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LATE DIAGENETIC INDICATORS OF BURIED OIL AND GAS

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LATE DIAGENETIC INDICATORS OF BURIED OIL AND GAS

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ABSTRACT

At least three hydrocarbon seepage mechanisms are interpreted to operate over oil and gas fields. These are: (1) effusion of hydrocarbons through inadequate caprocks and along faults and fractures, (2) low-molecular-weight hydrocarbons dissolved in water moving vertically through capping shales as a result of a hydrodynamic or chemical potential drive, and (3) diffusion of gases dissolved in water. Combinations of these mechanisms may also occur.

Seeping hydrocarbons are oxidized near the earth's surface, and the resulting carbon dioxide reacts with water producing bicarbonate ions, which combine with calcium and magnesium dissolved in ground waters to yield isotopically distinctive pore-filling carbonate cements and surface rocks. The passage of hydrocarbons and associated compounds such as hydrogen sulfide through surface rocks causes a reducing environment and consequent reduction, mobilization, and loss of iron from iron-bearing minerals commonly resulting in a discoloration. Other metals such as manganese are also mobilized and redistributed. These changes in the physical and chemical properties of surface rocks correlate with the subsurface distribution of petroleum, and potentially can be detected from both airborne and spaceborne platforms.

INTRODUCTION

Explorationists have long utilized seepages and other surface indicators of petroleum as guides to the location of exploratory drill sites (Owen, 1975; Thompson, 1926; Barton, 1927; Coomber, 1938; Illing, 1938; DeGolyer, 1940; Link, 1952). The most obvious and easily found petroleum deposits were discovered largely by the use of surface seepages, and by detailed mapping of the surface expression of structural traps. More recently sophisticated techniques geared to detection of trace amounts of hydrocarbons in soils and soil gases and the metabolic byproducts of microbial degradation of hydrocarbons at the surface have been employed (Laubmeyer, 1933; Sokolov, cited in Boyle and Garrett, 1970; Horvitz, 1939; Pirson, 1940; Rosaire, 1940; Kartsev and others, 1959; Davis, 1967; Boyle and Garrett, 1970). The difficulty in finding geologically inconspicuous deposits also stimulated the development of a highly sophisticated geophysical technology. The success of this technology, coupled with the fact that the "easy oil" largely had been found, was responsible for a decline in interest in surface indicators of buried petroleum. Recently, however, the large and increasing costs of geophysical surveying have spurred renewed interest in detection of subsurface accumulations of petroleum by surface or near surface indicators (McCulloh, 1969; Donovan, 1974; Donovan, Noble, and others, 1975).

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This paper describes several kinds of surface alteration phenomena over several midcontinent, Texas, California, and Rocky Mountain oil fields and one undrilled prospect, and proposes, schematically, the geochemical pathways whereby they may be developed.

INTERACTIONS BETWEEN WATER AND HYDROCARBONS

The subtle relationships between formation-water salinity and dispersal, transport, and remobilization of entrapped hydrocarbons are not always recognized. The origin of saline-formation waters (brines) is a major geochemical and hydrologic problem (Clayton and others, 1966), and important to many of the problems in the geology of petroleum. The conclusion that formation waters are "predominantly of local meteoric origin" (Clayton and others, 1966, p. 3869) is of special importance to the general problem of hydrocarbon-formation water interaction.

Hitchon (1969a, b; 1974), combined complex mathematical models of basin-wide flow of fluids of Toth (1962; 1963), Freeze (1966; 1969), and Freeze and Witherspoon (1966; 1967; 1968), to substantiate that the critical variables affecting fluid potential distribution in a basin are topography, lithology, and permeability. Thus, "the dominant fluid potential in any part of the basin corresponds closely to the fluid potential at the topographic surface in that part of the basin. Major recharge areas correspond to major upland areas, and major lowland regions are major discharge regions" (Hitchon, 1974, p. 539). Topography provides and maintains the initial differences of fluid potential by capturing precipitation at different elevations.

