research and Development Company for comparison with the auger hole technique and to gain a better understanding of the relationship between free gas and adsorbed gases liberated by the drilling process. To be an effective and viable technique, the disaggregation desorption method must be able to distinguish between oily and gassy areas. An area known to be predominantly oily, Rose Hill in Lee County, Virginia, and another known to be predominantly gassy, the Gulf Research Facility in Pittsburgh, Pennsylvania, were chosen as initial test sites. Both areas had been sampled previously using the auger hole technique, allowing the new data to be compared with the established data sets (Richers, 1984).

The Rose Hill test site includes 126 soil cores of which 51 fall within 300 m (1,000 feet) of the earlier auger holes. Despite differences in the sample locations and depths, both techniques correctly identify the area as oil-prone. Table 5-XII shows the relationship between the diagnostic gas ratios (Jones and Drozd, 1983) and the results of the two surveys (Richers, 1984). It is obvious that the ball-mill technique accurately describes the oil-prone nature of the Rose Hill oil field. However, the data of Table 5-XII suggest a slight difference in the composition of the hydrocarbons detected by the two techniques. In the auger holes the soil gas is slightly drier (methane-rich) than the soil gas obtained by ball-mill disaggregation-desorption. This shift may reflect the preferential loss of methane from the shallow cores compared to the deeper auger holes and the difference between core samples and free gas measurements. The other gases are essentially the same in both techniques: the C_4/nC_4 ratio for the disaggregation technique is 0.34, and the auger hole technique yields a value of 0.40; the C_2/C_3 ratios are comparable at 1.84 for the disaggregation technique and 1.76 for the auger hole technique. In addition, the intercorrelation of the various hydrocarbon gases in the disaggregation data set is higher than that for the auger hole data. This high degree of

TABLE 5-XII

Comparison of results of free soil-gas and disaggregated soil-gas surveys, Rosehill, Virginia (Richers, 1984)

Survey method	No. of sites	% methane	C_1/C_2	$(C_3/C_1) \times 1000$
Free soil gas	145	72	7	110
Disaggregated gas	128	70	7	117

correlation among the gases may reflect a near-equilibrium condition achieved through time for the adsorption-desorption process in soils. Hence, the signal seen by the desorption technique may effectively integrate and smooth rapid changes one might expect to see with a free-gas technique such as auger holes.

At the Gulf Research Facility in Pittsburgh, Pennsylvania, there are two producing gas wells, and 38 sites were selected to test the ability of the disaggregation technique to define gassy areas. Not only did the test yield gassier results than those obtained at Rose Hill, but also the results were again comparable to those obtained using the auger hole technique. Table 5-XIII is a compilation of these results. Clearly, the two data sets reflect a more gas-prone area for the Gulf Research Facility than for the Rose Hill area. Although the data set for the disaggregation technique is only half of the size of the data set from the auger holes, it still yields useful information regarding composition of the subsurface reservoirs.

Acid extraction

A technique which measures only the most tightly-bound gas was originally developed by Horvitz (1939, 1945, 1950, 1954, 1957, 1965, 1969). In this technique the sample is subjected to acid digestion under vacuum at an elevated temperature of about 80°C. Further developments by Debnam (1969) and Horvitz (1972, 1980, 1981) involved corrections for lithology to reduce the effect of acid-soluble minerals biasing the data. Debnam (1969) noted that soil samples could be dried, pulverised and sieved without affecting their hydrocarbon content. He also noted that sieving sand samples to <200 mesh gave analytical values comparable with those produced by clay samples from the same location. Horvitz developed a wet-sieving technique to concentrate the analysis on only the clay fraction of the sediment.

McCrossan et al. (1971) evaluated the acid-extraction technique in the western part of Alberta. This extensive survey of over 4561 samples covering 15 townships concluded that the distribution of anomalous points was random and was strongly biased by samples rich in carbonate minerals. Adequate corrections for amounts of acid-soluble material were not successful and it was concluded that this method could not be used in areas covered by glacial till.

TABLE 5-XIII

Diagnostic soil-gas ratios at the Gulf Research Facility, Pittsburgh, Pennsylvania

Survey method	No. samples	% methane	C_1/C_2	$(C_3/C_1) \times 1000$
Free soil gas	73	89	18	21
Disaggregated gas	38	91	25	22

As early as 1940, Sanderson had discussed a number of factors that affected adsorption of hydrocarbon gases by soils. He noted that the ability of the soil to adsorb any gas depends upon the type of gas, the characteristics of the soil and the conditions under which the soil is exposed to the gas. Adsorption will depend upon the type and surface area of particles and their chemical composition. The surface reactivity will be modified considerably by the presence of previously-adsorbed molecules, such as carbon dioxide, water and mineral ions. The condition of adsorption is complicated by temperature and pressure and length of exposure time in addition to concentrations and species of gases present. Adsorbed-gas data can, at best, be only approximations of the original mixture of migrated gases. Another possible problem lies in the quantitative desorption of the gases from the mineral components of the soil.

Sanderson (1940) observed up to six-fold differences in the ability of soils to adsorb hydrocarbons in his laboratory. He also noted that the adsorptive characteristics of the colloidal soil systems would vary slowly with moisture content, time and season. Of particular significance was his observation that the adsorptive capacity for hydrocarbons on wet soil was only a small fraction of that for dry soil. A further complication is created by near-surface biological activity that creates wide variations in the content of carbon dioxide, nitrous oxide and other biological gases. Overcoming all these problems is probably impossible; however, it will suffice if the gases are liberated in proportion to the amounts present so that the analytical results bear some relationship to one another, and allow identification of potentially prospective areas.

Various other approaches have been devised in attempts to overcome this problem. Bays (US patent no. 2,165,440) suggested correcting for the sorptive power of the soils and McDermott (US patent no. 3,120,428) suggested correcting for the surface area. An alternative technique proposed by Thompson (1971) used ethylenediaminetetracetic acid (EDTA) at about pH 7 and slightly heated in order to decompose the carbonate minerals under conditions that do not release such large quantities of carbon dioxide. Thompson reports that a comparison on duplicate samples shows that the EDTA technique consistently releases from 94-99.5% of the hydrocarbon gases released by the standard strong-acid treatment. A further refinement of this method by Thompson et al. (1974) separates a critical carbonate mineral before analysis. This critical mineral was almost always found to be dolomite, but occasionally is other carbonate minerals, such as iron or calcium carbonate. The ratio of hydrocarbons per unit of critical mineral is then plotted to form a geochemical prospecting map. This technique was reported to highlight a salt dome in the Gulf of Mexico on which a major oil discovery was made after the survey was conducted.

Poll (1975) addressed this problem of lithologic corrections by dividing data according to desorption efficiencies based on their physicochemical properties. The first step is to prepare a detailed lithological description of the samples. This involves a differentiation on sediment lithology, sample coherence, structure, cementation and mineral types, including carbonate and sand percentages. This information is used as shown in Fig. 5-26 to classify the samples into homogeneous sets for each of which the

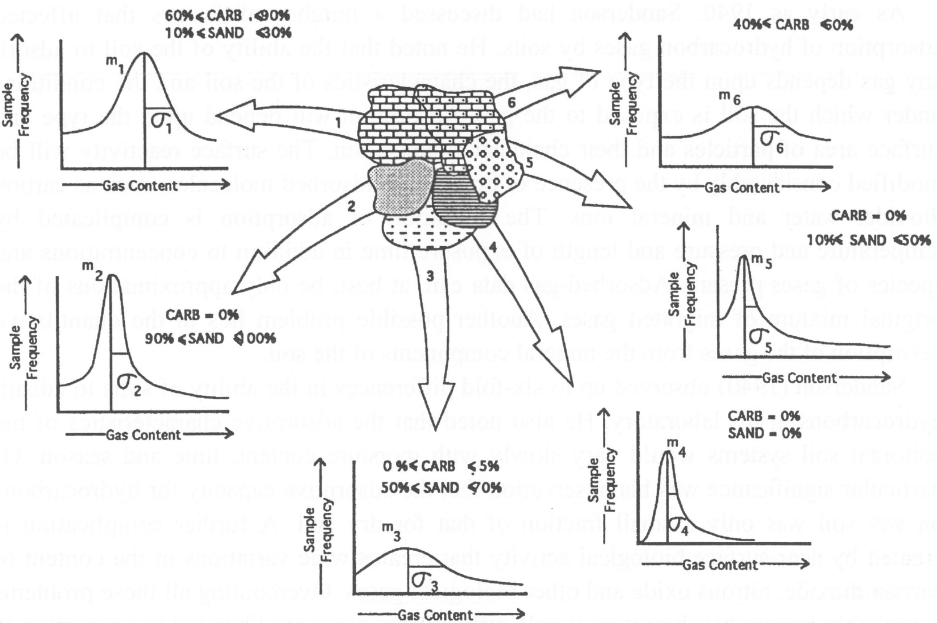


Fig. 5-26. Scheme for lithological classification of samples prior to interpretation of gases released by acid extraction (reproduced with permission of Australian Petroleum Production and Exploration Association from Poll, 1975).

average, or background, gas content is computed. The gas content in each group is assumed to be distributed according to a Laplace-Gauss law. Each subset is then assumed to have a uniform efficiency of desorption and its own background and anomaly threshold. As shown in Fig. 5-26, for calcareous sediments these are very high, due to the effectiveness of the acid attack. The mean normal standard can be computed for each set yielding dimensionless values that can be added together for mapping, regardless of the sediment type. This technique has been applied by Poll (1975) in the Gippsland Basin and by Devine (1977) and Devine and Sears (1985) in the Cooper Basin in Australia. Reasonably positive results were reported in all three cases.

The acid-extraction technique relies on the ability of soil and minerals to retain hydrocarbons that migrate past them through the soil pore system. It is therefore not subject to the fluctuation involved in the soil-air system but hopefully represents some averaged or integrated signal over time. As noted above, the samples must be corrected for lithologic effects by only making comparisons within a given lithology or by specifically analysing certain minerals. Corrections must always be applied because adsorption occurs in both the fine-grained fractions and in carbonates, which often release disproportionately large amounts of hydrocarbons.

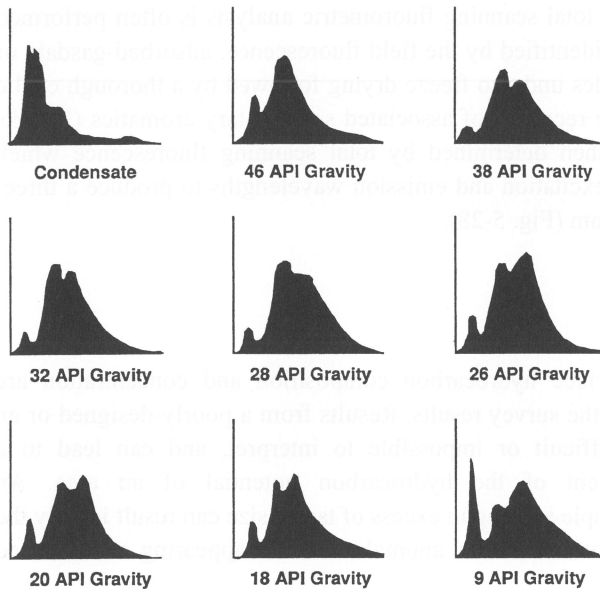


Fig. 5-27. Comparative fluorescence spectra of nine crude oils of different (from Purvis et al., 1977)

Fluorescence

As an extension of light hydrocarbon gas analysis, UV fluorescence spectroscopy can be used to measure the oil potential of near-surface sediments by analysing their aromatic hydrocarbons. This is highly sensitive and selective method for the analysis of oil components, particularly those containing one or more aromatic functional groups. Using spectroscopic scanning, complex molecular aggregates, such as those found in crude oils, can be rapidly characterized and quantified on the basis of their combined intensity wavelength distribution or “fingerprint”.

The fluorescence spectra of nine crude oils of different gravity are shown in Fig. 5-27 (Purvis et al., 1977). These two-dimensional fluorograms were produced by exciting at 265 nm and scanning from 250 nm toward the red end of the spectrum. The accepted procedure for illustrating the change in the emission spectrum associated with different-gravity crude oils is to measure the intensity of fluorescence at two wavelengths: 320 nm for light aromatic compounds; and 365 nm for the heavier, multiple-ring aromatic compounds. The intensity of the fluorescence emission is proportional to the quantity of aromatics in the extracted sample. The standard field method employs a rapid wet extraction process which dissolves loosely-bound trace aromatics into hexane. This extract generally favours the heavy oil fraction, which is in hydrophobic association with the sediment.

A second phase of in-depth, total scanning fluorometric analysis is often performed on selected anomalous samples identified by the field fluorescence, adsorbed-gas data or interstitial-gas data. These samples undergo freeze drying followed by a thorough cyclic extraction in hexane to optimise recovery of associated sedimentary aromatics (Brooks et al., 1986). The oil type is then determined by total scanning fluorescence which employs step-wise scanning of excitation and emission wavelengths to produce a three-dimensional fingerprint fluorogram (Fig. 5-28).

