

# Hydrocarbon-Induced Alteration of Soils and Sediments

**Dietmar Schumacher**

*Earth Sciences and Resources Institute  
University of Utah  
Salt Lake City, Utah*

## Abstract

The surface expression of hydrocarbon-induced alteration of soils and sediments can take many forms, including (1) microbiological anomalies and the formation of "paraffin dirt"; (2) mineralogic changes such as formation of calcite, pyrite, uranium, elemental sulfur, and certain magnetic iron oxides and sulfides; (3) bleaching of red beds; (4) clay mineral alteration; (5) electrochemical changes; (6) radiation anomalies; and (7) biogeochemical and geobotanical anomalies.

Bacteria and other microbes play a profound role in the oxidation of migrating hydrocarbons, and their activities are directly or indirectly responsible for many of the surface manifestations of hydrocarbon seepage. These activities, coupled with long-term migration of hydrocarbons, lead to the development of near-surface oxidation-reduction zones that favor the formation of a variety of hydrocarbon-induced chemical and mineralogic changes. This hydrocarbon-induced alteration is highly complex, and its varied surface expressions have led to the development of an equally varied number of surface exploration techniques, including soil carbonate methods, magnetic and electrical methods, radioactivity-based methods, and remote sensing methods.

Exploration methods based on what are assumed to be hydrocarbon-induced soil or sediment alterations have long been popular. Many claims of success have been made for these methods. However, well-documented studies are rare, and the claims are seldom substantiated by a scientifically rigorous program of sampling and analysis. The cause of these altered soils and sediments may well be hydrocarbon-related, but hydrocarbons are an indirect cause at best and not the most probable cause. Although the occurrence of hydrocarbon-induced geochemical alteration is well established, considerable research is needed before we understand the many factors affecting the formation of these anomalies in the near surface. Only then will we realize their full value for hydrocarbon exploration.

## INTRODUCTION

The objective of this paper is to provide an overview of the major hydrocarbon-induced changes affecting soils and sediments and their implications for surface exploration methods and applications. Long-term leakage of hydrocarbons, either as macroseepage or microseepage, can set up near-surface oxidation-reduction zones that favor the development of a diverse array of chemical and mineralogic changes. The bacterial oxidation of light hydrocarbons can directly or indirectly bring about significant changes in the pH and Eh of the surrounding environment, thereby also changing the stability fields of the different mineral species present in that environment.

These changes result in the precipitation or solution and remobilization of various mineral species and elements, such that the rock column above a leaking petroleum accumulation becomes significantly and measurably different from laterally equivalent rocks (Pirson, 1969; Oehler and Sternberg, 1984; Price, 1986). This alteration chimney or plume has been documented empirically, and its surface expression can range from subtle biogeochemical anomalies, such as in Wyoming's Recluse field (Dalziel and Donovan, 1980), to the dramatic hydrocarbon-induced diagenetic aureoles (HIDAs) described from the Cement field area of Oklahoma (Donovan, 1974; Lilburn and Al Shaieb, 1983, 1984). Because such changes are measurable and mappable, they have formed the

basis for many different surface exploration methods over the years. Unfortunately, our understanding of the complex physical, chemical, and biological processes responsible for these phenomena remains incomplete, with the result that these methods are viewed with skepticism and remain underutilized.

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## EARLY OBSERVATIONS

The association of mineralogic changes and hydrocarbon seepage has been recognized since the earliest days of petroleum exploration. Many of the early explorationists noted the correlation of productive areas with seeps, paraffin dirt, saline or sulfurous waters, surface mineralization, and topographic highs. Sawtelle (1936) reported that such features were instrumental in the discovery of about 70% of American Gulf Coast oil fields.

Harris (1908) was among the first to report the presence of pyrite and other sulfides in strata overlying oil fields associated with some Louisiana salt domes. Reeves (1922) observed the discoloration of surface red beds in the Cement field area of southwestern Oklahoma and noted the intense carbonate cementation over the crest of the Cement structure. Thompson (1933) observed that sulfur and pyrite are commonly associated with oil accumulations, and he reported that in the presence of hydrocarbon gases, gypsum and anhydrite are replaced by limestone in salt dome cap rocks in the Persian Gulf–Iraq oil belt. He also described another of the common alteration products found in Persia known as Gach-i-turush, an association of seepage petroleum, gypsum, jarosite, and sulfur caused by the interaction of petroleum with evaporites (Thompson, 1933).

McDermott (1940) and Rosaire (1940) reported the occurrence of secondary mineralization such as soil carbonates, caliche, and silicification in the vicinity of some Texas oil fields. Feely and Kulp (1957) demonstrated that the sulfur present in the cap rocks of Gulf Coast salt domes originated by bacterial action on the anhydrite and that calcite replaced anhydrite as a result of bacterial oxidation of petroleum. More recent studies have documented these and other changes and discussed the processes involved (Oehler and Sternberg, 1984; Matthews, 1986; Price, 1986; Klusman, 1993; Thompson et al., 1994).

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## MICROBIAL EFFECTS

Bacteria and other microbes found in the soils and sediments above hydrocarbon accumulations play a profound role in the oxidation of migrating hydrocarbons. Their activities are directly or indirectly responsible for the varied and often confusing surface manifestations of hydrocarbon seepage. Their role is still largely unknown, or at least not fully recognized, by most of the investigators of hydrocarbon seepage and surface exploration technology.

Kartsev et al. (1959), Davis (1952, 1956, 1967), Krumbein (1983), and Atlas (1984) have discussed in great detail the oxidation of hydrocarbons by bacteria. In addition to the many varieties of aerobic bacteria that oxidize hydrocarbons, important anaerobes also exist (e.g., sulfate-reducing bacteria and denitrifying bacteria). Also, certain fungi and actinomycetes readily oxidize hydrocarbons in soil (McKenna and Kallio, 1965). Although bacterial activity is most pronounced in surface soils, it can occur at all depths above a leaking hydrocarbon accumulation. The most obvious result of hydrocarbon oxidation is a decrease in the concentration of free soil gas hydrocarbons (interstitial), hydrocarbons dissolved in pore fluids, occluded hydrocarbons, and adsorbed hydrocarbons. In addition, bacteria produce carbon dioxide and organic acids from hydrocarbon oxidation; the sulfate reducers produce hydrogen sulfide, and the denitrifiers produce free nitrogen and nitrous oxide.

One of the byproducts of bacterial oxidation of hydrocarbons is *paraffin dirt*, a yellow-brown waxy-appearing soil commonly associated with gas seepages in the onshore U.S. Gulf Coast, as well as in other areas with tropical to temperate climates such as Colombia, Romania, and Burma (Milner, 1925; Davis, 1967). Davis (1967) was able to create paraffin dirt in the laboratory that was indistinguishable from natural samples by encouraging bacterial growth by passing hydrocarbon gas through moist soils. He determined that paraffin dirt was an accumulation of dead cell walls of fungi and bacteria, consisting chiefly of carbohydrates (Davis, 1967).

In offshore areas, bacterial mats and suspensions are commonly associated with petroleum seepage, especially oil seepage. Such bacterial mats (*Beggiatoa*) have been reported from the North Sea (Gullfaks, Statfjord, and Tommeliten fields), the Santa Barbara Channel, and the Gulf of Mexico (Hovland and Judd, 1988; Sassen et al., 1993). *Beggiatoa* mats are also known from onshore seepages in Tunisia, Iraq, Papua New Guinea, the Congo, and Colombia. In addition to bacterial mats, offshore seep sites in the Gulf of Mexico also support a diverse chemosynthetic community including mussels, lucinid clams, and tube worms, all of which depend on methane and hydrogen sulfide seepage (Kennicutt et al., 1985; Childress et al., 1986; Brooks et al., 1987; MacDonald et al., 1989, 1990; Reilly et al., this volume).

Microbial hydrocarbon oxidation consumes either free oxygen or chemically bound oxygen ( $\text{SO}_4^{2-}$  or  $\text{NO}_3^{2-}$ ) via one of two main metabolic pathways. First, aerobic bacteria oxidize hydrocarbons to form carbon dioxide or bicarbonate that eventually precipitates as carbonate. Second, once oxygen is depleted within the sediment or pore fluid, other bacteria reduce sulfate to produce hydrogen sulfide. These changes can significantly alter the oxidation-reduction potential (Eh) of the environment and can affect the pH of the system. Such pH/Eh changes can result in new mineral stability fields in which some minerals become unstable and are dissolved and mobilized, while others are precipitated from solution. In this setting, bacteria can produce minerals either through passive growth or as a result of metabolic activity.

Examples of passive microbial biomineralization include bacterial precipitation of amorphous silica in hot springs, as well as formation of some forms of authigenic iron oxides, phosphates, carbonates, and clays (Krumbein, 1983; Ferris et al., 1994; Ferris, 1995). Microbial mineral precipitation can also result directly from metabolic activity of microorganisms whereby bacterial activity simply triggers a change in the solution chemistry that leads to mineral precipitation. For example, an increase in pH can initiate the precipitation of calcium carbonate. Similarly, sulfide production by sulfate-reducing bacteria can bring about the precipitation of a number of iron sulfides and oxides, including pyrite, greigite, pyrrhotite, and maghemite (Reynolds et al., 1990; Ferris, 1995). Still other mineral phases precipitate directly from bacterial enzyme action, such as the formation of magnetite particles inside the cells of magnetotactic bacteria (Krumbein, 1983; Ferris, 1995).