However, it is because most sedimentary rocks are anisotropically permeable that ground-water flow lines tend to parallel bedding; such anisotropy is usually insignificant in unconsolidated sediments. These facts enable sedimentary basins to be divided into two vertical zones (Toth, 1972): the unconfined flow zone has its flow distribution controlled by the configuration of the overlying water table and the confined zone has its flow system bounded by rock layers of low permeability; its flow distribution is not significantly influenced by the potential of the water table. Total dissolved solids (TDS) in the waters increase in the direction of flow and at the join of two flow systems; at points where three or more systems diverge, stagnant water forms which may be signalled by an increased total dissolved solids content. In areas of upward flow, accumulation of mineral salts may be expected in soils (Toth, 1972).

The capacity of clays and shales to act as salt-concentrating membranes is well established (DeSitter, 1947; Berry, 1959; Bredehoeft and others, 1963). Complementary studies of the effects of shale micropore systems on the isotopic fractionation of water provide additional evidence for regional recharge of subsurface waters by meteoric input (Graf and others, 1965; Graf and others, 1966; Hitchon and Friedman, 1969; Coplen and Hanshaw, 1973). Graf and others (1965) noted the difference in Deuterium and Oxygen isotopic composition between pairs of samples taken from different depths but geographically similar positions, as an indicator of the direction of cross-formational flow in that area. Their data clearly indicate large meteoric-water input. The idea that oils can be altered by contact with low-salinity (meteoric) waters has been discussed for some time (Estabrook, 1925; Uspenskii and others, 1947; Hunt, 1953; Weeks, 1958; Krejci-Graf, 1963). Furthermore, it has recently been documented that

low-salinity waters play an important role in the *in situ* biodegradation of crude oil (Winters and Williams, 1969; Bailey, Jobson, and Rogers, 1973). The selective removal from petroleum reservoirs of the low-molecular-weight components implies intricate subsurface relationships between major segments of the hydrologic and carbon cycles.

Figure 1 demonstrates the relationship between aqueous solubility and the molecular weight of homologous series compounds characteristic of crude oils at 25°C and 1 atmosphere pressure. The data clearly indicate that the low-molecular-weight members of any homologous series present in crude are more soluble in water. For any given molecular weight, aromatic compounds are more soluble in water than normal paraffins (because of the polar character of the aromatic ring) and cycloparaffins with low- to moderate-molecular weights have intermediate aqueous solubilities. Further, the aqueous solubilities of branched-chain paraffin hydrocarbons are somewhat greater than normal paraffin hydrocarbons. McAuliffe (1963, p. 1093) stated that, with the exception of methanes, "it appears that to a first approximation the weight of a normal or branched-chain paraffin hydrocarbon which dissolves in water is proportional to the vapour pressure of the hydrocarbon." These kinds of data are broadly useful in hypothesizing how selected hydrocarbons might overcome physical barriers (such as low permeability and/or high capillary pressure) to escape from petroleum reservoirs.

Complications arise when one considers interactions between hydrocarbons and impure water under a temperature and pressure regime such as is found in subsurface environments. Published data indicate that hydrocarbon solubility in water varies inversely with salt concentration, and is also dependent upon the kind of hydrocarbon and salt (Euchen and Hertzberg, 1950; McDevitt and Long, 1952; Paul, 1952; McAuliffe, 1963). The study of Price (1976) indicates that the increase of aqueous-solubility with temperature at systems' pressure is uniform but slight in the range 25° to 100°C, above which there is a pronounced increase. According to Price, salinities in excess of 150,000 ppm NaCl concentration effect drastic exsolution of hydrocarbons, and at 350,000 ppm there is about a 95 percent reduction in solubility. However, a semi-log plot of some of Price's data (fig. 2) indicates that a change from gradual to drastic exsolution begins at about 25,000 ppm. This is probably the result of abrupt transition between two different solution mechanisms. Therefore, drastic dissolution of hydrocarbon might be expected even with moderate dilution of formation waters.

The effects of increased temperature and pressure are counteractive to aqueous salt concentration; however, at conditions common to moderate-to-shallow depths, pressure and temperature effects appear relatively unimportant (Price, 1976, figs. 2-9). Within the moderate-to-shallow depth range greatly variable formation water salinities are observed, however, they are commonly low (DeSitter, 1947; Bredehoeft and others, 1963; Dickey, 1966; Zaitsev and Baskov, 1969). Significant fresh-water dilution of brine systems can markedly affect the aqueous solubility of any hydrocarbons with which they are in contact, as well as introduce other complicating factors such as microbes, dissolved molecular oxygen, and sulfate.