SAMPLING STRATEGY

Spatial patterns of near-surface hydrocarbon composition and concentration are prime factors when interpreting the survey results. Results from a poorly-designed or an uncontrolled survey can be difficult or impossible to interpret, and can lead to a completely erroneous assessment of the hydrocarbon potential of an area. An improperly-spaced grid with sample spacing in excess of target size can result in only the most cursory assessment of potential, with anomalous areas appearing as localised single-point anomalies.

The distribution of sample sites in a geochemical survey is largely governed by the purpose and budget of the survey. For regional surveys a sampling density of one sample per 2-5 km² seems adequate. Such a density still allows for the discrimination of regional ambient backgrounds from secondary backgrounds. Detailed diagnostic work requires a close-spaced grid, sometimes with a sample interval of only a few tens of m. Regional sampling is generally performed using a modified grid because a regular grid, on which samples are taken at the intersections of a straight lines, does not minimise cost or maximise information. We recommend that sample positions be chosen within grid cells according to ease of access (minimum cost) and along zones of known or inferred fracturing and faulting (maximum information). Satellite imagery, aerial photography, seismic data and other data are useful when attempting to site samples on or near fractures and faults. The analytical results from a regional survey should yield some indication of compositional and/or magnitude "sweet-spots", either as isolated data points or small clusters. If the objective is merely to evaluate whether a basin has a source section, and general trends of where it is mature and focused to the surface, a regional study may be all that is required. A more detailed follow-up survey, however, is recommended if the objective is to highlight the zones of higher hydrocarbon potential.

One method commonly employed for detailed surveys is to sample seismic shot holes, further providing a means to easily tie the geochemistry to subsurface structure. Because seismic lines are not normally placed on a close-spaced grid, infill sampling between seismic lines is usually recommended. It should be emphasised that in order to define a target adequately, approximately 70% of the data should be collected in presumed background areas beyond the immediate target area. An embarrassingly large number of surveys have been performed in which sample locations do not extended

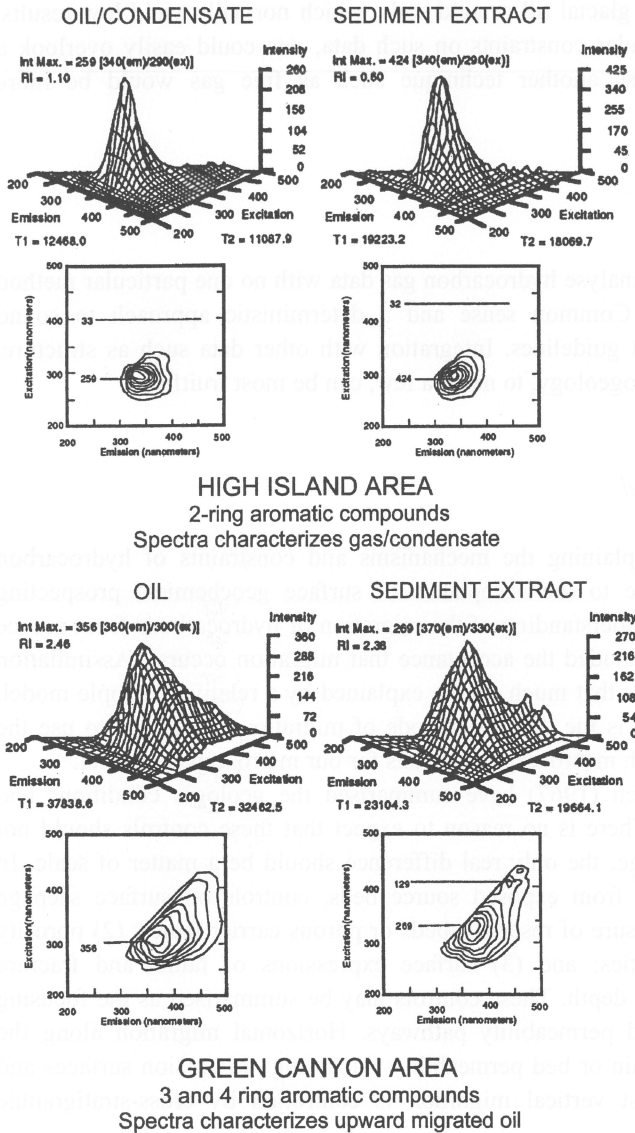


Fig. 5-28. Fluorograms of reservoir hydrocarbons and corresponding hydrocarbons extracted from sediments in the Gulf of Mexico.

more than one or two sites beyond the anomaly. The result of this misplaced desire to save money is often an ambiguous survey interpretation.

The selection of a technique that is inappropriate for the surface geologic conditions in part of the survey area can also lead to erroneous results. An example is the use of the

acid extraction technique on glacial till or acid soils, which normally yield low results. Without regard to the particular constraints on such data, one could easily overlook a favourable area. In this case another technique such as free gas would be more representative.

DATA INTERPRETATION

There are many ways to analyse hydrocarbon gas data with no one particular method being correct or incorrect. Common sense and a deterministic approach to sound geologic models are the best guidelines. Integration with other data such as structure, lithology, soil types and hydrogeology, to name a few, can be most fruitful.

Preferential pathway model

The lack of a model explaining the mechanisms and constraints of hydrocarbon leakage is often an obstacle to the acceptance of surface geochemical prospecting (although a similar lack of understanding of the migration of hydrocarbons from source beds to reservoir has not precluded the acceptance that migration occurs). Assimilation of the data, however, suggests that much can be explained by a relatively simple model. The conclusion that effusion is the dominant mode of migration enables us to use the visual patterns associated with macroseeps as a basis for our microseepage model.

Link (1952) and Levorsen (1967) have summarised the geologic conditions and controls on macroseepage. There is no reason to expect that these controls should not apply as well to microseepage; the only real difference should be a matter of scale. In addition to seepage directly from exposed source beds, controls on surface seepage include: (1) the surface exposure of reservoir beds or porous carrier facies; (2) porosity associated with unconformities; and (3) surface expressions of faults and fracture systems that are pervasive to depth. These controls may be summarised as the focusing of migration along preferred permeability pathways. Horizontal migration along the pathway is dominated by grain or bed permeability (including old erosion surfaces and other unconformities), whilst vertical migration is controlled by cross-stratigraphic discontinuities.

Horizontal pathways deflect the surface location of the anomaly laterally away from its subsurface origin. Thus if an anomaly is associated with the surface expression of a porous formation, one should suspect a down-dip source (or down-groundwater gradient source). The same conclusions can be inferred for anomalies associated with unconformities, low angle faults and listric faults.

Vertical pathways are dominated by the intersection of high angle faults and fractures with reservoir and carrier beds. In this case the surface expression of the source of the hydrocarbons will lie directly above, or only slightly displaced from the source. The

presence of multiple, stacked porous zones also often results in a surface geochemical expression that is approximately vertically above its subsurface origin.

The role of faults and fractures is particularly important for microseepage and some further comment is in order. The close association of near-surface geochemical anomalies with faults and fractures has been pointed out by, amongst others, Horvitz (1939), Sokolov (1971b), Richers et al. (1982), Jones and Drozd (1983) and Matthews et al. (1984). McCrossan et al. (1971) point to the close association of high concentrations of hydrocarbons in the surface environment with photolineaments. McDermott (1940) suggests that the permeability of shale is dominated by microfractures and that these fractures are preferentially normal to the bedding plane. This potentially important role of microfractures is emphasised by Rosaire (1938), who correctly points out that the failure to observe displacement does not eliminate the existence of a fault or fracture.

The high permeability of fractures causes them to preferentially focus fluid flow. The effectiveness of fractures as mass transport systems for fluids is evident from a casual examination of mineralisation in fractured rocks and leakage of groundwater at fracture outcrops. Similarly, these fractures act as preferential hydrocarbon pathways, focusing their flow from source beds to surface.

Faults and interconnected fracture systems have a significant effect on the magnitude and, less commonly, composition of the near-surface gases. The effect on magnitude is generally to increase concentrations in fractured areas, whilst the effect on composition theoretically should be preferential loss of lighter gases compared to heavier gases. In practice, gas compositions on faults are often lighter or heavier than those at neighbouring sites. This is believed to be controlled primarily by the depth of the fault and the composition of the subsurface gases it conducts. Thus deep, basement-related faults are often gassy because they tap deep over-mature sediments. Shallower faults are often oily because large molecules migrate more easily than the lighter compounds.

The increase in magnitude in fracture systems can often be abrupt and localised. It commonly spans several orders of magnitude, going from nil to macroseep levels in the extreme cases. In an area where there is no significant source of subsurface hydrocarbons, there are no high-magnitude soil-gas signals, even on faults and fractures.

In a hydrocarbon-bearing environment, however, overall high variance in the data is more often the case, but the anomaly-to-background ratio is smaller in non-producing areas than in producing areas. Some of these anomalous zones are associated with preferential leakage directly from a source bed, while others are from reservoirs. Since some faults and fractures are sealed locally along their lengths, high-magnitude signals do not occur everywhere along their length. Thus, we often observe "hydrocarbon spots", similar to the "helium spots" discussed by Wakita (1978). Naturally, those faults penetrating only source beds will show a signal that reflects the source beds, whereas those penetrating a reservoir or both reservoir and source beds will exhibit a larger anomalous signal. It is not known, however, if one can truly distinguish between the two types in all instances, although extremely high magnitudes are felt to be more diagnostic

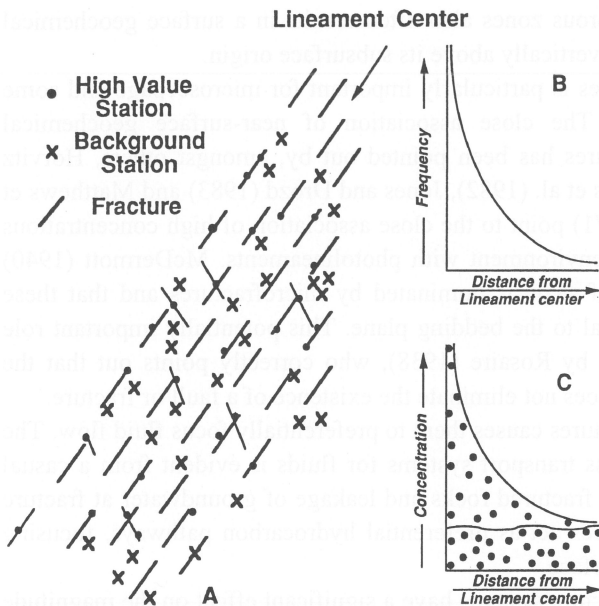


Fig. 5-29. Relation between fracture intensity and gas leakage: (A) plan showing lineament, fractures and gas sample sites; (B) distribution of fracture intersections with distance from lineament; (C) distribution of anomalous gas sample sites with distance from lineament (reproduced with permission of the American Association of Petroleum Geologists, whose permission is required for future use, from Richers et al., 1986, AAPG Bull., vol. 70, no. 7, Fig. 13, p. 885, AAPG©1986).

of reservoirs, as seepage volumes are expected to be larger from reservoirs than from a source bed (Hunt, 1981).

The expectation that all samples in a leaking fracture zone are higher than those outside the zone is simplistic, and is not always realised in practice. A fault or fracture is rarely one discrete plane, but zones of broken or disrupted strata, separated by relatively-unaffected competent strata. It is analogous to a fractured pipe: certain portions of the conduit are solid, whereas the fractured section is composed of both intact fragments and cracks. Fluids flowing through the pipe are going to leak in the fractured areas of the pipe but not in the solid-walled portions. Similarly, even in the fractured zones, the fragmented areas will leak only through the fractures, not through the fragments of pipe between the fractures. Extrapolating this model up to geologic scales, sampling outside the fracture zone is expected to give values that are typical of the background of the area. Within the fractured sample zone, sample sites may intersect discrete fractures or encounter coherent blocks between the fractures (Fig. 5-29A). The intensity of fracturing, and hence the probability of the fractures interconnecting, increases toward the centre of the fracture zone, as shown in Fig. 5-29B. Therefore, samples taken near the centre would be expected to be a mixture of high values (intersecting fractures that connect), median values (intersecting fractures that do not connect) and low values (not

intersecting fractures). Further from the centre of the fracture zone, the maximum values fall until they merge with those typical for the background of the area. This distribution of free soil-gas magnitudes as a function of distance from the centre of the fracture zone is shown in Fig. 5-29C (Richers et al., 1986). Disaggregation data from Patrick Draw exhibit a similar pattern, although the increase near the centre of the fracture zone is not as great; acid extraction data from this example show no obvious relationship, clearly suggesting that different analysis techniques are extracting gases from different sources.

The following examples illustrate the means of interpreting what are often referred to as direct anomalies using preferential pathway models. These direct anomalies may be either vertically over their subsurface source, or laterally displaced by varying amounts (Sokolov, 1971b; Pirson, 1969; Laubmeyer, 1933). What is generally not realised is that most areas contain microfractures to the extent that they allow gases to escape vertically.