Bacteria play a profound role in determining the nature and direction of physical, chemical, and biological changes in near-surface soils and sediments. Nowhere is their role more significant than in the presence of hydrocarbon seepage. Not only are bacteria responsible for the destruction of hydrocarbons at seeps, but they are also responsible for the formation of large volumes of authigenic minerals, including carbonate, elemental sulfur, and iron oxides and sulfides.

## HYDROCARBON-INDUCED DIAGENETIC ALTERATION

Although the close association between surface mineralization or discoloration and oil accumulations has long been noted, detailed investigations of these changes and the processes that produce them have been conducted only since the 1970s. Donovan (1974) published the first of a series of studies describing the complex chemical and mineralogic changes observed in red beds over a number of Oklahoma oil fields. Lilburn and Al-Shaieb (1984) proposed the term *hydrocarbon-induced diagenetic aureole (HIDA)* for these near-surface alterations.

These diagenetic zonations are particularly well developed over Cement-Chickasha, Velma, Healdton, Eola, and Carter-Knox fields in southwestern Oklahoma. The geologic setting of these fields consists of tightly folded and faulted Pennsylvanian sedimentary rocks overlain by more than 600 m (2000 ft) of unfaulted Permian sandstones, red beds, and gypsum. Oil occurs in both the Pennsylvanian and Permian strata, with major production in the former. The geologic setting of these fields and their diagenetic relationships have been reviewed most recently by Al-Shaieb et al. (1994). Other studies of these near-surface diagenetic changes have been published by Olmstead (1975), Donovan and Dalziel (1977), Goldhaber et al. (1978), Ferguson (1979a, b), Donovan et al. (1981), Allen and Thomas (1984), and Reynolds et al. (1990).

Three major diagenetic facies are observed in the red beds and associated sediments overlying these oil fields

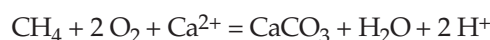
(Figures 1–4): (1) an innermost zone of intense carbonate cementation and/or carbonate-replacing gypsum whose distribution coincides with the pre-Permian fault system, (2) a central zone of pyrite mineralization which may not be well exposed at the surface but is well developed at depth, and (3) a zone of bleached red beds surrounding the carbonate zone. Unaltered sediments occur beyond the zone of discolored red beds. The areal extent of these alteration zones approximates the productive limits of the reservoirs in the subsurface.

Figures 1 and 2 illustrate the observed diagenetic zonation at Velma field, southwestern Oklahoma. Identical diagenetic facies occur over nearby Cement-Chickasha field, as shown in Figures 3 and 4. Similar hydrocarbon-induced alterations have been reported in places as diverse as the Baku region of Azerbaijan (Kartsev et al., 1959), Lisbon field in southeastern Utah (Segal et al., 1984), Ashland field in southeastern Oklahoma (Oehler and Sternberg, 1984), Turkey Creek seep in Colorado (Reid et al., 1992), Mist gas field in Oregon and Brown-Bassett field in Texas (Campbell, 1994), and the Gulf of Mexico (Roberts et al., 1990; Sassen et al., 1994).

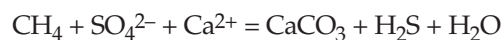
## Carbonates

Diagenetic carbonates and carbonate cements are among the most common hydrocarbon-induced alterations associated with petroleum seepage. In offshore settings, the carbonates can form as slabs and rubble, large mounds and pillars, hard grounds, or pore-filling carbonate cement. On land, pore-filling calcite and replacement calcite is most common. These near-surface diagenetic carbonates are formed principally as a byproduct of petroleum oxidation, particularly of methane, using one of two reaction pathways, as summarized below:

1. Aerobic:



2. Anaerobic:



When these reactions occur, carbon dioxide evolves and reacts with water to produce bicarbonate. The bicarbonate bonds with calcium and magnesium in groundwater and precipitates as carbonate, or carbonate cement, that has an isotopic signature matching that of the parent hydrocarbon(s).

Normal calcite, whether its carbon is derived from the atmosphere, freshwater, or the marine environment, has a carbon isotopic value of about  $-10$  to  $+5\%$  relative to the PDB standard (Fairbridge, 1972; Anderson and Arthur, 1983). The carbon isotopic composition of most crude oils ranges from about  $-20$  to  $-32\%$ , whereas that of methane can be range from  $-30$  to  $-90\%$ . Calcite formed from oxidized petroleum incorporates carbon from the organic source which typically has an isotopic composition more negative than  $-20\%$ . Depending on

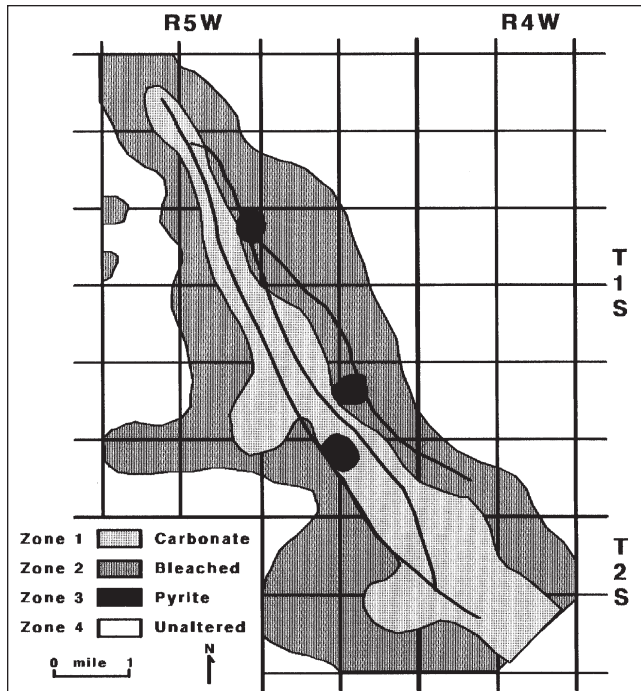


Figure 1—Surface diagenetic alteration zones and traces of pre-Permian faults over Velma field, Stephens County, Oklahoma. (From Al-Shaieb et al., 1994; reprinted by permission.)

the proportion of oxidized hydrocarbon incorporated, the isotopic composition of the resultant carbonate can range from  $-10$  to  $-60\%$ .

In Cement-Chikasha, Velma, and other southwestern Oklahoma oil fields, the Permian sandstones at the surface are highly cemented by secondary calcite and dolomite in the crestal areas of the field, but they contain little or no carbonate cement away from the field. A local gypsum-bearing formation grades from pure gypsum on the flanks of the field to gypsum entirely replaced by calcite along the structural axis of the field. The increased resistance to erosion of these carbonate-cemented units forms topographic highs along the anticlinal crest. Diagenetic carbonates present over these fields include calcite, ferroan calcite, high-Mg and high-Mn calcite, dolomite, ankerite, aragonite, siderite, and rhodochrosite (Donovan, 1974). The carbon isotopic composition of diagenetic carbonates at Cement-Chikasha field ranges from  $-2$  to  $-35\%$  (Donovan, 1974; Lilburn and Al-Shaieb, 1984), with the lightest (most negative) values occurring along the structural axis of the field (Figure 5). Donovan et al. (1981) report carbon isotope values for carbonate cements from Velma field of  $-7$  to  $-36\%$ . This wide range in isotopic composition reflects more than one carbon source or a mixture of sources. For these fields, the data suggest a hybrid carbon source from both freshwater and hydrocarbons (oil and gas).

Diagenetic carbonates are also well developed over Ashland gas field in the Arkoma basin of southeastern

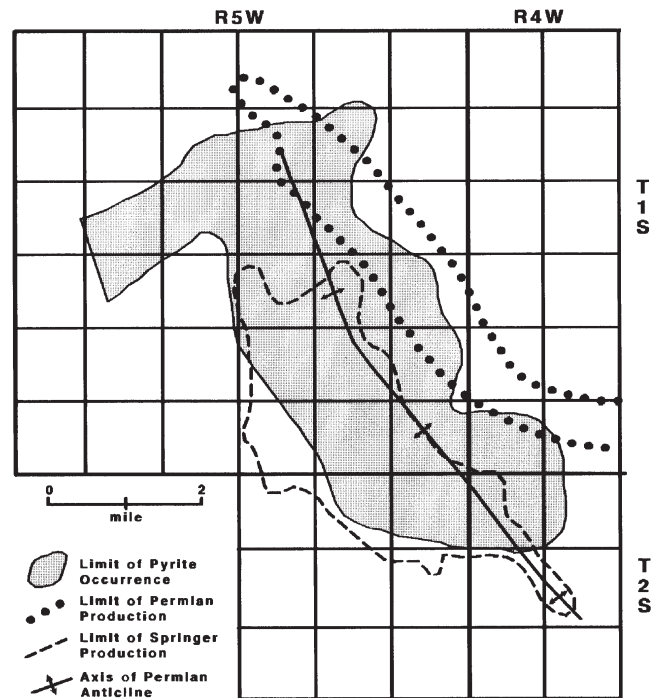


Figure 2—Subsurface limits of pyrite mineralization over Velma field, Stephens County, Oklahoma. The pyritization limits coincide with production and fault boundaries. (From Al-Shaieb et al., 1994; reprinted by permission.)