Considered broadly, the introduction to a petroleum reservoir of relatively fresh water, possibly bearing dissolved oxygen or sulfate and hydrocarbon-

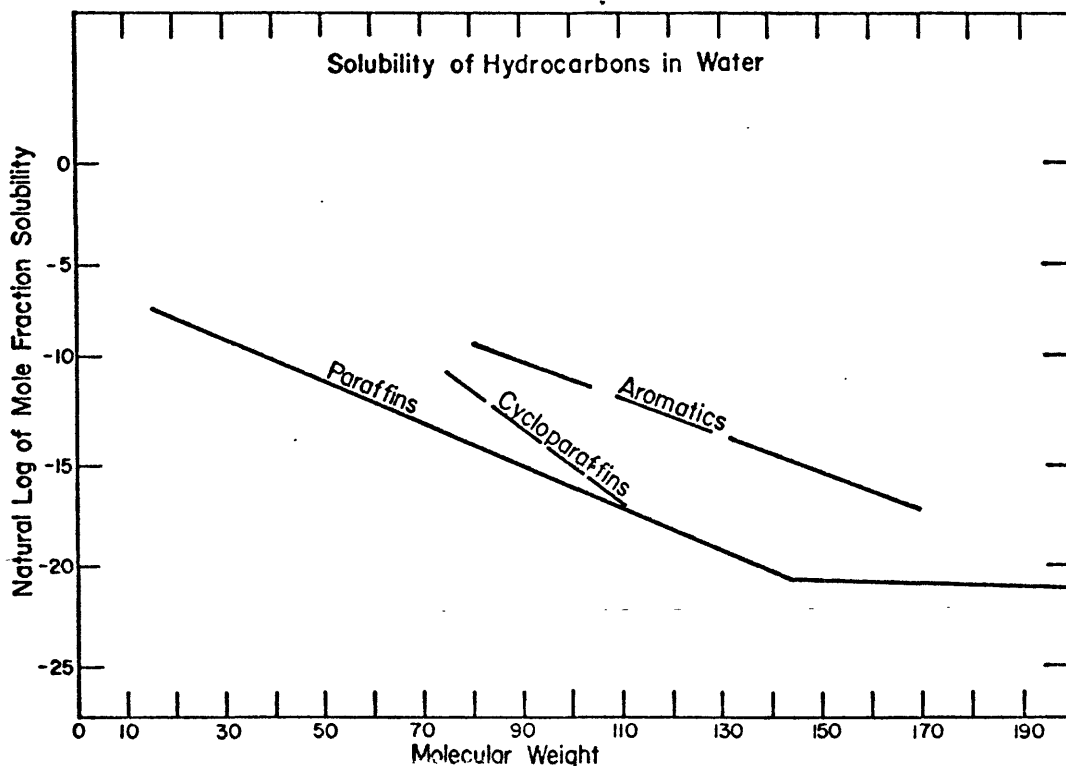


Figure 1.--Relation between molecular weight and aqueous solubility of homologous series compounds at 25°C and 1 atm pressure. Data from Bohon and Claussen (1951); McAuliffe (1963); and Baker (1969). The tabulated values of Price (1976, table 2) should also be consulted.