Using a coal-burn experiment in the central Wyoming coal region, Jones and Thune (1982) showed that a definite vertical-migration component could be identified. In that experiment, gases formed during combustion appeared both in soil gases directly above the retort and up-dip along the bedding planes of the strata involved in the burn. Thus, vertical signals from a known subsurface origin were shown to exhibit cross-stratigraphic migration, presumably due to the presence of fractures in the system. A second horizontally-displaced component also migrated along the bedding planes at the same time.

An example of the use of direct anomalies and the preferential pathway model is shown in Fig. 5-30, which shows an idealised subsurface cross-section through the Lost River field in West Virginia along with a propane profile (Matthews et al., 1984). From this profile and with some knowledge of the geology, it can be seen that a large anomaly is probably caused by updip leakage of the fractured Devonian Oriskany reservoir at depth. This outcrop anomaly is due to updip leakage along the bedding plane of the reservoir facies. A smaller but significant anomaly is related to leakage from a fault that strikes along and to the east of the crest of the producing anticline. Blind drilling on the outcrop anomaly would have resulted in a dry hole, whereas drilling just west of the fault anomaly would have encountered the producing structure. Appropriate geological modelling identifies the location at which to drill.

An alternative to the direct anomaly interpretation method relies on identifying one of two types of halo: (1) local lows, source background areas surrounded by highs; or (2) extremely low areas, surrounded by areas of moderate concentration. These halos are consistent with the initial results obtained with soil-gas analysis techniques (Rosaire, 1938; Horvitz, 1939, 1945, 1954, 1985; McDermott, 1940; Rosaire, et al., 1940), which indicated that adsorbed and occluded hydrocarbons occur in greater quantities around the edges of production, whereas relatively lower values are found directly above production. Halo anomalies have been recognised in many regions of the former USSR (Kartsev et al., 1959). Horvitz (1969, 1980) has emphasised that although other hydrocarbon distribution patterns are recognised, including direct anomalies, the halo

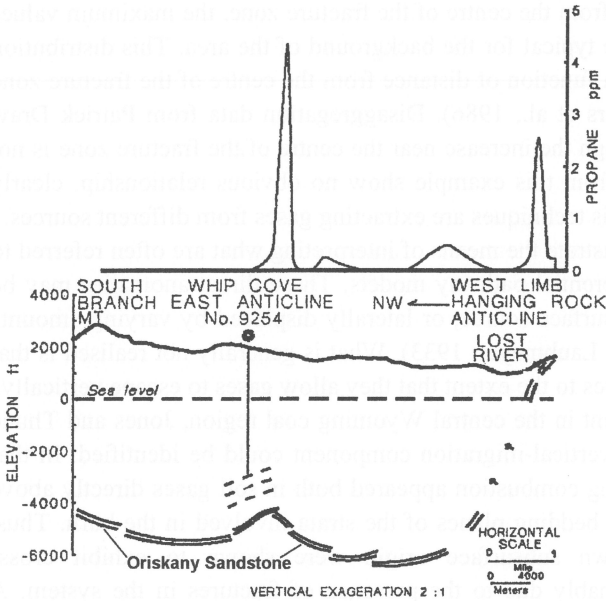


Fig. 5-30. Cross-section through the Lost River oil field, West Virginia, and profile of propane in soil-gas (reproduced with permission of Veridian-ERIM International from Matthews et al., 1984).

pattern continues to be the most common type found in conjunction with important oil and gas accumulations.

Numerous explanations have been put forth as to why halos form around hydrocarbon accumulations. Most of these link the phenomena to the impedance effect of a diagenic mineralisation zone overlying the main part of the petroleum accumulation. Such a zone would tend to reduce the ability of gases to seep vertically, except along well-pronounced fracture systems. Hence, most transport would be deflected around the edges of the occluded zone. The occluded zone could form by any number of diagenic processes. Rosaire (1940) suggested that the greater solubility of carbon dioxide in petroleum, as compared to water, results in the conversion of bicarbonates to less soluble carbonates over an accumulation. An initial chimney effect would result in a greater supply of bicarbonate being present above an accumulation resulting in the cementation. Rosaire (1940) also proposed the reduction of sulphates to sulphides over an accumulation. Fenn (1940) reintroduced another process that was first introduced by Mills and Wells (1919). This model is based on the evaporation of ground moisture as the result of gas expansion which results in the subsequent precipitation of minerals at shallow depths. The origin of the blocked central portion over an accumulation implies that gas-induced evaporation occurs more effectively over an accumulation than along its margins. This model is consistent with results on the variations in unusual chemical

and isotopic compositions of carbonate-cemented surface rocks over oil and gas fields (Donovan, 1974; Donovan and Dalziel, 1977). Stroganov (1969) has confirmed that the deeper distribution of hydrocarbons only rarely yields a halo pattern, suggesting the halos have a near-surface origin. Matthews (1985) suggested that diagenetic blockage related to hydrocarbon emplacement may originate at intermediate depths and then be exhumed by erosional processes.

Although direct anomalies and halos have conflicting explanations, both appear to be valid. Indeed, the controversy is significant only if it is assumed that lateral displacement has not occurred during subsurface leakage. This is certainly a valid assumption in some, but definitely not all, cases. If the halo pattern is interpreted as a subset of several preferential pathways, one can assume that at least one major flowpath could become blocked by diagenetic cement, resulting in a bias of leakage, with a false halo forming as the gases are diverted around this blockage in an area that previously yielded a direct anomaly. In one study the occurrence of halos was suggested by adsorbed soil-gas samples, whilst direct anomalies were observed using free soil-gas samples (Richers et al., 1986). One must speculate that these techniques measure different aspects of the leakage phenomena. For this reason, it is felt prudent to always collect both types of samples whenever economically feasible. In addition one would be well advised to incorporate geological and geophysical data into the model.

A significant portion of near-surface hydrocarbon survey results appear to be compatible with the mechanisms of macroseepage, particularly leakage occurring along preferential pathways. Those anomalies seemingly not coincident with known faults, fractures, unconformities, bedding planes or other obvious pathways may lie on pathways unrecognised due to limited or incorrect mapping. Alternatively, some occurrences may represent processes not completely understood, or processes not validly extrapolated from macroseepage to microseepage.

The preferential pathway model summarises the movement of hydrocarbon fluids through the subsurface to their final destination as a surface seep, either directly or by way of an intermediate trap. It is certainly not definitive nor complete, but illustrates some of the challenges confronting the petroleum geologist in his quest for new resources.

Geochemical populations

An alternative to modelling hydrocarbon gas migration as a basis for data interpretation is to decompose data into geochemical populations. On this basis surface geochemical data can be interpreted with respect to both composition and magnitude.

The goal of compositional analyses is to be able to characterise the type or types of subsurface accumulations present and to be able to predict the location at which they occur. This can be achieved through using ratios of the various hydrocarbon constituents that are detected in the soil-gas sample. In general, gas reservoirs are commonly

TABLE 5-XIV

Concentrations of unsaturated hydrocarbons (10^{-4} vol. %) generated during oxidation of gaseous hydrocarbons by a culture of *Myc. Flavum* incubated at 30-32°C (Telegina and Cherkinskaya, 1971)

Day	Experimental conditions	Aerobic (21.2% O ₂)			Anaerobic (1.4% O ₂)		
		C ₂ =	C ₃ =	C ₄ =	C ₂ =	C ₃ =	C ₄ =
0	<i>Myc. Flavum</i> present	0	0		0	0	0
	Control, no bacteria	0	0	0	0	0	0
8-10	<i>Myc. Flavum</i> present	0.004	0	0	0.227	0.062	0
	Control, no bacteria	0	0	0	0.158	0	0
30	<i>Myc. Flavum</i> present	0	0.003	0	0.064	0.114	0.003
	Control, no bacteria	0	0	0	0.500	0	0

dominated by the presence of methane, whereas oil reservoirs usually contain additional quantities of hydrocarbon gases heavier than methane (Nikonov, 1971).

There are three potential origins for gases detected in the near-surface environment: biogenic, thermogenic (or katogenic) and igneous (including mantle degassing); and irrespective of the origin, the gases tend to migrate towards the surface due to pressure and buoyancy effects. Gases from several sources may mix or undergo other compositional changes such as chromatographic separation, during this migration. Thus the measured compositions may not always reflect the original subsurface composition. In most areas mixing presents little problem because gases of thermogenic origin are by far the most abundant. Furthermore, the tendency for gases of biogenic and igneous origin to be extremely dry and of a different isotopic composition from thermogenic gases enables recognition of their presence. Extreme chromatographic separation may only be recognised by careful isotopic analysis and through the close comparison of near-surface gas with known reservoir gas in the region. The presence of gas of igneous origin generally indicates the occurrence of deep, pervasive faulting, and/or the presence of igneous activity in the area. This association, as well as the extremely methane-rich character of such gases, allows for the facile distinction between gases from thermogenic and igneous sources.

Telegina and Cherkinskaya (1971) found that the olefin content of soil gases decreased relative to saturated hydrocarbons until depths of about 300 m. Experimentally, as illustrated in Table 5-XIV, olefins can be formed from saturated compounds in areas of low oxygen content (0.5-3.2 %). The presence of these olefins may be biogenic (Smith and Ellis, 1963), although Starobinets (1976) showed a linear relationship between the concentrations of saturated and unsaturated gases derived from the thermogenic alteration of organic matter. Sokolov (1971b), among others, suggested a relationship between the generation of unsaturated compounds and drilling activity.

Gleezen (1985) showed that there is promise in using the olefin contents of soil gases as a scaling factor to separate seep signals from ambient signals. He was able to define areas with signatures similar to those of the reservoir gases. It would appear that in some cases the presence of olefins may merely represent the breakdown of saturated hydrocarbons by some yet-undetermined process during the migration of gases to the surface and/or some activity such as biogenic degradation of the saturates in the near-surface environment (Telegina and Cherkinskaya, 1971).

Compositional information in soil gases has been related to subsurface accumulations through the application of specific ratios (Jones and Drozd, 1983). Methane-dependent ratios (Table 5-VIII) are reliable unless multiple sources of gas are present in the area. An independent methane-rich source biases an oilier composition toward a drier gas composition. This can sometimes be overcome by plotting histograms of the compositional data and noting multiple populations in the data. Another set of diagnostic ratios that are not methane dependent has also been defined and further aid in properly defining the true potential of an area (Drozd et al., 1981; Williams et al., 1981). In general, the agreement between the surface compositions with reservoir compositions is the strongest evidence that surface prospecting can accurately define the potential of an area.

In addition to compositional information, soil-gas data can yield useful information according to the presence or absence of anomalously-high magnitudes. To understand the concept of anomalously-high magnitudes, one must understand the general distribution of gases in nature. Basically these can be reduced to three main populations for any given region.

- 1) An ambient background population (which represents a detectable level of non-significant hydrocarbon concentrations). This includes mantle-derived hydrocarbons, contamination, instrumental noise, sampling error, etc.

- 2) A source background population representing hydrocarbons derived from the presence of organic-rich source beds in a region. These are generally areal in extent, and they may or may not be relatively consistent throughout the area depending on local geologic variations, regional trends or multiple sources.

- 3) An anomalous population of higher-than-normal concentrations of hydrocarbons that represent the subsurface presence of concentrated hydrocarbons such as those found in reservoirs.

Ambient levels, by their very nature, are encountered everywhere, and are always a component of the total soil-gas signal regardless of the overall hydrocarbon potential of an area. Their presence may be due to natural catagenesis of organically-poor rocks during the processes of diagenesis and lithification, and can be thought of as being syngenetic. Another source is the biogenic alteration of organic matter in the near-

TABLE 5-XV

Hydrocarbon content of Palaeogene formations in productive and non-productive areas of western Siberia (Starobinetz, 1983)

	Nekrasovskaya	Cheganovskaya	Dulinvorskaya
<u>North Vargau (productive)</u>			
No. samples	7	10	20
C ₅ -C ₈ (10 ⁻⁴ cc/kg)	129	131	133
C ₅ -C ₈ / C ₂ -C ₄	42	47	21
C ₅ -C ₈ %	2.73	1.90	0.08
No. samples	7	4	9
MCA 10 ⁻⁴	50	21	19
Aromatics, C ₆ +C ₇ (10 ⁻⁴ cc/kg)	41	17	13
C ₆ / C ₇	0.6	0.5	0.4
<u>Pokrovskaya (non-productive)</u>			
No. samples	10	14	17
C ₅ -C ₈ (10 ⁻⁴ cc/kg)	90	16	24
C ₅ -C ₈ / C ₂ -C ₄	65	4.4	4.3
C ₅ -C ₈ %	0.24	0.01	0.01
No. samples	5	6	9
MCA 10 ⁻⁴	5	6	11
Aromatics, C ₆ +C ₇ (10 ⁻⁴ cc/kg)	4	4	7
C ₆ / C ₇	0.3	0.3	0.3

surface. Typically, ambient background areas contain a little methane and virtually no other hydrocarbon gases. An illustration of ambient background levels is shown after Starobinetz (1983) in Table 5-XV.