Oklahoma (Oehler and Sternberg, 1984). Geochemical analyses indicate that about 45% more total carbonate occurs (chiefly as calcite) in near-surface sandstones located over the field as compared to the same stratigraphic interval in off-field locations. The carbon isotopic composition for shallow calcites at Ashland ranges from  $-22$  to  $-29\%$ , indicating that they have derived a significant portion of their carbon from oxidized hydrocarbons. These isotopically anomalous calcites are present in both on-field and off-field wells, although their concentration is greater in the on-field wells.

Isotopically light carbonates have been widely documented in salt dome cap rocks in the U.S. Gulf Coast and in modern hydrocarbon seep sites in the Gulf of Mexico. Roberts et al. (1990) report carbon isotope values of  $-16$  to  $-48\%$  for authigenic carbonates in the Green Canyon area, northern Gulf of Mexico. Sassen et al. (1994) report values of  $-22$  to  $-29\%$  for carbonate cements and  $-24$  to  $-31\%$  for carbonate cap rock in salt domes. Other values reported for calcite cap rocks of Gulf Coast salt domes range from  $-12$  to  $-53\%$  (Posey et al., 1987; Prikryl, 1990). Since the volume of diagenetic carbonate that can form at seafloor seep sites can be considerable, some workers have even suggested that some carbonate reefs might owe their origin to hydrocarbon seepage (Hovland, 1990).

Other areas with isotopically light carbonate include Recluse oil field in Wyoming (Dalziel and Donovan, 1980), Gulf of Alaska (Barnes et al., 1980), Davenport oil field in Oklahoma (Donovan et al., 1974), Ocho Juan field

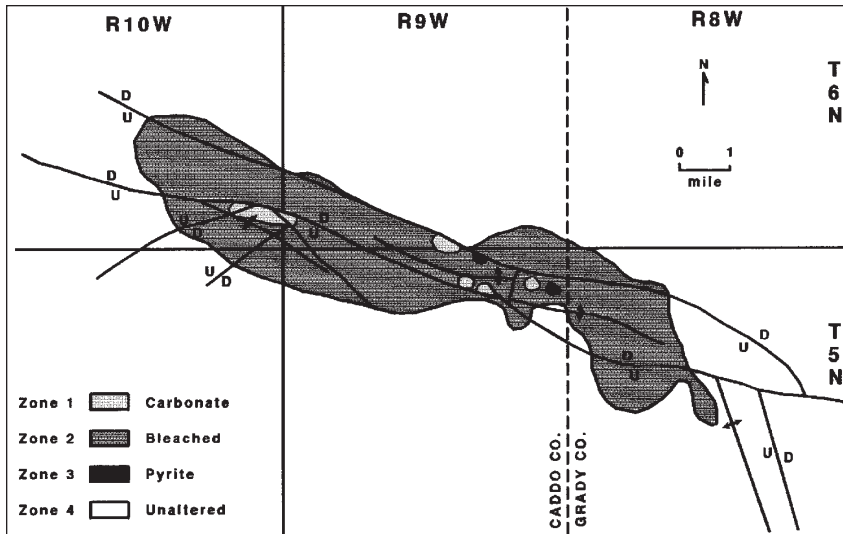


Figure 3—Surface diagenetic alteration zones and pre-Permian structural configuration of Cement-Chickasha field, Caddo County, Oklahoma. (From Al-Shaieb et al., 1994; reprinted by permission.)

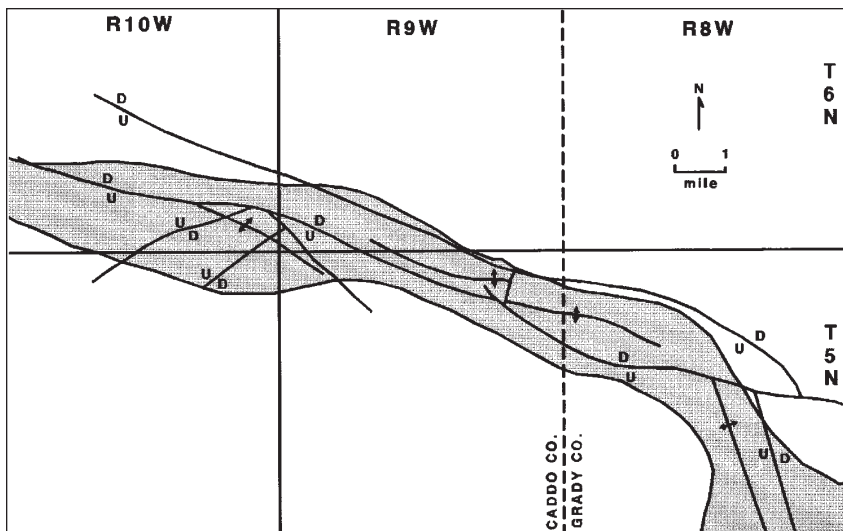


Figure 4—Subsurface limits of pyrite mineralization in Cement-Chickasha field, Caddo County, Oklahoma. The limits of the pyritized zone coincide with the pre-Permian structure. (From Al-Shaieb et al., 1994; reprinted by permission.)

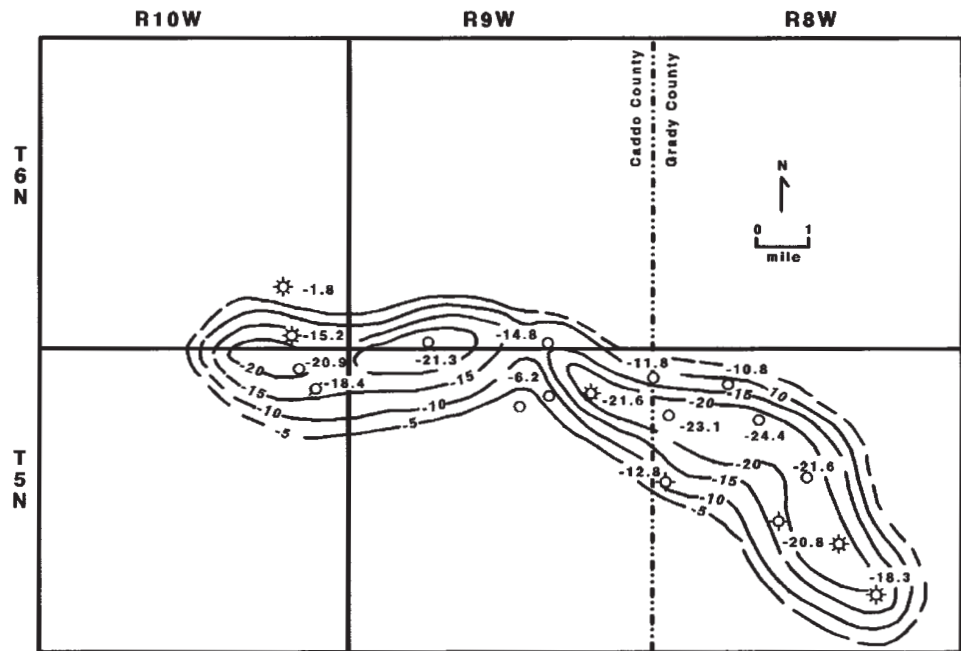
in Texas, Fox-Graham field in Oklahoma (Duchscherer, 1984), and the carbonate hardgrounds formed around modern gas seeps on the Carolina continental rise (Paull et al., 1995) and near Fredrikshavn, Denmark (Dando et al., 1994).

Diagenetic carbonates related to hydrocarbon seepage appear to be widespread, although not all fields or hydrocarbon seep areas possess isotopically anomalous carbonates. Hydrocarbon microseepage is well documented for Patrick Draw field in Wyoming and Lisbon Valley field in Utah, but the carbon isotopic composition for their soil carbonates ranges from 0 to  $-9\text{‰}$ , indicating that little if any of the carbon is derived from the oxidation of hydrocarbons (Conel and Alley, 1985; Lang et al., 1985a). Similarly, calcite cements from outcropping sandstones in the Little Buffalo Basin oil field of Wyoming have isotopic values heavier than  $-10\text{‰}$ , suggesting little contribution from oxidized hydrocarbons, although the occurrence of the most negative values over the crest of the structure suggests that there may be some contribution (Bammel et al., 1994). Other fields, such as Coyanosa in west Texas,

show no evidence of hydrocarbon seepage, and carbonate cements from over the field have isotopic compositions of  $-1$  to  $-9\text{‰}$ , results consistent with a nonpetroleum carbon source (Lang et al., 1985c).

It is tempting to relate near-surface carbonate diagenesis to leakage of reservoir hydrocarbons, but we should remember that geochemical anomalies caused by abnormal amounts of carbon dioxide are nonspecific for petroleum. Abnormal  $\text{CO}_2$  concentrations in soils and sediments can result from processes other than microbial oxidation of hydrocarbons, such as hydrothermal activity, volcanic activity, catagenesis of organic matter, micropore filtration, and thermochemical sulfate reduction (Kartsev et al., 1959; Matthews, 1986; Sassen et al., 1994). Different mechanisms can yield similar end-products, and the formation of near-surface carbonates and carbonate cements may be more heavily dependent on the area's geology and groundwater chemistry. Unless each mechanism has a distinctive geochemical or isotopic "fingerprint," careful analysis is required to determine the nature and origin of shallow carbonates and carbonate cements.

Figure 5—Variation in the carbon isotopic composition of subsurface carbonate cements from Cement-Chickasha field, Caddo County, Oklahoma. (From Al-Shaieb et al., 1994; reprinted by permission.)