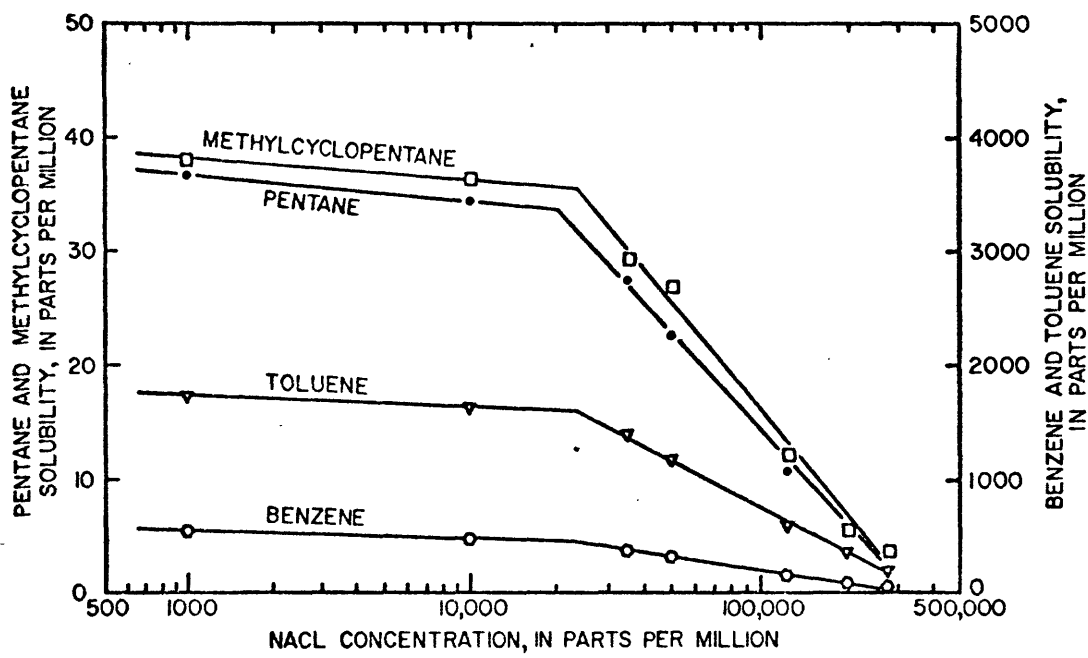


Figure 2.--Relation between aqueous solubility of various hydrocarbons and salt concentration. Data from Price (1976).

oxidizing microbes can result in the following: (1) *in situ* biodegradation of hydrocarbons, especially the paraffins in approximate proportion to their chain length; and (2) dissolution and removal (water-washing) of the more water-soluble components (Winters and Williams, 1969; Bailey, Jobson and Rogers, 1973; Bailey, Krouse, and others, 1973; Donovan, 1974). These mechanisms plus the escape by direct communication with the surface (Hunt, 1953, p. 1870) leave behind a residual oil different in composition than the original material. Other factors affecting alteration, such as gas-deasphalting (Evans and others, 1971) or the addition of microbial metabolites (Winters and Williams, 1969), should also be considered.

IDENTIFICATION OF ALTERED CRUDE OILS

It is of interest to determine if microseepage from petroleum accumulations is common enough to make exploration techniques, based upon detection of this seepage, useful. The problem can be addressed by assuming that crude oils will be detectably altered if selective loss of the low-molecular-weight liquid components ("light-ends") has occurred. Leaky systems are expected to contain a residual petroleum substantially different than the "starting" substance. The following discussion describes processes which bring about this alteration.

Petroleum displays a wide variety of compositions and physical characteristics which are dependent upon the source materials and environment at the place of origin, the environment at the place of accumulation, and any subsequent chemical or biochemical changes (Andreev and others, 1968). The actual processes of generation, migration, and alteration are poorly understood, and empirical evidence for them is difficult to obtain. The general improvement in the quality of crude oil through a decrease in density with increasing depth and temperature is well known (Barton, 1934; Brooks, 1949; McNab and others, 1952) as is the general correlation in most basins between increasing specific gravity of petroleum and decreasing water salinity (Weeks, 1958). These variations have most commonly been interpreted as the result of thermal maturation of the crude oil, although Haeberle (1951) has related variations in crude properties in the Gulf Coast region to changes in depositional facies. The inverse relation between petroleum specific gravity and depth or temperature is highly variable and is qualitatively true only in restricted areas or some geologic provinces (for instance, in areas such as the Texas Gulf Coast). Reversals of the trend are common (Levorsen and Berry, 1967, p. 162; Schmidt, 1973; Kharaka and others, 1977).