Zinger et al. (1983) provide data that are typical of a sourced background from the Kuybyshev oil-bearing area of the former USSR. Here the methane content varies between 20% and 57%, with heavier homologs consistently present. The backgrounds that occur in such areas are considered to be sourced backgrounds because the effects of the pooled hydrocarbons are superimposed on the lower ambient background signal.

The anomalous population comprises only a very small portion of the overall data set, typically only a few percent. Values for these samples generally are 2-3 times the magnitude of the sourced background. In some instances, concentrations may reach the percentage level, in which case the locations border on the macroseepage rather than microseepage. At the other end of the spectrum are those samples that are 5 or 10 times above the background concentration. These may represent either a separate population from the sourced background, or merely high-frequency fluctuations in the sourced background.

There are two fundamentally-different approaches to defining anomalous magnitudes. The traditional technique focuses solely on the distribution of hydrocarbon

concentrations, regardless of location. A magnitude threshold, or series of thresholds, is chosen and those locations with values above this threshold (anomalously-high concentrations) are identified on a map. The second technique focuses on the spatial clustering of anomalous stations. This is accomplished by the identification of regions where the number of stations with magnitudes above a threshold is statistically significant.

The traditional method of identifying a magnitude threshold has been accomplished by a variety of techniques. These include: (1) the mean plus two standard deviations of a normally-distributed data set; (2) arbitrarily selecting the 90th percentile or 95th percentile, etc., of the data; (3) identifying the inflection point on a cumulative frequency plot that deviates from a straight line (Sinclair, 1976).

In the opinion of the authors it is dangerous to select any hard-and-fast rule for defining an anomalous population, although the approach of Sinclair (1976) is the most appropriate for a mixed mode data set. Sample populations should be normal, or at least log normal, for many of the statistical tests to be valid, and bias in sample sites should be avoided if possible. Ideally a training set made up of a data subset with known hydrocarbon potential should be employed. This gives a means to tie-in data to a known feature, whether it be a source bed, a reservoir or a barren area. Once the results are available, a first step is to construct histograms to determine the spread of the data. The data can then be plotted on cumulative frequency plots to determine the different populations. Scatter plots of key components, such as methane *versus* propane, or iso-butane *versus* normal butane, often yield multiple trends for multiple populations in the data. Pearson correlation analysis also yields useful information on the "cleanliness" of the data, with single populations generally showing a high degree of inter-correlation. Filtering or screening the data according to composition prior to applying statistics is also an effective means of determining areas of favourable potential.

The method of identifying regions of anomalously-high leakage by clustering (Dickinson and Matthews, 1993) is accomplished by first identifying a magnitude threshold and a search area. The magnitude threshold, which is somewhat arbitrary, is used to transform the distribution of magnitudes into a binomial population (above the threshold "heads" and below the threshold "tails"). The size of the search area (the "cell") is such that it includes 20 or more sample stations regardless of its location within the surveyed area. Once these parameters are chosen, the cell is placed at one position on the map, usually in one corner, and the percentage of heads and the total number of stations within the cell are recorded. The cell is then translated to a new location and the same parameters are recorded. This process is repeated until the entire survey area has been examined. Because the properties of the binomial distribution are well known, statistical tests of the chance of a particular cell having a particular percentage of heads can be made and probability maps contoured. Thus, regions of anomalously-high frequency of magnitudes above the threshold can be identified, and their chance of arising due to random processes, instead of focused leakage, can be estimated. There is,

TABLE 5-XVI

Success rates of surface gas geochemistry in petroleum prospecting in Azerbaijan (Zorkin et al., 1982)

Province	Positive prognosis			Negative prognosis		
	Areas	Correct	%	Areas	Correct	%
Apsheronkaya	8	7	87	-	-	-
Nizhniekurinskaya	4	3	75	-	-	-
Kirovobadskaya	10	7	70	8	7	87
Kobystano-Shemahinskaya	4	2	50	6	6	100
Total	26	19	70	14	13	90

however, the risk that information about spatial variability within a cell is lost and so is the information about the absolute magnitude of individual samples.

On the basis of anomalous magnitudes, Zorkin et al. (1982) showed that, in 90% of cases, the soil-gas technique correctly identified areas lacking hydrocarbon potential in Azerbaijan, and correctly identified areas with hydrocarbon potential in 70% of cases (Table 5-XVI). Although the distinction of ambient from secondary background is often relatively straightforward, the distinction becomes ambiguous in areas with effective seals, such as stable intracratonic salt basins.

CASE HISTORIES

Numerous case histories illustrating the relationship of surface seeps to their associated production are given in the cited references. Four surveys, three onshore and one offshore, are selected here to demonstrate and confirm the compositional relationships defined above. The first onshore example consists of calibration grids conducted over two fields in the Neuquen Basin of Argentina, and the second example is a sniffer survey conducted for calibration purposes over gas-productive areas in the High Island area of the Gulf of Mexico. The two other onshore surveys are located in the Great Basin of Nevada and in the Overthrust Belt of Wyoming-Utah.

Neuquen Basin, Argentina

Detailed soil gas geochemical surveys were conducted for calibration purposes over two fields, Filo Morado and Loma de La Lata, in the Neuquen Basin in Argentina. These two fields were chosen for this calibration study because of their differences in both reservoir composition and entrapment mechanisms.

Filo Morado is an anticlinal oil field producing from the Agrio Formation at a depth of 3000 m (10,000 feet). Loma de La Lata consists of two stratigraphically-trapped

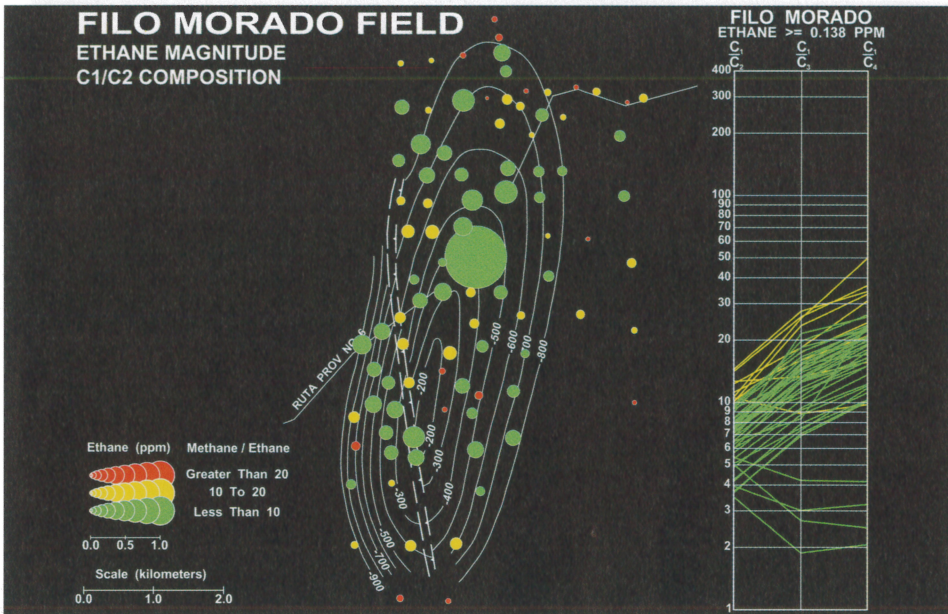


Fig. 5-31. Spatial distribution of soil gas hydrocarbons at Filo Morado, Argentina (arbitrary coordinates): dot size indicates ethane concentration; dot colour indicates C_1/C_2 ratio, such that green = low (oil), yellow = intermediate, red = high (gas).

reservoirs formed on a homocline which dips to the northeast. Oil production comes from the Quintuco Formation at 2000 m (6600 feet). This reservoir is partially underlain by a separate gas to gas condensate reservoir producing from the Sierras Blancas formation at 3000 m (10,000 feet). The three separate reservoirs from these two fields provide two oil reservoirs and one gas to gas condensate reservoir for calibration of the soil-gas geochemical data.

The geochemical data come from 239 shallow probe (1.2 metre, 4 feet) soil-gas samples collected on 500 - 1000 m grids placed directly over these two fields, with 95 sites over Filo Morado and 144 sites over Loma de La Lata. The free soil gases were analysed for methane, ethane, ethylene, propane, propylene, iso-butane and normal butane by gas chromatography using a flame ionisation detector.

In order to illustrate the distribution and compositions of the light hydrocarbon seepage, compositional dot maps which combine both the light hydrocarbon magnitudes and compositional information are shown in Fig. 5-31 for Filo Morado and in Fig. 5-32 for Loma de La Lata. Each dot is coloured according to the C_1/C_2 ratio to reflect the composition of soil gases as indicative of oil (green), gas (red) or intermediate (yellow). The dots, including those at localities with only background magnitudes, vary in size according to their ethane magnitudes.

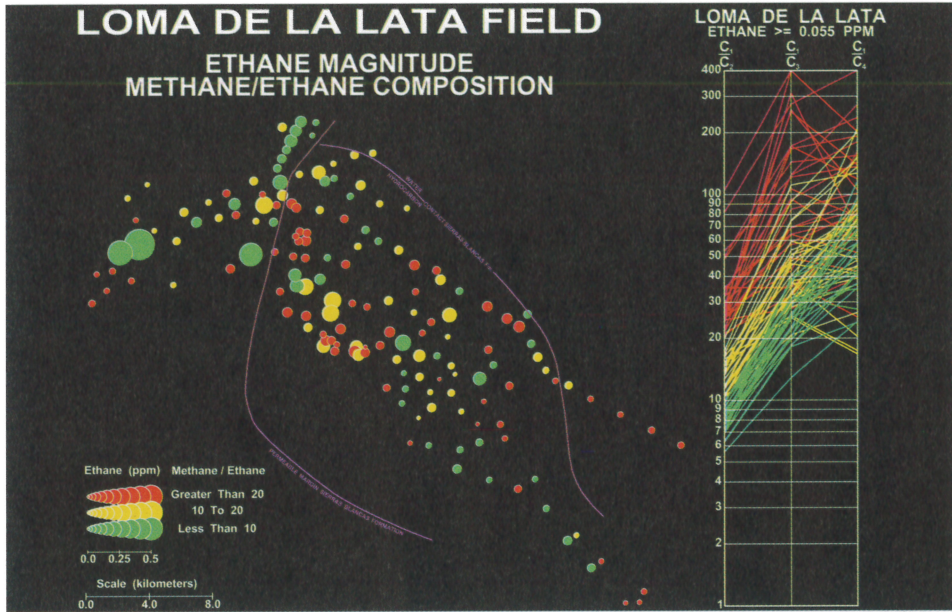


Fig. 5-32. Spatial distribution of soil gas hydrocarbons at Loma de La Lata, Argentina (arbitrary coordinates): dot size indicates ethane concentration; dot colour indicates C_1/C_2 ratio, such that green = low (oil), yellow = intermediate, red = high (gas).

The compositional subdivisions are derived from the published literature (Nikonov, 1971; Jones and Drozd, 1983) and are the same as those shown in Table 5-VIII. The shade of each of the anomaly clusters suggests the oil *versus* gas potential of the anomaly according to these empirical divisions alone.

Ratios of methane/ethane, methane/propane and methane/total butanes for all sites that exceed the median of the data are also shown in Figs. 5-31 and 5-32, in order to provide a visual illustration of the composition of the anomalous data. The bimodal nature of the Loma de La Lata soil-gas data is clearly shown by the red (gas) and green (oil) populations whilst Filo Morado stands in stark contrast, with its unimodal oily (green) population and lack of gas-type anomalies.

Examination and comparison of these ratio plots and dot maps for each of the two fields indicate that the more anomalous magnitude sites (large dots) match the composition of the known underlying reservoirs. The areal groupings and Pixler ratio plots of these specific components with their appropriate reservoirs lends confidence to the deduction that these soil-gas anomalies are the result of migration of petrogenic hydrocarbons from the underlying sedimentary sources.