## Sulfides

The formation of secondary pyrite and other sulfides has been documented for many petroleum fields, including the Cement-Chickasha, Velma, Eola, and Ashland fields (all in Oklahoma) by Ferguson (1979a, b), Lilburn and Al-Shaieb (1983, 1984), Donovan et al. (1981), Oehler and Sternberg (1984), and Hughes et al. (1986). Pyrite is the dominant sulfide mineral in these hydrocarbon-induced alteration zones, but pyrrhotite, marcasite, galena, sphalerite, and native sulfur are also found and may be locally abundant. The mechanisms responsible for the formation of sulfides in the hydrocarbon seep environment have been discussed by Sassen (1980), Oehler and Sternberg (1984), Sassen et al. (1988, 1989), Goldhaber and Reynolds (1991), and Reynolds et al. (1990, 1993).

Pyrite can be precipitated in a reducing environment, given a source of sulfur and iron. The major source of sulfur in a petroleum province is hydrogen sulfide gas from the petroleum itself, from anaerobic bacterial activity, or from the oxidation of petroleum in the near-surface. Sources of iron include iron oxide grain coatings in sandstone, pore-filling clays such as chlorite, rock fragment inclusions, and deeper meteoric waters. The reaction of hydrogen sulfide and iron (from hematite) to precipitate pyrite or marcasite can be summarized as follows (Oehler and Sternberg, 1984):



The development of a pyrite alteration zone depends on the sulfur content of the oils, the geology and groundwater geochemistry of the sedimentary sequence, and the nature of the bacterial degradation (Hughes et al., 1986). For example, if the sulfur content of oils is high and the groundwater is rich in iron, pyrite could be precipitated

at any depth within the migration plume that possesses sufficient porosity. If oils are free of sulfur, the sulfur required for the reaction must be derived from bacterial degradation, in which case pyrite precipitation would occur in the near-surface sediments due to environmental restrictions on bacterial activity. In each case, however, seepage-related pyrite would be concentrated in the reduced plume of hydrocarbon leakage (Hughes et al., 1986).

The pyrite zone is well-developed in Velma, Healdton, and Cement-Chickasha fields in Oklahoma (Figures 2, 4). Pyrite mineralization is concentrated in sandy intervals in the uppermost 100 m (330 ft) of section, and its distribution approximates the surface projection of the productive reservoirs. Pyrite is abundant in cuttings from on-field wells and generally absent in cuttings from off-field wells. The concentration of pyrite in the cuttings ranges from 5–20% over Cement field to 2–4% over Velma, Chickasha, and Eola fields (Campbell, 1994). The average value of the sulfur isotopic composition of the pyrite (–3.6‰) compares favorably with that of the sulfur in the associated oil (–4.7‰), strongly suggesting that the H<sub>2</sub>S associated with the oil is the major source of the sulfur in the pyrite (Goldhaber et al., 1978; Lilburn and Al-Shaieb, 1983, 1984).

The presence of a pyrite zone has also been documented for Ashland gas field, a stratigraphic trap in the Arkoma basin, southeastern Oklahoma. A comparison of on-field and off-field pyrite and marcasite content shows that the on-field wells average nearly twice as much iron sulfide within the same sandy stratigraphic interval as the off-field wells do, 1.5–3.5% versus 0.5–1.5% (Oehler and Sternberg, 1984). Campbell (1994) has documented the development of pyrite zones in near-surface sediments overlying Mist gas field in Oregon, Hogback Ridge gas field in Utah, and Brown-Bassett gas field in west Texas.

For Brown-Bassett field, Campbell (1994) reports that the average concentration of pyrite in cuttings from on-field wells is more than three times as high as observed in off-field wells, 5.7% versus 1.7%.

Not all shallow pyrite anomalies result from hydrocarbon leakage. Oehler and Sternberg (1984) have described a “false” pyrite anomaly over a nonproductive petroleum prospect in Texas in which the pyrite mineralization was associated with fine-grained organic-rich mudstones and unrelated to petroleum accumulation or leakage. While high concentrations of pyrite have been observed over many oil and gas fields, such mineralization only occurs where the shallow stratigraphy and its geochemical environment are favorable.

### Bleached Red Beds

The presence of bleached and discolored red sandstones at the surface above petroleum accumulations has been widely noted, but detailed studies are few. Bleaching of red beds occurs whenever acidic or reducing fluids are present to remove ferric oxide (hematite). Such conditions also favor the formation of pyrite and siderite from the iron released during the dissolution of hematite. The possible reducing agents responsible for bleaching red beds above petroleum accumulations include hydrocarbons, H<sub>2</sub>S, and CO<sub>2</sub>.

In the Cement field area of Oklahoma, Donovan (1974) reported that the color of the Permian Rush Springs Formation grades from reddish-brown for unaltered sandstone adjacent to the field, to pink, yellow, and white along the flanks of the Cement anticline, and to gray and white along the anticlinal axis, where maximum bleaching and iron loss occur. Similar changes are observed at nearby Velma, Eola, Healdton, and Chickasha fields (Ferguson, 1979a,b; Donovan et al., 1981).

The geology and geochemical alteration associated with Lisbon Valley field in southeastern Utah have been described in considerable detail by Segal et al. (1984, 1986) and Conel and Alley (1985). They report that the distribution of the bleached outcrops of the Triassic Wingate formation approximates the geographic limits of the oil and gas reservoirs at depth. The red color of the unbleached Wingate was found to result from a pervasive hematite-clay mixture coating virtually all sand grains, whereas the bleached Wingate appears white or gray due to the absence of these hematite grain coatings. Hematite is present in the bleached rocks at Lisbon Valley field, although it occurs only as pseudomorphs of pyrite and siderite rather than as hematite grain coatings (Segal et al., 1984, 1986; Conel and Alley, 1985).

Other petroleum fields associated with bleached red beds include those near Baku in Azerbaijan (Kartsev et al., 1959), several Wind River basin oil fields in Wyoming (Love, 1957), and Garza field in west Texas (Donovan et al., 1979). While the presence of bleached red beds over oil and gas accumulations is a highly visible manifestation of hydrocarbon-induced alteration, one must remember that the reducing fluids causing the observed discol-

oration are not limited to hydrocarbons and, even if hydrocarbons, might represent shallow biogenic methane rather than thermogenic oil or gas.

### Clay Mineral Alteration

The production of CO<sub>2</sub>, H<sub>2</sub>S, and organic acids resulting from the microbial oxidation of hydrocarbons in near-surface soils and sediments can create reducing, slightly acidic conditions that promote the diagenetic weathering of feldspars to produce clays and may lead to the conversion of normally stable illitic clays to kaolinite. Clays thus formed remain chemically stable unless their environment is changed.

In Utah’s Lisbon Valley field, Segal et al. (1984, 1986) report that bleached portions of the Wingate Sandstone directly overlying the field contain primarily kaolinite clays, whereas the unbleached areas of the sandstone located away from the field contain fresh plagioclase and muscovite. The bleached Wingate contains three to five times more kaolinite than the unbleached rock. The geographic distribution of the kaolinite is inversely related to that of the mixed-layer illite-smectite clays, suggesting that the enrichment of kaolinite is also related to the depletion of other clay minerals and not only to the alteration of feldspars (Conel and Alley, 1985).

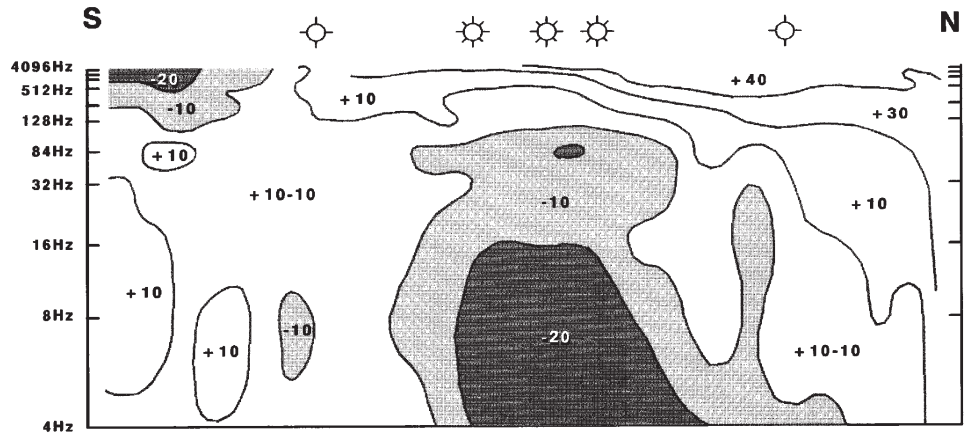
Clay mineral diagenesis has also been documented at Cement-Chickasha field in Oklahoma, where kaolinite and mixed-layer illite-smectite clays of late origin have replaced detrital illite in red beds (Lilburn and Al-Shaieb, 1983, 1984). A third occurrence of hydrocarbon-induced formation of kaolinite has been described by Reid et al. (1992) from the Turkey Creek oil seep near Denver, Colorado. Turkey Creek is the site of an oxidation-reduction front that developed in the outcrop of the Cretaceous “J” sand due to active oil seepage. Coarse-grained authigenic kaolinite in concentrations up to 2.0 wt. % is present in the altered rocks of the outcrop.

### Uranium

The occurrence of uranium has been linked to petroleum by many authors (Eargle and Weeks, 1961; Al-Shaieb, 1977; Goldhaber et al., 1978, 1983; Curiale et al., 1983). The association between petroleum and heavy metals such as uranium (as well as lead, zinc, and even gold) is due to the fact that the reducing environment created by migrating hydrocarbons and associated fluids favors the precipitation of uranium and other heavy metals. Oxidized uranium (UO<sub>2</sub><sup>2+</sup>) is soluble in groundwater, although when reduced, it precipitates from solution as uraninite (UO<sub>2</sub>), which is relatively insoluble.