Study of data tabulated in U.S. Bureau of Mines Routine Crude-Petroleum Analyses (Hempel-method analyses) suggests a more than casual relationship between the volume percent of Total Gasoline and Naphtha (TG+N) fraction (hydrocarbons distilling between 50° and 200°C at 760 mm Hg) and that fraction's specific gravity. Low volumes are characteristically associated with high specific gravities and the opposite is true. Because specific gravity is a measure of hydrocarbon composition, it is apparent that as the volume percent of TG+N varies so does its composition. A normalization technique was devised to preclude comparisons of TG+N volumes which are compositionally different:

$$TG+N^* = TG+N \left(\frac{Sp.g.}{Sp.g.} \right),$$

where TG+N* is the normalized volume percent of the total gasoline and naphtha reported in the U.S. Bureau of Mines Routine Analysis, Sp. g is the specific gravity of that fraction, and $\overline{\text{Sp. g}}$ is the mean specific gravity (.746) calculated from all the data used (154 analyses).

Cursory inspection of the normalized data suggests that TG+N* varies with salinity, for in general there is a small TG+N* associated with low-salinity waters as expected, but the relationship is neither simple nor linear. A plot of log TG+N* against the log of the square of salinity (in percent) suggests strongly a relation exists but a marked heterogeneity is exhibited (fig. 3).

If alterations as outlined above have occurred in a reservoir, it is reasonable that no consistent relation should exist between TG+N* and salinity, except that TG+N* will be small for the corresponding total salinity. The test of this presumption is data plotted (fig. 3) for crudes known from chemical (and geological) analysis to be both "normal" and peculiar (and presumably altered) with respect to their compositions. The location of samples used for control are tabulated in table 1. Thus, although the data for the oils plotted in figure 3 are from Hempel analyses, the assessment of their altered or unaltered nature is from other sources. Salinities of formation waters are taken from U.S. Bureau of Mines published and unpublished sources. Only salinities for a formation water that is associated with a crude oil were used.

Figure 4 is a plot of unaltered crudes from figure 3 as a function of salinity demonstrating a good correlation. The gentle slope of the regression curve testifies to the sparing solubility of hydrocarbons in salt water.

It is emphasized that the dashed line drawn on figure 3 is not a statistically fitted curve, rather it is a subjective separation of data points representing two distinct classes of oils: those essentially in equilibrium with their associated waters (above the line), and those in disequilibrium (below the line). The latter are the result of some unusual post-accumulation history. An inequality can be calculated from these empirical data which is useful for estimating unaltered crude oils:

$$\text{TG+N*} > [\text{TDS}] \quad 0.082 \quad + 25.7,$$

where [TDS] represents the percentage of total dissolved solids in the associated formation waters. We conclude from figure 3 that altered crude oils are probably as common as unaltered ones, and a significant proportion may have been altered through the selective loss (in contrast to biodegradation) of light-ends.

CUMULATIVE EFFECTS OF HYDROCARBON SEEPAGE THROUGH SURFACE AND NEAR SURFACE ROCKS

Our data and analysis indicate that at least three seepage mechanisms operate. These are: (1) effusion of small to large amounts of gaseous and liquid hydrocarbons through relatively thin overburden along faults and fractures and through poorly compacted and permeable caprocks, (2) low-molecular-weight hydrocarbons dissolved in water moving vertically through capping shales behaving as semi-permeable membranes with either hydrodynamic pressure or differences in