The geochemical soil gas data exhibit clearly defined compositional sub-populations which match the composition of the underlying reservoirs and change in direct response to the major structural and/or stratigraphic features that control the location of the subsurface reservoirs. Predictions of oil *versus* gas from these soil gas data are in

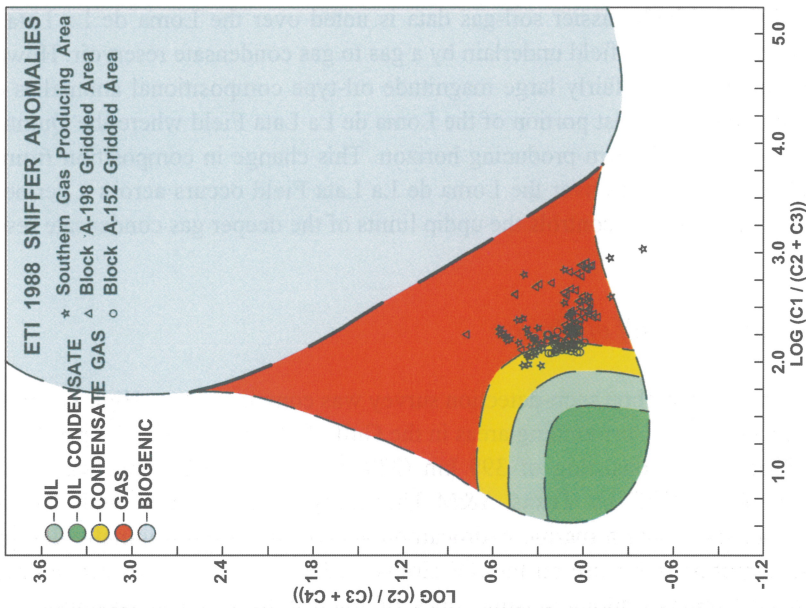
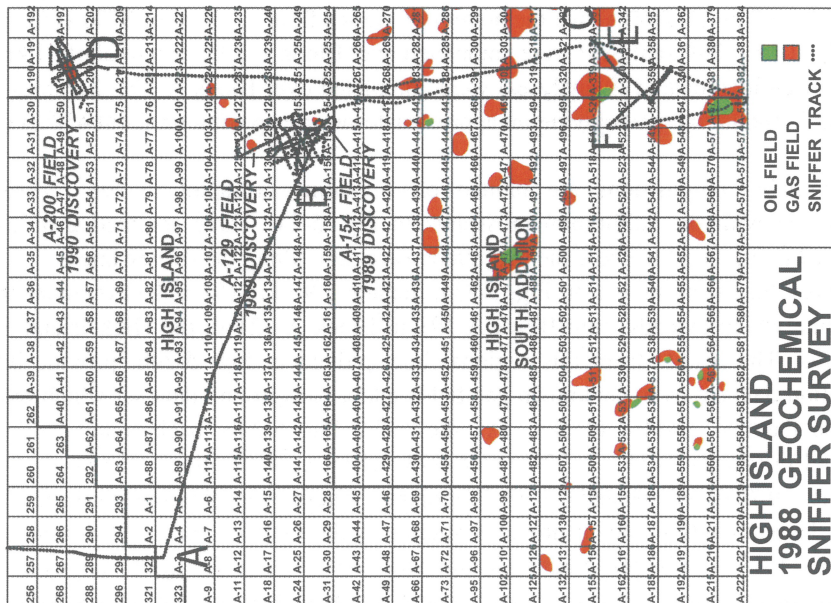
excellent agreement with published soil gas and reservoir data (Jones and Drozd, 1983; Nikonov, 1971). A single oil source is predicted at Filo Morado, in agreement with the known oil field. Much gassier soil-gas data is noted over the Loma de La Lata Field, where there exists an oil field underlain by a gas to gas condensate reservoir. However, a very striking change to fairly large magnitude oil-type compositional anomalies occurs directly over the northwest portion of the Loma de La Lata Field where the Quintuco oil reservoir is the only known producing horizon. This change in composition from oil to gas condensate signatures over the Loma de La Lata Field occurs across a permeability pinchout at depth, which controls the updip limits of the deeper gas condensate reservoir.

High Island area, Gulf of Mexico

A marine hydrocarbon seep-detection survey was completed over High Island Blocks A-152 and A-198 and surrounding areas in the Gulf of Mexico on 22-23 April 1988 (Fig. 5-33a). This study, consisting of 399 km (239 miles) of sniffer data, was conducted aboard the RV GYRE by Texas A&M University in conjunction with Exploration Technologies Inc. using a marine hydrocarbon analytical system originally designed by Gulf Oil Corporation for use on the RV Hollis Hedberg. Light hydrocarbon data were collected continuously along seismic lines of interest from a water-sampling system towed about 9 m (30 feet) above the bottom of the sea floor. A total of 87 km (52 miles) of gridded data (259 analyses) were completed over Block 152A and a total of 51 km (31 miles) of gridded data (129 analyses) were completed over Block A-198. Samples were taken at 3-minute intervals giving an approximate sample spacing of about 450 m (1500 feet)

Anomaly compositions are plotted on a marine crossplot in Fig. 5-33b for comparison with the calibration crossplots in Fig. 5-24. Three regional profiles are presented in Fig. 5-34 to show the magnitude variations along the survey lines.

Survey tracks, as shown on Fig. 5-33a, include a 90 km (54 miles) regional south-north line which extends from Block A-198 to Block A-321 in the High Island South extension. The results from this regional line, plotted in Fig. 5-34b, provide both a calibration data set over the known gas fields and a background data set which extends between the two gridded blocks. As shown by Fig. 5-34b, background values are observed in Blocks A-237, A-224 and A-223, where concentrations are about 100 nl/l methane, <0.70 nl/l ethane and <0.50 nl/l propane. These concentrations correspond with typical backgrounds found in previous studies in the Gulf of Mexico (Mousseau and Williams, 1979). The largest magnitude anomalies observed on this entire survey are also noted on this regional line (Fig. 5-34b), where it crosses the centre of Block A-268 and traverses the major trend of the known gas-producing fields. Within this producing trend, methane values exceed 500 nl/l, ethane ranges from 1-5 nl/l and propane rises from 0.50-1 nl/l. In addition, iso-butane and normal butane reach a combined total of about 1 nl/l in anomalies associated with these known gas fields.



b)

a)

The presence of butanes in the sniffer data clearly separates the southern gas-producing trend from the area to the north of Block A-252. The grids over both Block A-152 and Block A-198 and the profile data north of Block A-252 exhibit a clear lack of propane and butane anomalies. The presence of mainly methane in the northern area suggests that these anomalies are derived from biogenic gas sources.

Marine compositional crossplots from the anomalies observed in Block A-152 and A-198, and from the regional profile are compared in Fig. 5-34d. All three areas fall exactly as expected, based on the known oil and gas producing reservoirs within this survey area. Blocks A-152 and A-198 are similar to the fairly dry gas type Pleistocene reservoirs found in West Cameron, in the Louisiana offshore area, and are indicative of only gas potential. Block A-198 anomalies appear to contain even drier gas data than those in Block A-152. Data from both of these blocks plot below the cluster associated with the major Pliocene gas-producing trend that lies to the south of Blocks A-152 and A-198. The increase in ethane, propane and butanes in this southern gas-producing area suggests that these gas fields contain Pliocene gas from a more petrogenic source, whereas the areas to the north appear to be dominated by biogenic gas sources that do not contain C₂₊ components. It should be noted that the new field discoveries (A-129, A-154 and A-200), highlighted in Fig. 5-33a, were made after the sniffer survey was completed.

Great Basin, Railroad Valley, Nevada

The third example in this chapter is an onshore survey conducted in Railroad Valley, Nevada. This example is abstracted from an integrated two-year (1984-85) remote-sensing and surface-geochemical research project which provides an excellent example of the exploration value of combined remote-sensing and geochemical studies in frontier basins (Jones et al., 1985; Burtell et al., 1986). The variability of sample spacing used over this two-year programme, coupled with repeated, even-closer detailed sampling on grids in 1985, allows a demonstration of the sampling artifacts that can be created by over-interpreting a low-density regional survey. In addition, the repeatability of soil-gas surveys is demonstrated. The compositional correlations predicting oil *versus* gas, as shown in the two previous examples, are extended to differentiating non-commercial heavy-oil deposits from their lighter counterparts, neither of which contains any significant gas production.

Fig. 5-33. High Island geochemical sniffer survey 1988: a) sniffer track map; b) marine compositional crossplot.

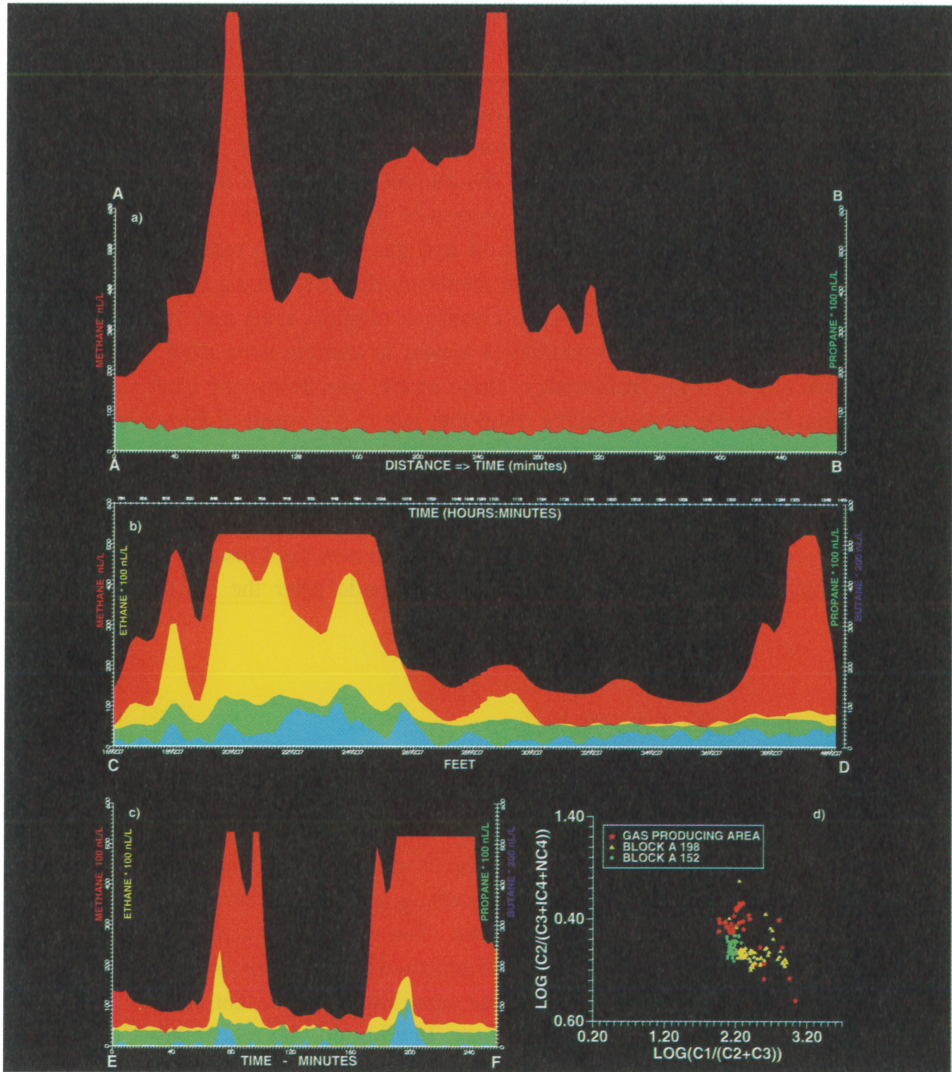


Fig. 5-34. Profile of dissolved hydrocarbon data from High Island sniffer survey; a) east-west line A-B; b) south-north line C-D; c) north-south-north line E-F; d) marine compositional crossplot for 1988 sniffer anomalies.

The first-year study in Railroad Valley, conducted in 1984, consisted of a regional lineament evaluation made from Landsat Thematic Mapper (TM) imagery, Synthetic Aperture Radar (SAR) imagery and regional soil-gas probe sampling to identify areas of significant hydrocarbon seepage (Jones, et al. 1985). Railroad Valley was chosen for this research study because of the excellent surface expression of structural features,

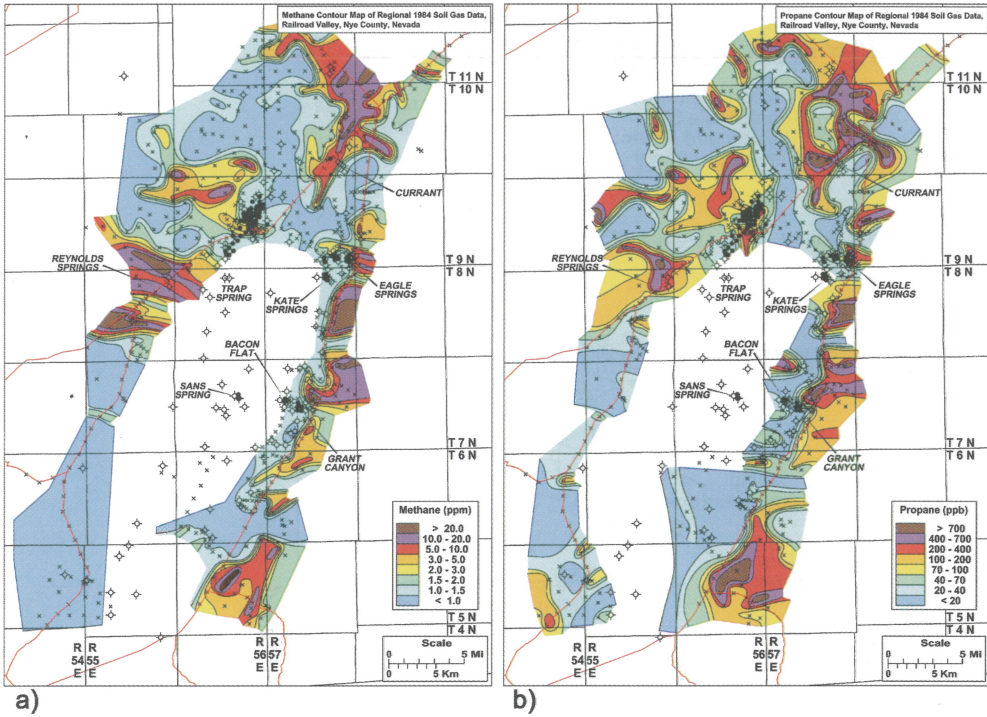


Fig. 5-35. Contour maps of 1984 regional soil-gas data, Railroad Valley, Nevada: a) methane contour map; b) propane contour map.

including both lineaments and circular geomorphic anomalies, which have been used by Dolly (1979) and Foster (1979) to locate drainage anomalies, interpreted as reflecting differential subsidence of subsurface structural blocks. The first three producing fields discovered in Railroad Valley (Eagle Springs, Trap Spring and Grant Canyon) occur in circular features mapped by Dolly (1979) and Foster (1979). Subsequent discoveries in Railroad Valley have not discounted this proposed association, but the discovery of Paleozoic reservoirs has added considerably to the complexity of the model.