A commercial uranium deposit occurs at Cement field, Oklahoma (Olmstead, 1975; Allen and Thomas, 1984). In Lisbon Valley field, Utah, the close spatial correspondence of uranium deposits in the Triassic Chinle Formation, outcrops of bleached Wingate Sandstone, and the geographic limits of the subsurface oil and gas accumulation suggests a genetic relationship among them (Conel

**Figure 6—Controlled-source audiofrequency magnetotellurics (CSAMT) residual resistivity profile across Ashland gas field, Arkoma Basin, Oklahoma. Note the well-developed low-resistivity zone at depth that overlies the gas field and closely approximates the productive limits of the field. The shallow high-resistivity zone corresponds to an interval of carbonate-cemented sandstone. (After Oehler and Sternberg (1984) and Phoenix Geophysics.)**



and Alley, 1985). The Turkey Creek oil seep near Denver, Colorado, has geologic and geochemical characteristics similar to uranium roll-front deposits in Texas and the Colorado Plateau, many of which are related spatially to petroleum accumulations (Reid et al., 1992). Eargle and Weeks (1961) reported an association between uranium roll-fronts in Karnes County, Texas, and oil and gas fields located down-dip; they speculated that  $H_2S$  seepage created the reducing environment responsible for deposition of uranium and the accompanying pyrite. A similar association was described from Live Oak County, Texas, where many uranium mines occur along the Oakville fault (Eargle and Weeks, 1973). Oil, gas, and  $H_2S$  leak up the fault and create the reducing environment that promotes pyrite and uranium deposition (Goldhaber et al., 1978, 1983).

## Magnetic Minerals

The presence of magnetic anomalies over oil and gas fields has been noted for several decades, but it is only in relatively recent years that the phenomenon has been critically examined. The same hydrocarbon-induced reducing environment that promotes the formation of uranium and pyrite can lead to the precipitation of a variety of magnetic iron oxides and sulfides, including magnetite ( $Fe_3O_4$ ), maghemite ( $\gamma-Fe_2O_3$ ), pyrrhotite ( $Fe_7S_8$ ), and greigite ( $Fe_3S_4$ ).

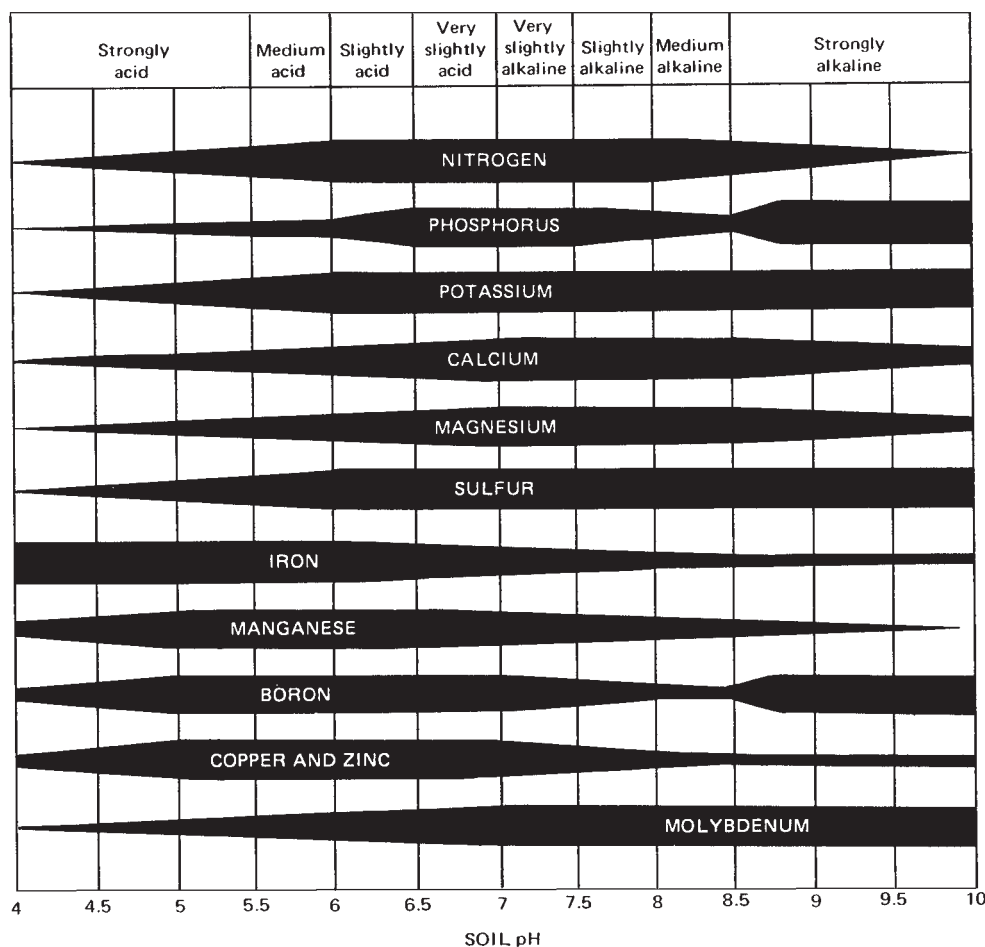
Donovan et al. (1979) reported magnetite in altered Permian rocks overlying Cement field, Oklahoma, and speculated that hydrocarbon-related brines migrating from depth caused reduction of hematite to form magnetite. Reynolds et al. (1984, 1988, 1990) reexamined the occurrence of magnetite at Cement field and concluded that it represented drilling contamination. However, they did document the presence of ferrimagnetic pyrrhotite in the section and suggested that it precipitated as a result of hydrocarbon seepage and degradation. Although authigenic magnetite is absent at Cement field, its occurrence has been documented at many hydrocarbon seep sites by Elmore et al. (1987) and McCabe et al. (1987). The formation of pyrrhotite and other metals in hydrocarbon seep

environments at several U.S. Gulf Coast salt domes has been described by Sassen et al. (1988, 1989). Other studies have documented the presence of greigite and maghemite in near-surface sediments above petroleum accumulations and suggest that these minerals may be responsible for most of the magnetic anomalies associated with oil and gas fields (Foote, 1987; Foote and Long, 1988; Foote, this volume).

The presence, origin, and exploration significance of magnetic mineralization associated with petroleum accumulations remain controversial and have recently been addressed by Gay and Hawley (1991), Machel and Burton (1991a, b), Gay (1992), Reynolds et al. (1993), and Machel (this volume). The general agreement of elevated magnetic susceptibility of soils and sediments with light hydrocarbon soil gas anomalies supports the hypothesis that hydrocarbon microseepage may generate magnetic anomalies in near-surface soils and sediments (Henry, 1988; Saunders et al., 1991; Ellwood and Burkart, this volume). Gay (1992) agrees that recent measurements of soil magnetic susceptibility in oil fields constitutes evidence for anomalous near-surface magnetization associated with hydrocarbon leakage plumes. He urges caution, however, in ascribing the origin of all shallow magnetic anomalies to seep-induced alteration without considering possible syngenetic magnetic sources such as detrital magnetite, magnetic sedimentary formations, and burned coal seams. To further confuse the issue, it has been documented that increases in soil magnetic susceptibility can be due to pedogenic formation of magnetite and maghemite in soils and that such formation is closely tied to rainfall and climate, not hydrocarbon seepage (Maher and Thompson, 1991, 1992; Liu et al., 1994).

## Electrochemical Changes

Considerable evidence has been cited to demonstrate that hydrocarbon-induced changes alter the mineralogy and chemical composition of the sediments and fluids overlying a petroleum accumulation. While these near-surface manifestations of hydrocarbon migration are varied and complex, only a few of these alterations have the



**Figure 7—The effect of soil pH on the availability of nutrients to plants. The width of the horizontal band reflects relative solubility. (From Bidwell, R. G. S., *Plant Physiology*, ©1974, p. 252. Reprinted by permission of Prentice Hall, Upper Saddle River, New Jersey.)**

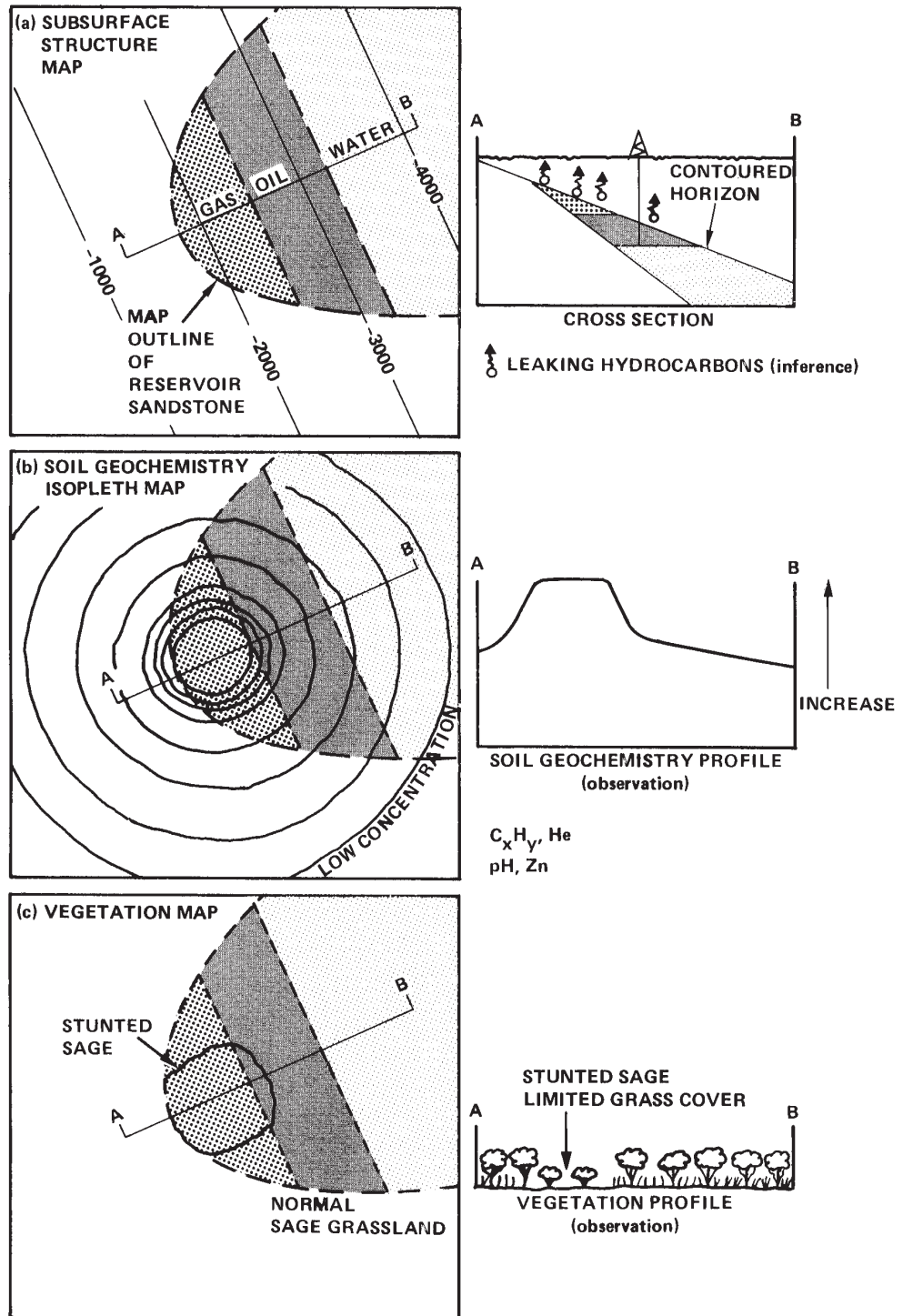
potential to significantly affect the electrochemical properties of the rock column above an oil or gas accumulation. Hughes et al. (1986) described and discussed five such phenomena: pyrite mineralization, calcite cementation, clay alteration, brine effects, and redox potential cell. The first three effects have already been discussed in this paper and were shown to be important alteration products associated with petroleum migration and seepage. The existence of the two remaining phenomena is less well documented. The upward migration of brines has been postulated by Donovan et al. (1981) and others to explain the numerous conductive anomalies measured over known oil fields. There is, however, little published documentation for the existence of brine plumes, and that mechanism remains speculative (Hughes et al., 1986). Pirson (1969, 1976) proposed that the generation of a reducing plume or chimney above a hydrocarbon accumulation produces an excess of free electrons within the plume and that this produces the electrically conductive zone within the plume. However, there appear to be few if any quantitative studies to document the existence of redox potential cells.

Electrical measurements of oil and gas fields aim to detect one or more of the following hydrocarbon-induced alterations by their electrical response: (1) shallow pyrite and marcasite, which provide the source of induced

polarization anomalies; (2) pore-filling carbonate cements, which provide the source of shallow high-resistivity anomalies, and (3) the presence of a deeper low-resistivity zone representing the conductive plume or inferred hydrocarbon leakage chimney. The best documented study to date is probably that of Oehler and Sternberg (1984) for Ashland gas field, a stratigraphic trap in southeastern Oklahoma. Their results document the presence of a near-surface pyrite-marcasite zone and a shallow calcite-cemented zone. They show that these mineralized zones correspond to induced polarization and shallow high-resistivity anomalies, respectively, in surface electrical surveys. Furthermore, their results show excellent correlation between the lateral extent of the induced polarization and resistivity anomalies and the productive limits of the field. The resistivity anomaly for Ashland field is shown on Figure 6.

Results of other induced polarization and resistivity surveys have been reported for Red Oak and South Pine Hollow gas fields in Oklahoma (Sternberg, 1991), Masrab field in Sirte basin in Libya (Sternberg, 1991), Mist field in Oregon and Brown-Bassett field in Texas (Campbell, 1994), and the Turkey Creek seep in Colorado (Reid et al., 1992). All of these examples demonstrate a close correspondence between induced potential and resistivity anomalies and deeper petroleum production. As encour-

Figure 8—Diagram illustrating the empirical remote sensing exploration model developed for the Patrick Draw, Wyoming, NASA/Geosat test site. The stunted sage brush anomaly coincides with soils characterized by high concentrations of light hydrocarbons, zinc, and elevated pH. (From Lang and Nadeau, 1985; reprinted by permission.)



aging as such examples are, significant problems and uncertainties remain, as shown by the results of induced potential and resistivity surveys over Whitney Canyon and Ryckman Creek fields in Wyoming. Hughes et al. (1986) found a striking correlation between the conductive anomalies and the areal extent of the fields. However, they determined from modeling studies that these same anomalies could be explained as the result of cultural, geologic, and topographic factors unrelated to the underlying

petroleum accumulations. The importance of minimizing cultural influences in electrical surveys has been most recently discussed by Carlson and Zonge (this volume).

### Trace Elements and Biogeochemistry

Hydrocarbon microseepage creates a chemically reducing zone in the soil column at depths shallower than would be expected in the absence of seepage. Such leak-

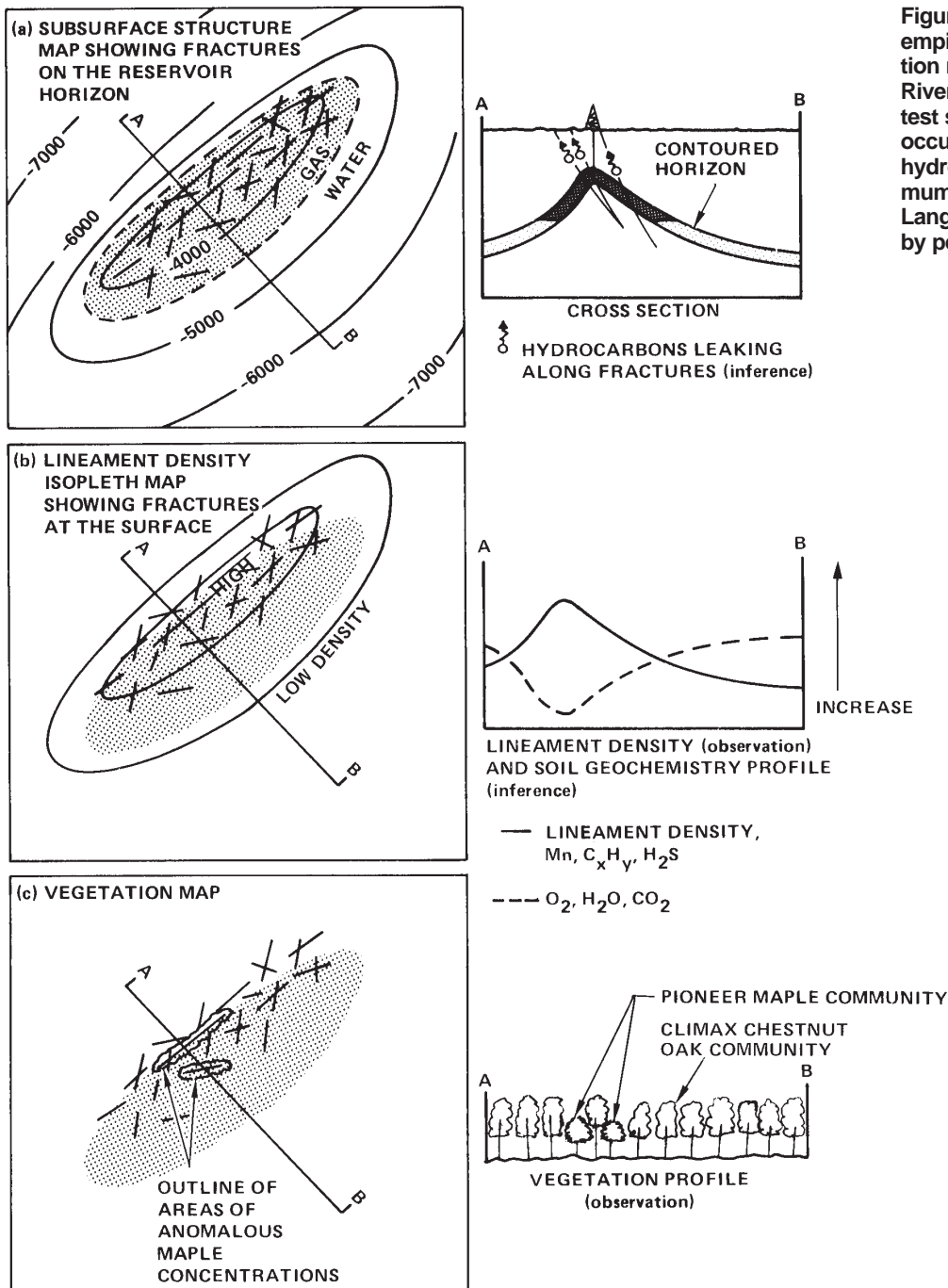


Figure 9—Diagram illustrating the empirical remote sensing exploration model developed for the Lost River, West Virginia, NASA/Geosat test site. The maple tree anomaly occurs in an area of maximum hydrocarbon seepage and minimum soil oxygen levels. (From Lang and Nadeau, 1985; reprinted by permission.)

age stimulates the activity of hydrocarbon-oxidizing bacteria, which decreases soil oxygen concentration while increasing the concentration of CO<sub>2</sub> and organic acids. These changes can affect pH and Eh in soils, which in turn affects the solubilities of the trace elements and consequently their availability to plants. Figure 7 illustrates the effect of soil pH on the relative solubility of common trace metals (Bidwell, 1979). This effect can be quite pronounced; for example, the solubility of iron at pH 6 is 10<sup>5</sup> times greater than at pH 8.5. The lack of essential nutrients such as iron, manganese, copper, and zinc—or their presence in excessively high concentrations—can lead to

physiologic and morphologic changes in plants and can alter their spectral reflectance.