Contour maps of the regional methane and propane soil-gas data gathered in 1984 are shown in Fig. 5-35, along with major structural and geomorphic features mapped by Dolly (1979) and Foster (1979). Both components exhibit large-magnitude geochemical anomalies that clearly originate at the basin-bounding fault and extend updip onto the adjacent pediment block. A very simplified cartoon explains how this updip migration might occur through fractures and/or draped sand lenses contained within the Tertiary fill (Fig. 5-36).

An alternative approach to contour maps is to generate a colour compositional dot map (Fig. 5-37), in which the size of each dot is proportional to the ethane magnitude and the colour is selected from the Pixler ratio plot (Fig. 5-37, inset, upper left).

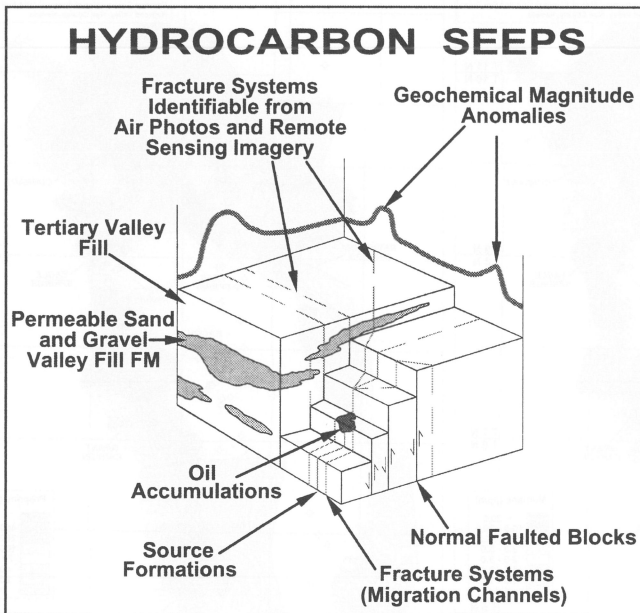


Fig.5-36. Geological/geochemical seep model illustrating possible migration pathways for Railroad Valley, Nevada.

Choosing the standard empirical classes from Table 5-VIII for these data shows that the producing oil fields fall within the yellow, rather than within the green areas, as would be expected for the heavy oils produced in Railroad Valley. This colour compositional dot map suggests that it is possible to differentiate between hydrocarbon types from the relative position of each site on these Pixler ratio plots. Eagle Springs, Trap Springs and Grant Canyon fields have well-controlled intermediate compositions (yellow dots), while the Currant well area exhibits much lower, oilier ratios (green dots). Thus hydrocarbon seep compositions observed in Railroad Valley appear to differentiate productive or potentially-productive reservoirs from non-productive heavy-oil accumulations at depth. These compositional changes are spatially closely related, suggesting that the compositional changes may occur across geologic boundaries, which control both the hydrocarbon reservoirs and their associated surface seepage.

The study in Railroad Valley also showed that a large number of high-magnitude seeps occur near to, or on, lineaments and lineament intersections (Jones, et al. 1985). This classic relationship reflects one of the most valuable uses of remote-sensing lineament studies in frontier basins. Preferential location of geochemical samples in the vicinity of active structural zones and their intersections will usually locate a large number of the hydrocarbon seeps in any basin. In addition, regions of intense fracturing

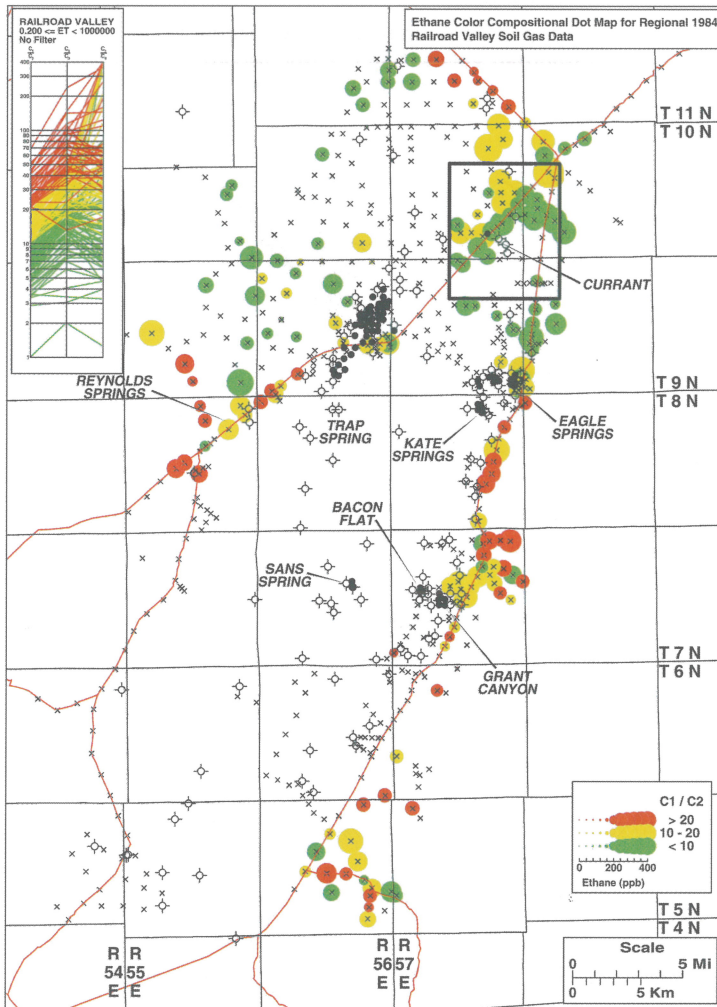


Fig. 5-37. Ethane colour compositional dot map for 1984 regional soil-gas data, Railroad Valley, Nevada; inset, Pixler ratio composition.

that do not exhibit hydrocarbon seepage strongly suggests a lack of source potential at depth in such areas.

This study in Railroad Valley demonstrates a unique surface geochemical expression of one particular lineament, herein named the Currant Lineament, which appears to have a dramatic effect on the commercial possibilities for a subsurface oil deposit. The non-commercial Currant No. 1 well is located just to the southeast of a NE-SW linear feature, which crosses the valley through the town of Currant in northern part of Railroad Valley. The location of this lineament is obvious on all of the regional remote-sensing products. Although the lineament is dramatically expressed both northeast and southwest of Currant, it is not as obvious in the centre of the study area. Even more detailed aerial

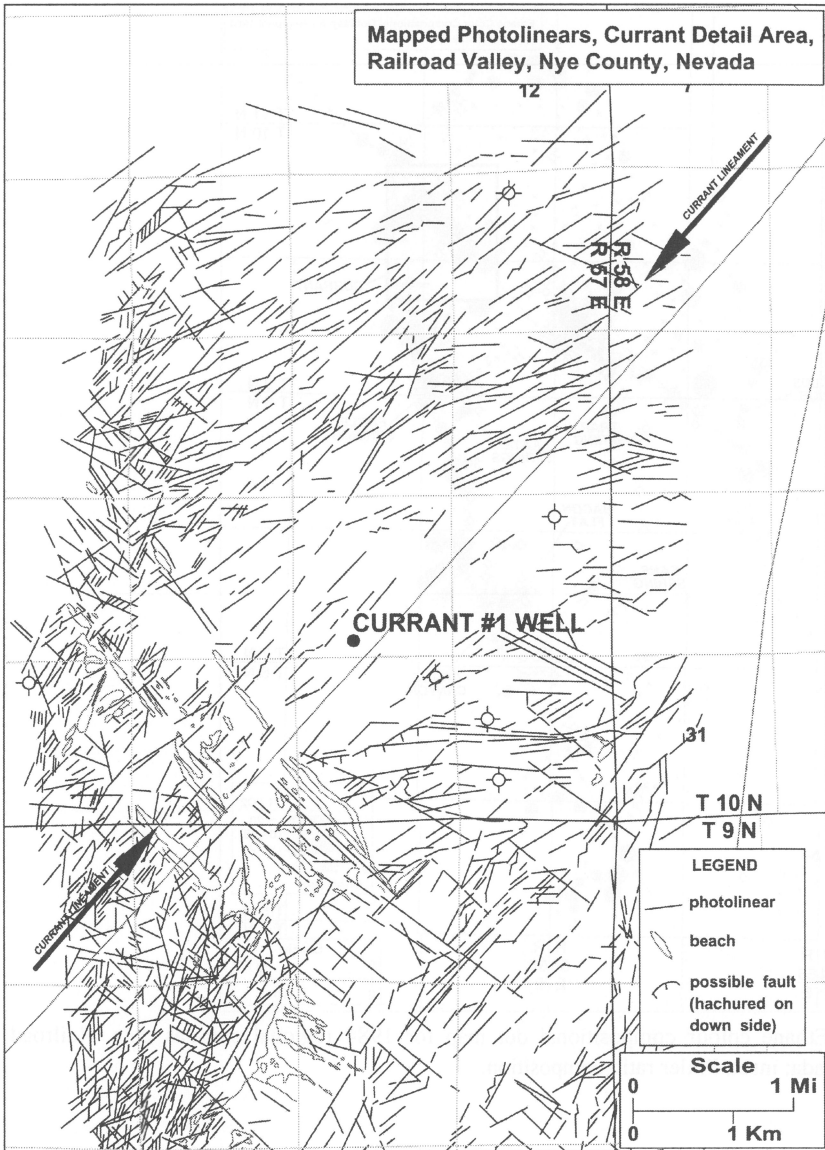


Fig. 5-38. Mapped photolinears, Currant detail area (from Jones et al., 1985).

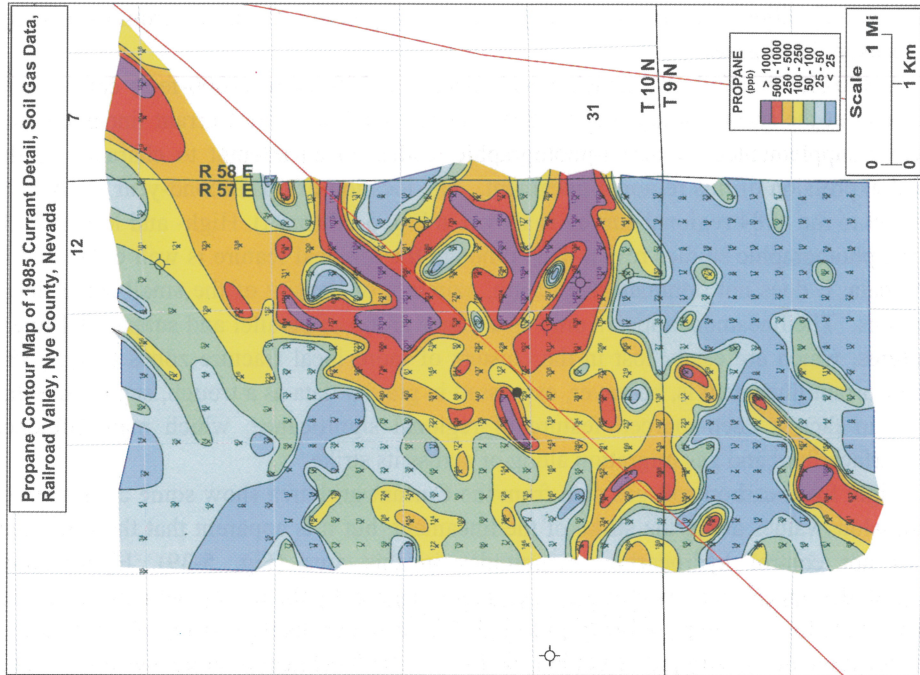
photography (Fig. 5-38) yields only a series of fairly short photolineaments, most of which are drainage segments not obviously related to the regional lineament. As shown by the colour compositional dot map in Fig. 5-37, hydrocarbon seeps to the northwest of the Currant lineament have compositions, as defined by Pixler ratio plots, that are quite similar to the productive fields in Railroad Valley. Sites to the southeast of the lineament

have a much oilier signature, suggesting a relative depletion of volatiles from the sources of measured soil gases.