Soil trace metal surveys have been used as indirect surface indicators of petroleum accumulations due to their ability to form organometallic complexes under the reducing conditions that can be found above petroleum accumulations. Duchscherer (1984) reports that V, Cr, Mn, Ni, Co, Cu, Mo, U, Fe, Zn, and Pb are among those trace metals found as geochemical halos over oil fields, and he cites examples of such anomalies from Ocho Juan field in Texas and Bell Creek field in Montana. Another element that has been cited as an indirect pathfinder for petrole-

um accumulations is iodine (Gallagher, 1984; Klusman, 1993; Tedesco, 1995). Iodine can be derived from clays or mineral assemblages in soil, from the breakdown of humic acids or humins, from the atmosphere, or from formation waters. Increases in soil iodine are thought to result from reactions between migrating hydrocarbons and iodine at the soil-air interface (Tedesco, 1995), but the mechanism is poorly understood and largely undocumented.

The most comprehensive investigation of the effects of hydrocarbon leakage on the chemistry of soils and vegetation was the joint NASA-Geosat study of Patrick Draw oil field in Wyoming, Lost River gas field in West Virginia, and Coyanosa field in west Texas (for summary, see Lang and Nadeau, 1985). The study documents a variety of hydrocarbon-induced effects on vegetation and soil over Patrick Draw and Lost River fields, but no apparent effect at Coyanosa. The most pronounced anomaly observed at Patrick Draw field was an area of stunted sagebrush and an associated tonal anomaly visible on Landsat imagery. The anomaly overlies the field's gas cap and occurs in a region of strong light hydrocarbon microseepage, as shown in Figure 8 (Lang et al., 1985a; Richers et al., 1982, 1986). The geology and production history of the field show that the sagebrush anomaly results from the upward migration of injected gases and waters used to maintain reservoir pressures in the field (Arp, 1992). These gases and waters produced anoxic, low-Eh (oxidation potential), high-pH, and high-salinity soils that are toxic to the overlying sagebrush (Lang et al., 1985a; Arp, 1992).

Hydrocarbon microseepage was also documented over the Lost River gas field in the Appalachian Mountains of West Virginia. The principal vegetation anomaly observed here was the presence of maple trees over the gas field at sites where more typical oak-hickory climax vegetation would be expected (Lang et al., 1985b). The results for the Lost River site, as summarized in Figure 9, show that the maple trees occur in an area of maximum hydrocarbon seepage (methane) and minimum soil oxygen content. The anomalous maple distribution may relate to anaerobic soil conditions that directly or indirectly influence the mycorrhizal fungi living on the trees' root hairs, favoring maple trees whose fungi appear to be better able to tolerate the anaerobic soils than their counterparts living on the roots of oaks (Lang et al., 1985b).

Applying biogeochemical techniques, Dalziel and Donovan (1980) measured reduced iron and manganese in the leaves of pine and sagebrush that grew over the Recluse oil field in Wyoming and found that the Mn:Fe ratio was highest over the field. Similar results were reported from Bell Creek oil field in Montana by Dalziel and Donovan (1980) and Roeming and Donovan (1985). At Bell Creek, as in most areas studied, soil and plant geochemical data are inversely related, with low concentrations of metals in soils from under plants with high metal concentrations in their leaves. McCoy and Wullstein (1988) analyzed leaves of sagebrush and greasewood from Blackburn oil field in Nevada and reported a halo

anomaly of high Mn:Fe ratios surrounding the productive part of the field. McCoy et al. (1989) revisited Blackburn field and determined that the spectral reflectance of sagebrush from the anomalous area was lower than that of sagebrush from background areas.

More recently, Klusman et al. (1992) compared the amounts of 20 trace elements in plants growing over and near two oil fields—Eagle Springs field in Nevada and Cave Canyon field in Utah. Klusman theorized that alkaline soil elements such as calcium, strontium, and barium are less available to plants growing in microseepage environments, whereas the transition trace elements such as iron, manganese, and vanadium increase in availability due to their increased solubility in the seep environment. Data from Eagle Springs field supported the expected relationship, but data from Cave Canyon did not.

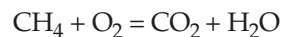
There is no doubt that hydrocarbon microseepage can have a pronounced effect on soils and vegetation, but the specific response is not consistent for different species and sites. In addition, factors such as bedrock geology, soil type, slope, soil moisture, and climate can have a more pronounced effect than that due to the presence of hydrocarbons (Rock, 1984; Klusman et al., 1992).

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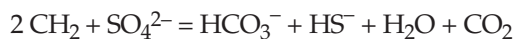
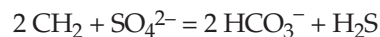
## MODEL FOR HYDROCARBON-INDUCED ALTERATION

Models and mechanisms to explain the diverse array of hydrocarbon-induced changes observed in soils and sediments have been widely proposed and discussed by Donovan (1974), Oehler and Sternberg (1984), Hughes et al. (1986), Price (1986), Klusman (1993), Al-Shaieb et al. (1994), and Thompson et al. (1994). A simplified summary of the basic reactions and processes is presented here and illustrated in Figure 10:

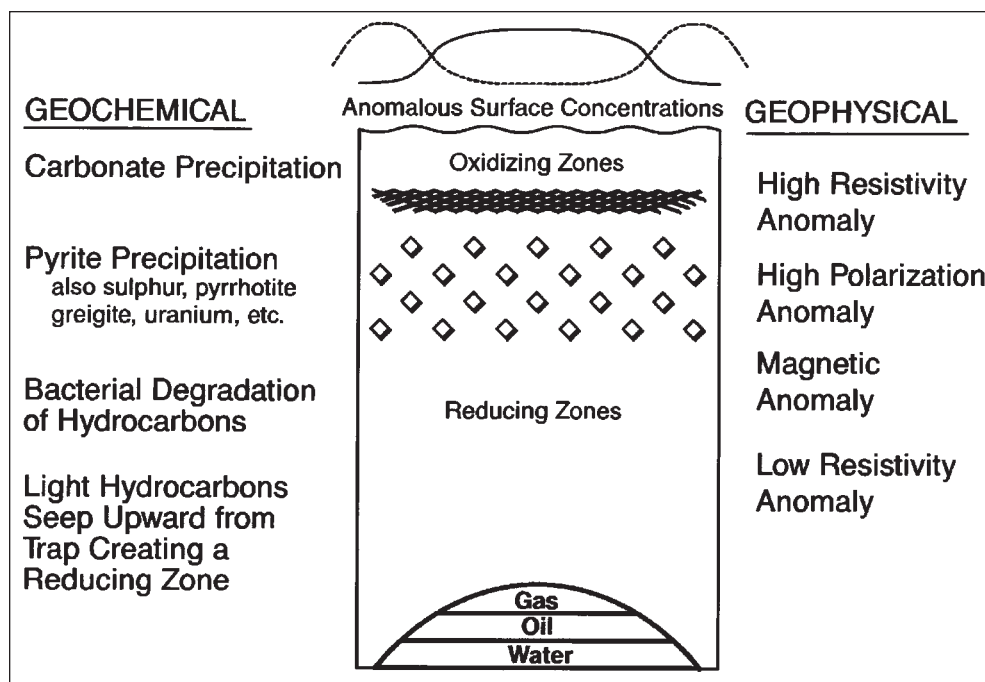
1. Hydrocarbons, chiefly methane through pentane, migrate upward from the reservoir to the surface.
2. When upward-migrating light hydrocarbons reach near-surface oxidizing conditions, aerobic hydrocarbon-oxidizing bacteria consume methane (and other light hydrocarbons) and decrease oxygen in pore waters:



3. With development of anaerobic conditions, the activity of sulfate-reducing bacteria results in sulfate ion reduction and oxidation of organic carbon to produce reduced sulfur species and bicarbonate ion:



4. Highly reactive reduced sulfur species then can



**Figure 10—Generalized model of hydrocarbon-induced geochemical and geophysical alteration of soils and sediments.**

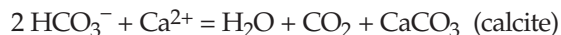
combine with available iron to form iron sulfides and oxides:



(Iron sulfide can be in the form of pyrite, marcasite, magnetite, pyrrhotite, greigite, or maghemite.)