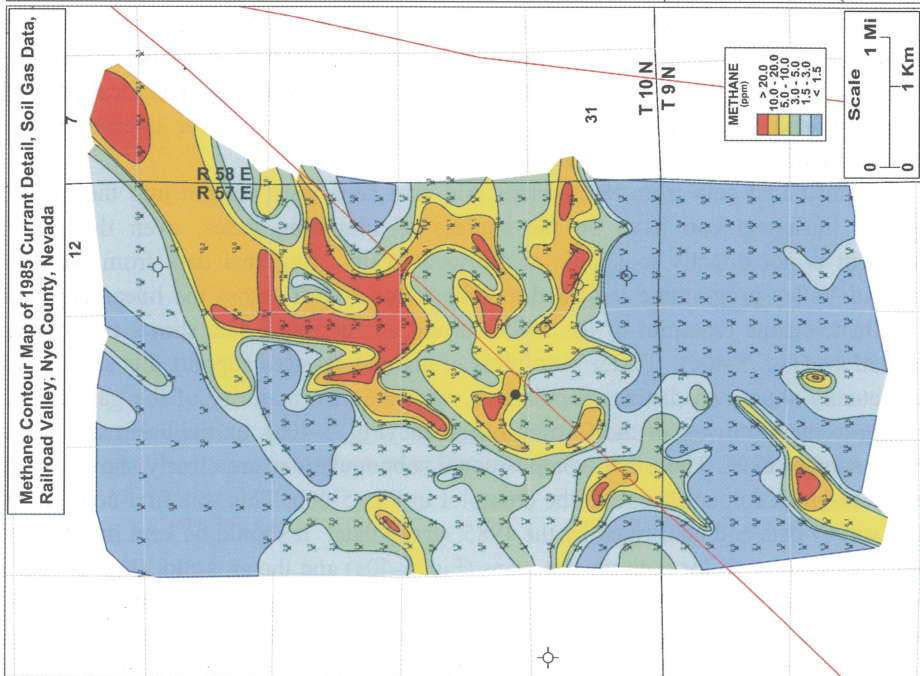
A 400-site detailed grid geochemical survey on 300-metre (1000-foot) centres was carried out the second study year (1985) over this section of the Currant lineament and further supplemented by aerial-photographic studies in an attempt to characterise the local expression of this regional lineament. The location of this second-year study with respect to the 1984 regional survey is shown in Fig. 5-37 (inset). High- and low-altitude aerial photographic studies reveal that, although the regional feature is well expressed in TM data, it does not dominate the length, azimuth, or density of the small-scale linear features. The lineament appears only as a minor group of parallel and subparallel linear features, which are easily lost in the clusters of more local fracture zones (Fig. 5-38). The Currant lineament is, however, expressed in gravity data as a trough, suggesting that it is, in fact, a deep-sourced feature of regional significance, which may influence subsurface fluid and gas migration along or across its strike.

Light hydrocarbon soil-gas data from the Currant grid area show some alignment of anomalous values along the strike of the lineament, but it is apparent that the lineament does not control hydrocarbon magnitudes in this area (Fig. 5-39). Hydrocarbon magnitudes appear to be controlled, to a greater degree, by the north-south and east-west small-scale linear features (shown in Fig. 5-38), which probably reflect, to some extent, the location of subsurface structural faults and fault-related fracture systems. This relationship is quite important because structures identified by lineament zones are generally not the sole controlling factor for light hydrocarbon seepage; rather they simply provide enhanced pathways of migration for gases and fluids. The local geologic framework and source potential are the most important factors for interpreting the relationship of hydrocarbon seeps and lineaments.

Compositional data from the Currant grid area adds great insight into the effect a regional lineament can have on the sources of migrating gases, even though the lineament is not directly mappable at the local scale. Regional data from the 1984 Railroad Valley programme indicated a compositional shift across the lineament zone. A methane-ethane crossplot of the 1985 Currant detailed grid data shows two distinct populations (Fig. 5-40c). Pixler ratio plots of anomalous sites support this subdivision and actually show two distinct populations, with the vast majority of the gassier sites plotting to the northwest of the Currant lineament (Fig. 5-40a), on the basin side where deeper sources exist. These two compositional subpopulations are clearly shown by the yellow-to-green colour change in the crossplot in Fig. 5-40b. This was first noted in the 1984 survey data and confirmed by the 1985 survey data. It should be kept in mind that the colour code used for both the dot maps (Fig. 5-40a) and the crossplot (Fig. 5-40b) is determined by plotting the raw soil-gas data on the Pixler diagram. Thus the colour compositions are selected to be similar to analyses of samples from actual producing reservoirs. The combination of both spatial and compositional clustering clearly demonstrates the stability, and repeatability of light soil-gas data that are properly collected and analysed.



b)



a)

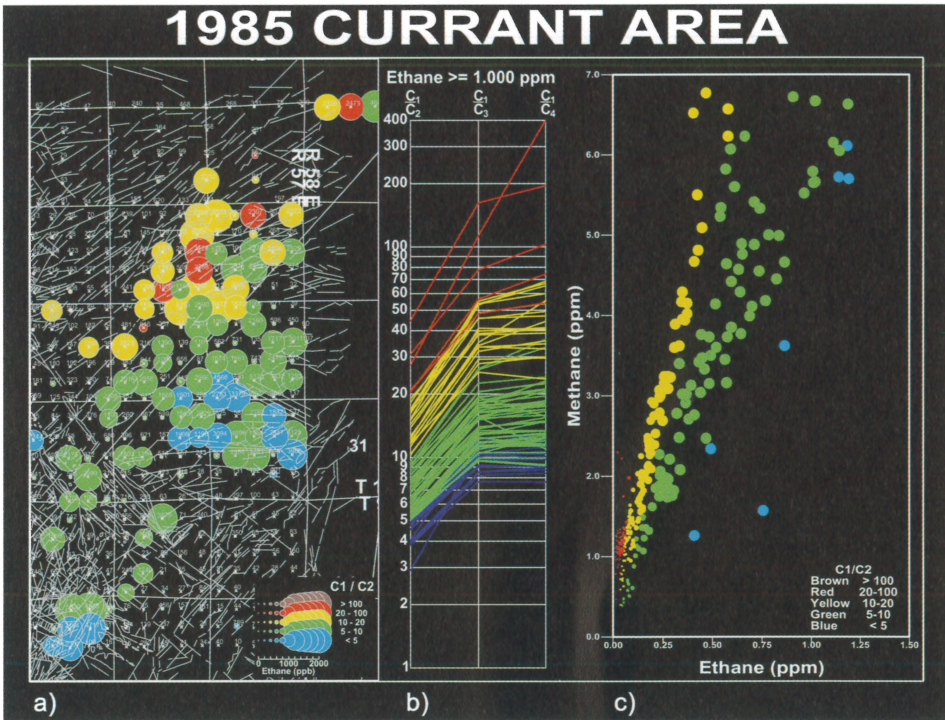
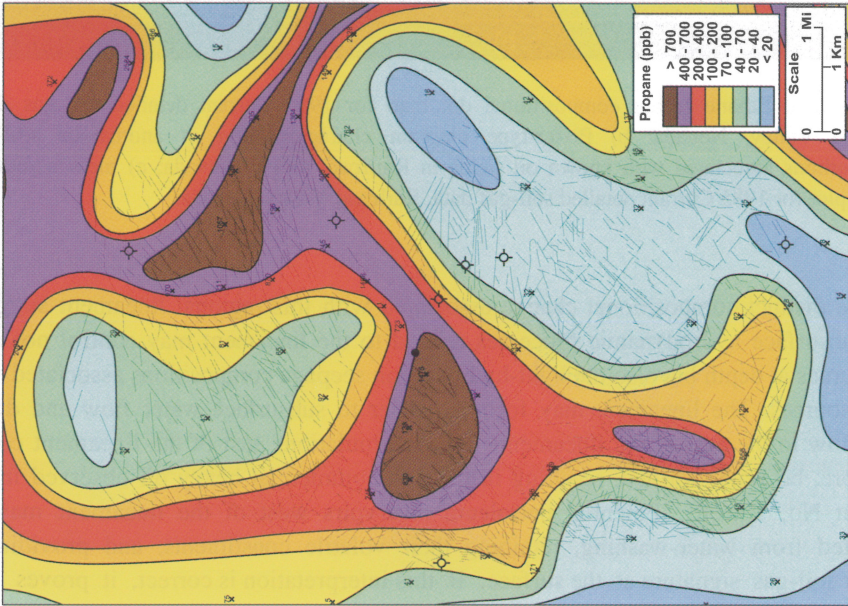


Fig. 5-40. a) Ethane colour compositional dot map for 1985 Currant detailed soil-gas data, Railroad Valley, Nevada; b) Pixler-type diagram characterisation of anomalous soil-gas hydrocarbons associated with known oil fields in Railroad Valley, Nevada; c) methane/ethane scatter plot for 1985 Currant detailed soil-gas data, Railroad Valley, Nevada.

The distinct compositional change associated with this regional lineament suggests that subsurface hydrodynamic processes related to the lineament may control not only the sources at depth but also the light-hydrocarbon seepage compositions associated with these sources. The lineament may form a barrier to subsurface water flow and divert fluid flow to the east of the lineament. Oil accumulations east of the lineament could, therefore, be water-washed, resulting in the non-commercial heavy oil observed in the Currant No. 1 well. Potential petroleum reservoirs west of the lineament may be protected from water-washing, retaining their volatile constituents, and providing a gassier soil-gas signature at the surface. If this interpretation is correct, it proves the

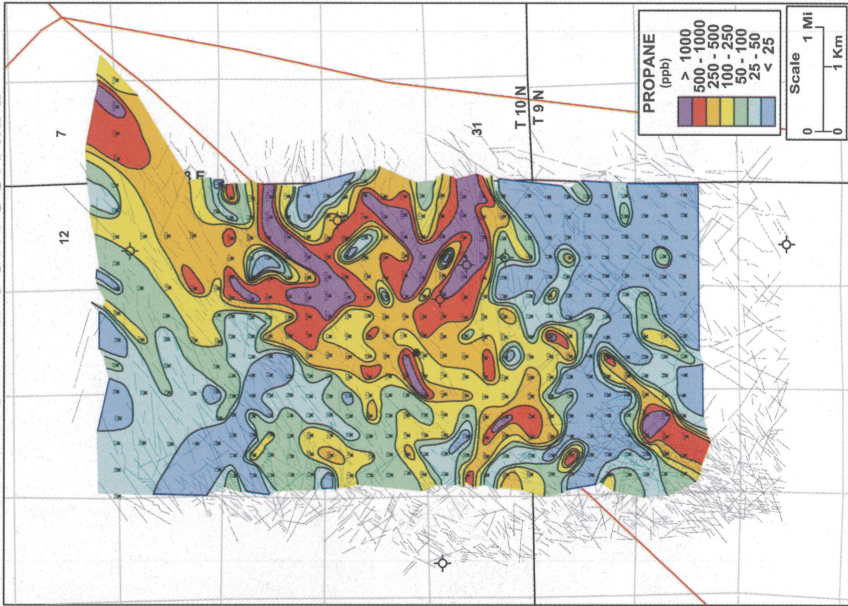
Fig. 5-39. Railroad Valley, Nevada: a) methane contour map of 1985 Currant detailed soil-gas data; b) propane contour map of 1985 Currant detailed soil-gas data.

1984 PROPANE CONTOUR MAP



a)

1985 PROPANE CONTOUR MAP



b)

local significance of this regional lineament system, even though the feature is not immediately obvious from small-scale remote-sensing data alone. It is also important to note that the regional geochemical study conducted in 1984 would not have been sufficient to support this interpretation, and that close detailed data gathered in 1985 were required to properly confirm the relationships between lineaments and hydrocarbon seepage in this case.