- As a result of bacterial sulfate reduction, sulfate ion concentration is decreased. In addition, bicarbonate is added to pore waters, raising pH and thus promoting precipitation of isotopically light, pore-filling carbonate cements:



This alteration model is not meant to represent all possible reactions and processes occurring in the chemically and biologically dynamic near-surface environment. Rather, it is intended to provide a general framework within which a wide range of reactions can occur.

## IMPLICATIONS FOR EXPLORATION METHODS

The surface and near-surface expression of hydrocarbon seepage can take many forms, ranging from elevated hydrocarbon concentrations in soils and water to complex chemical, mineralogic, microbial, and botanical

changes. These various surface manifestations have led to the development and marketing of an equally diverse number of surface exploration methods. Some are geochemical, some are geophysical, and others come under the category of remote sensing. Although this is not the place to discuss the advantages and limitations of each of the many commercially available exploration methods, it seems appropriate to comment on the major categories of exploration methods as they relate to the alteration phenomena on which they are based.

## Soil Carbonate Methods

Near-surface diagenetic carbonates and carbonate cements are among the most common and widespread manifestations of hydrocarbon seepage, although geochemical anomalies caused by abnormal amounts of  $\text{CO}_2$  are nonspecific for petroleum. High concentrations of  $\text{CO}_2$  in soils and sediments can result from processes other than microbial oxidation of hydrocarbons, such as volcanic or geothermal activity, catagenesis of organic matter, micropore filtration, and thermochemical sulfate reduction (Kartsev et al., 1959; Price, 1986). Also, even if the  $\text{CO}_2$  is a product of hydrocarbon oxidation, the hydrocarbon source could be shallow biogenic methane rather than thermogenic oil or gas from depth. If the origin is biogenic methane, the resulting alteration phenomena will have no relationship to deep subsurface exploration objectives.

Two of the more widely used surface geochemical exploration methods that depend on the presence of soil carbonate are Duchscherer's delta-carbonate ( $\Delta\text{C}$ ) method and Horvitz's "adsorbed" soil hydrocarbon method. The  $\Delta\text{C}$  method measures the amount of  $\text{CO}_2$

evolved from the thermal decomposition of soil carbonates at high temperature (Duchscherer, 1981, 1984, 1986). The Horvitz method utilizes an acid extraction technique to release hydrocarbons from the fine-grained fraction of the soil sample (Horvitz, 1945, 1985). Horvitz believed the hydrocarbons to be adsorbed onto clays or incorporated into soil calcites; the latter is more likely based on recent studies by Price (this volume). Price has found that the Horvitz technique is moderately dependent on soil calcite concentration, whereas Duchscherer's method is completely dependent on calcite concentration. Although soil calcite is nonspecific for thermogenic hydrocarbons, the Horvitz technique measures the concentration of ethane through pentane in the sample and is therefore specific for thermogenic hydrocarbons. Duchscherer's  $\Delta C$  method cannot by itself discriminate thermogenic from nonthermogenic calcites.

## Magnetic Methods

The presence of magnetic anomalies over oil and gas fields has been noted for several decades, but it is only in recent years that the phenomenon has been critically examined. Analysis of data from geologically and geographically diverse regions shows (1) that authigenic magnetic minerals may occur in near-surface sediments above petroleum accumulations; (2) that this hydrocarbon-induced mineralization is detectable with low-level, high-resolution aeromagnetic data; and (3) that magnetic susceptibility analysis of well cuttings (and sometimes soils) confirms the existence of the aeromagnetic anomalies.

While shallow sedimentary magnetic anomalies appear to be associated with many petroleum accumulations, hydrocarbon-induced mineralization is but one of several possible causes for such anomalies. Gay and Hawley (1991) and Gay (1992) urge caution in the interpretation of such anomalies and cite examples of many false anomalies caused by cultural contamination, geologic structure, and syngenetic magnetic sources such as detrital magnetite and burned coal seams. Not only is the interpretation of some shallow magnetic anomalies open to question but their very existence can be short-lived. Investigations by Ellwood and Burkart (this volume) document that nonmagnetic phases such as hematite, pyrite, and siderite can be oxidized to magnetite or maghemite, and more significantly for the explorationist, magnetic phases can revert to nonmagnetic pyrite or siderite under highly reducing conditions. The fluctuation in oxidizing and reducing conditions required to bring about these changes is most pronounced in soils and in the shallow subsurface.

## Electrical Methods

Electrical geophysical methods have gained acceptance in recent years due to advances in both hardware and software technology. The electrical tools most appro-

priate for oil and gas exploration include induced polarization (IP), spectral IP, magnetotellurics (MT), and controlled-source audiofrequency magnetotellurics (CSAMT). Each of these methods is designed to detect electrochemically altered sediments, that is, the conductive plume or alteration chimney that may extend from the accumulation to the surface. Magnetotelluric data are the result of measuring natural fluctuations in magnetic and electrical fields at the earth's surface. CSAMT is a more recent electrical geophysical application that uses an artificial signal source, unlike MT, which uses naturally occurring signals. CSAMT now appears to have sufficient resolution to image the subsurface alteration plume across a wide range of geologic conditions. Despite encouraging reports, there are still relatively few published studies documenting electrochemical alteration over petroleum accumulations, and most have not fully addressed the possible contribution of geologic, topographic, and cultural effects.

Sternberg (1991) states that the IP-resistivity method for hydrocarbon exploration has significant limitations. Many areas do not appear to have the required geologic and geochemical conditions for the formation of IP or resistivity anomalies. IP and resistivity anomalies may also need to be tested with surface geochemistry and shallow drill holes to separate anomalies caused by hydrocarbon seepage from false anomalies due to other causes.

## Radioactivity Methods

The existence of gamma radiation lows over oil and gas fields has long been known and forms the basis for radiometric surveys utilizing airborne or ground-based gamma ray spectrometers. Potassium-40 in clay is generally thought to be the major source of soil radioactivity, with lesser contributions from bismuth-214 and thallium-208. The low radiation values over petroleum accumulations have been attributed to either (1) precipitation of uranium salts at the oxidation-reduction boundary at the edge of the inferred hydrocarbon leakage plume, or (2) conversion of K-bearing clays and feldspars to kaolinite or other K-deficient clays (Pirson, 1969; Heemstra et al., 1979; Price, 1986; Saunders et al., 1993).

Despite numerous claims of success for surface radiation surveys by Weart and Heimberg (1981) and Curry (1984), among others, there have been few scientifically rigorous investigations of radiation surveys and the many factors that can influence their results. One such study by Heemstra et al. (1979) conducted in Kansas found no correlation between petroleum production and surface radiation. They did, however, find correlations among gamma radiation and topography, soil type and thickness, bedrock outcrops, and other factors. There seems little doubt that anomalous gamma radiation values are associated with some oil and gas fields, but the processes that produce them are poorly understood and even less well documented.

## Remote Sensing Methods

Satellite-based remote sensing of hydrocarbon-induced alteration holds great promise as a rapid, cost-effective means of detecting anomalous diagenesis in surface soils and rocks. Research in the vicinity of Patrick Draw, Lost River, and Lisbon Valley fields during the NASA-Geosat test case project demonstrates that Landsat MSS and Thematic Mapper (TM) data can be used to detect three types of hydrocarbon-induced geochemical changes: (1) reduction of ferric iron (red bed bleaching), (2) conversion of mixed-layer clays and feldspars to kaolinite, and (3) anomalous spectral reflectance of vegetation. The potential for application of these techniques is greatest in areas of sparse vegetation and susceptible surface clays and red beds.

The outlook for trace element and biogeochemical surveys seems less encouraging. Anomalous distributions of iodine and trace metals have been reported in some oil and gas fields, but the mechanisms responsible for these anomalies are neither well known nor well documented. Hydrocarbon microseepage can have a pronounced effect on soils and vegetation, but the specific response appears to be inconsistent for different species and sites. Also, factors such as bedrock geology, soil type, soil moisture, topography, and climate can have a greater effect than that due to the presence of hydrocarbons.

## CONCLUSIONS

Exploration methods based on what are assumed to be hydrocarbon-induced soil and sediment alterations have long been popular, but the processes that produce the observed effects are not well understood and even less well documented. The nature and extent of the alteration can vary significantly not only laterally and vertically but also temporally.

The cause of these altered soils and sediments may well be hydrocarbon related, but it is an indirect cause at best and may not be the most probable cause. We must evaluate seemingly "significant" alteration anomalies carefully to determine if they are related to hydrocarbon seepage. This requires answers to the following questions. Is the anomaly a function of geology or an artifact of culture? If geology, is the observed alteration syngenetic or authigenic? If authigenic, is the anomaly seep-related or of nonseep origin? If seep-related, does the anomaly result from an active hydrocarbon seep or a paleoseep? Finally, if the anomaly at the surface is to be related to a drilling objective at depth, does the anomaly result from mainly vertical migration or does the migration path follow a more complex route?

Numerous claims of success have been made for various exploration methods based on soil and sediment alteration anomalies. Well-documented case studies are rare, however, and the claims are seldom substantiated by a scientifically rigorous program of sampling and analysis. Although the occurrence of hydrocarbon-

induced alteration is well established, considerable scientific research is needed before we understand the formation of these anomalies in the near-surface and realize their full value for hydrocarbon exploration.

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