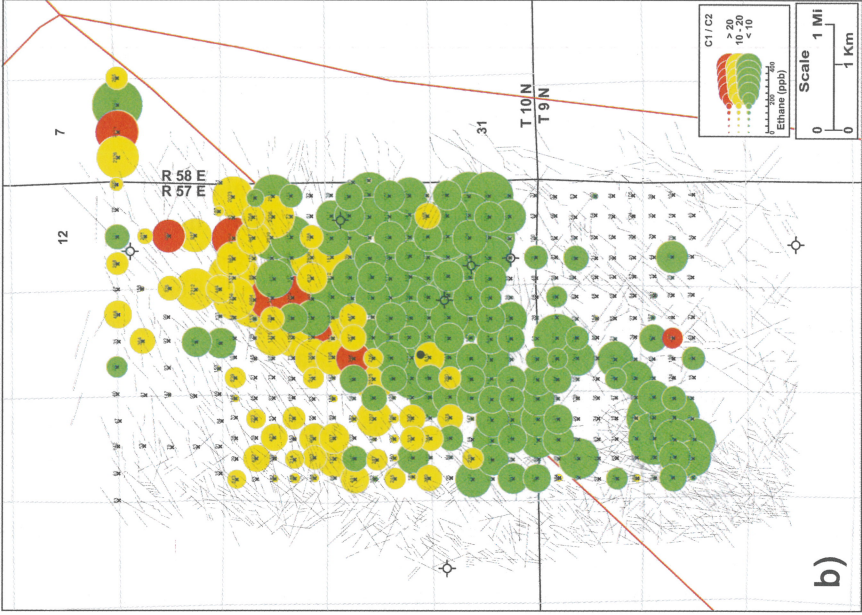
It is very important to realise that a regional geochemical survey on 1.6-km (1-mile) or even 5-km (3-mile) grids represents a low-resolution approximation to the actual size or shape of any geochemical anomaly. As shown in Fig. 5-39, the C_1 and C_3 patterns from the survey on 300-metre (1000-foot) centres are very different from those in the 1984 regional contour maps. The sharp geochemical boundaries observed in the detailed study cannot be mapped from the regional geochemical data. This is shown very clearly in Fig. 5-41, which expands the regional survey propane contour for direct comparison with the detailed grid data. Comparison of the magnitudes and compositions in these two data sets using the colour compositional dot maps (Fig. 5-42) proves that the regional data are valid and of good quality. However, using the regional data to draw contours is a serious mistake, which results in an erroneous interpretation in terms of the location of this complex anomaly. The data of the more detailed survey are essential before comparison with seismic data is attempted. Fracture orientations from the aerial-photography overlay define and control the sharp boundaries of the geochemical anomalies (Jones et al., 1985). The Currant lineament cuts through the centre of this major seep anomaly and appears to have some influence on fluid flow at depth (it appears to control the economics of the potential reservoirs). The shape of the geochemical anomaly is controlled by the bounding fractures, which are obviously not controlled by this regional lineament.

A comparison of the regional lineament interpreted from satellite remote-sensing data with the detailed composite interpretation from aerial photography shows that the azimuth of the Currant lineament is expressed only in the short photolineaments.

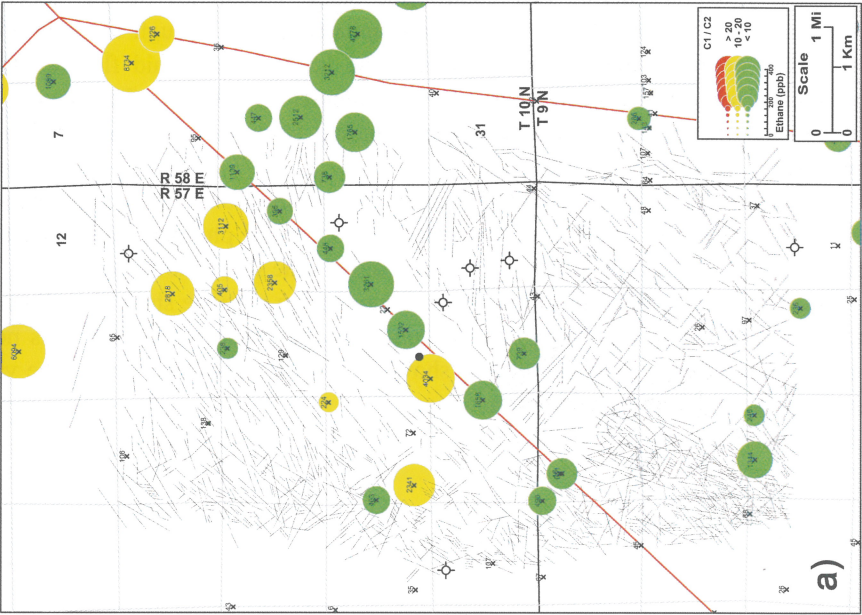
However, the regional lineament is not obvious from only the short photolineaments. Based on only the aerial photography we might suggest that this lineament is not real; the geochemical data, however, clearly shows otherwise and clearly shows the value of integrated multidisciplinary interpretations.

Fig. 5-41. Comparison of propane contour maps for soil-gas data, Currant area, Railroad Valley, Nevada, illustrating importance of sample spacing: a) 1984 regional survey; and b) 1985 detailed survey.

1985 ETHANE MAGNITUDE DOT MAP



1984 ETHANE MAGNITUDE DOT MAP



Overthrust Belt, Wyoming-Utah

The final example is one of the largest regional applications of light-gas surface studies ever published (Dickinson and Matthews, 1993). Some 3300 km² (1280 square miles) of the Wyoming-Utah overthrust belt, including the Clear Creek, Ryckman Creek and Whitney Canyon-Carter Creek fields, plus several small fields, was investigated using 1890 free soil-gas measurements (Fig. 5-43). The effective source rocks in the area are believed to be within the subthrust Cretaceous (Warner 1982). The maturity of these source rocks increases westward and appears responsible for the change in production from mixed oil, condensate and gas in the east, to dry gas, wet gas and some condensate in the middle, to dry gas in the west.

The compositional information derived from the surface gas study falls within the gas/condensate-mixed oil/gas classification of Jones and Drozd (1983). Further, there is a trend towards a more gas prone character from east to west, in agreement with both the production trends and increasing source rock maturity. A comparison of the light gas analysis of produced hydrocarbons with the surface free gases shows that the $(C_2/C_3) \times 10$ values are in very good agreement for the Ryckman Creek and Clear Creek fields and in general agreement with respect to the ranges of values for the multiple reservoirs in the Whitney Canyon-Clear Creek field. The $(C_3/C_1) \times 1000$ ratios, however, are considerably more methane rich in the surface than in the subsurface at Ryckman Creek and Clear Creek. This suggests that there is an independent source of methane in the region which is mixing with the leakage of the Cretaceous-reservoired gases. This independent source is either absent or much less effective at Whitney Canyon-Carter Creek.

In designing this study, Dickinson and Matthews (1993) decided that a sampling density of two samples per 2.5 km² (1 square mile), with approximately uniform distribution of locations, would represent a good compromise between the need for detail and cost. The regional focus of this study precludes the identification of all but very broad regions of interest because of the possibility of the occurrence of single point anomalies due to the coarse sample spacing. As a result, Dickinson and Matthews (1993) developed their cell technique, which we have previously described as an anomaly-probability map. Figure 5-44 shows a composite cell map in which the technique has been applied to methane, ethane and propane; the regions where all three of these gases are above their respective medians has been highlighted. The average number of sites within a cell was 18. Thus, binomial theory suggests that cells with more than 75% of the values above the median would be expected to occur only 5% of the time. The 75% contour line clearly identified several large areas that occupy more

Fig. 5-42. Comparison of ethane colour dot maps for Currant area, Railroad Valley, Nevada, illustrating repeatability of soil-gas compositional data: a) 1984 regional survey; and b) 1985 detailed survey.

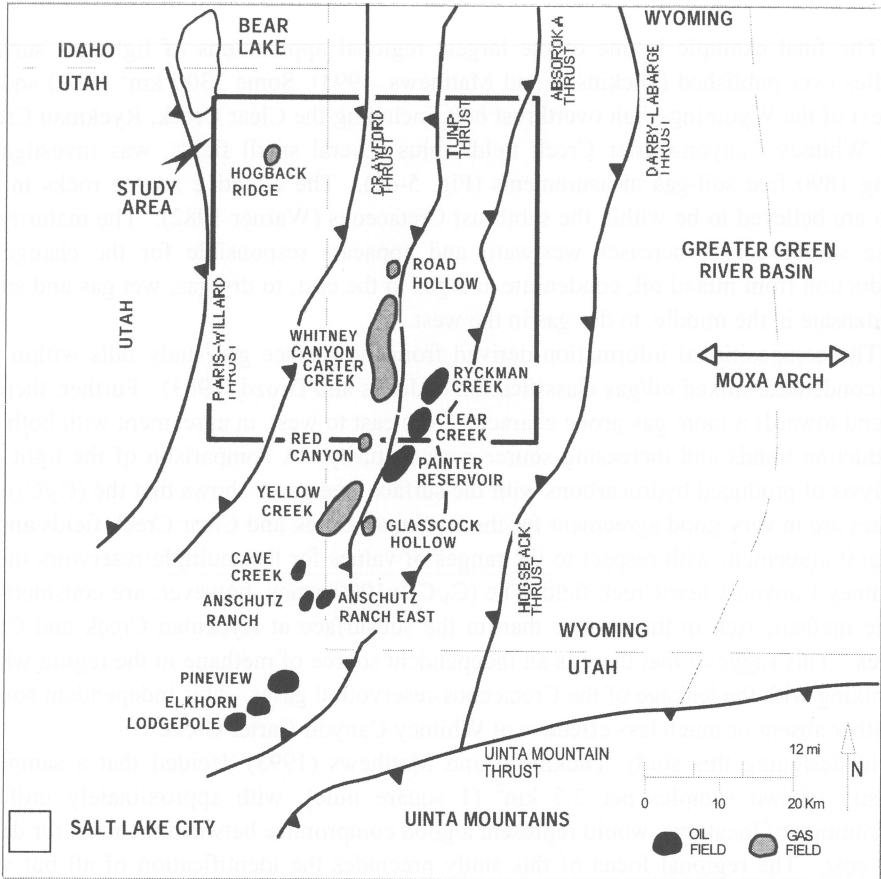


Fig. 5-43. Oil fields and gas fields of the Overthrust Belt, Wyoming-Utah.

than 5% of the total area. These regions are statistically anomalous, suggesting the occurrence of above-average seepage in these areas. Note the association of these anomalous areas with the Whitney Canyon-Carter Creek, Ryckman Creek and Clear Creek fields and with the surface trace of the major thrust faults. If this information had been available prior to the discovery of these fields, exploration could have been concentrated in the currently-productive region, saving costs. In addition, the general type of production and trend of composition would have been correctly predicted.

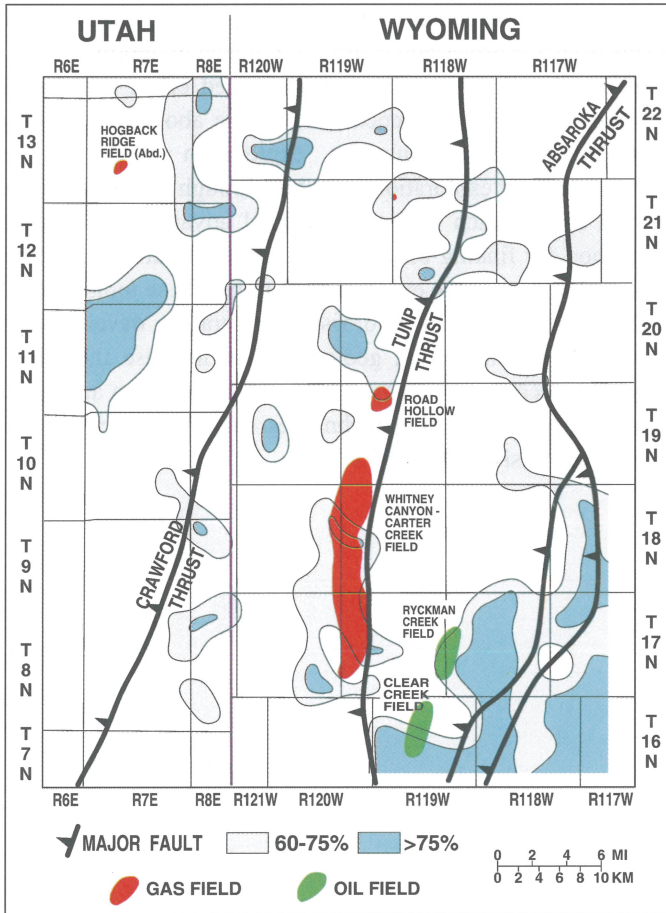


Fig. 5-44. Composite cell map in which the Monte Carlo simulations have been applied to methane, ethane and propane anomalies in the Overthrust Belt, Wyoming-Utah, highlighting the regions where all three of these gases are above their respective medians.

CONCLUSIONS

Surface and near-surface hydrocarbon occurrences arise as a result of a complex series of events and interrelationships. Except in rare instances, surface prospecting cannot reveal the outline of subsurface accumulations, nor indicate the potential commercial worth of a prospect. It can allow the explorationist a means to high-grade prospects, but should never be used as the sole criteria for delineating drilling locations. Surface soil-gas anomalies exist for many understandable reasons, although some do appear rather random. The interpretation of such data is derived from the general ability to extrapolate from macroseepage to microseepage, and the fact that often the surface

signal detected is directly correlated to gross subsurface hydrocarbon composition. Thus surface soil gas prospecting techniques utilising hydrocarbons can be a reliable test for indicating the presence of subsurface hydrocarbon source and/or accumulation.

Present day exploration for oil and gas requires a coordinated effort based on all useful techniques of geophysics, geology, and geochemistry. The above discussion on geochemical-prospecting techniques is useful for exploration geologists and geophysicists who wish to enhance their exploration activities through the use of surface geochemistry. We must avoid hailing each new technological advance as a panacea, because 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 programme 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. Given appropriate limitations, established geochemical prospecting techniques can be applied to aid a rational exploration program in any basin in the world.

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