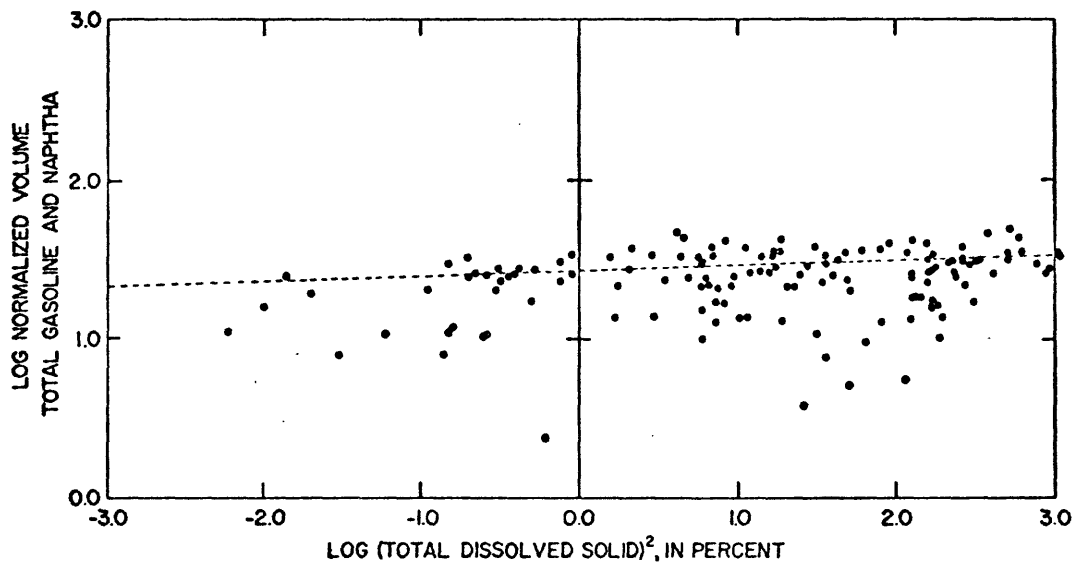


Figure 3.--Relation between normalized volume of Total Gasoline and Naphtha (TG+N) in crude oil and total dissolved solids of associated formation waters. Dashed line separates unaltered crudes above from altered crudes below.

Table 1.--Altered and unaltered crude oil data

Unaltered	Altered	Reference
	Montana	
Bell Creek (southwest end)	Bell Creek (northeast end)	Winters and Williams, 1969
	Alaska	
McArthur River (W. Foreland ss.)	Trading Bay (Tyonek Fm)	Claypool, written commun., 1976
	Louisiana	
Hackberry, W., deep	Hackberry, E., shallow	Winters and Williams, 1969
	Oklahoma	
	Cement, all zones	Donovan, 1974
	California	
Dos Cuadras, deep (Questionably unaltered?)	Dos Cuadras, shallow	McCulloh, 1969
	Texas-New Mexico	
Several	Several	Jones and Smith, 1965
	Saskatchewan	
Forget (marginally altered?)		Bailey, Jobson, and Rogers, 1973 Bailey, Krouse, and others, 1973

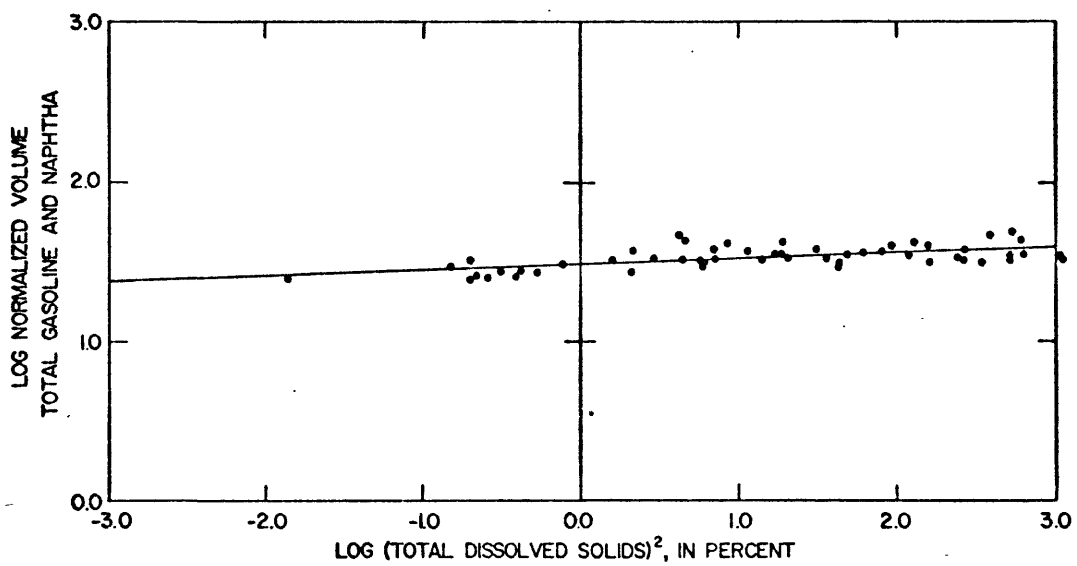


Figure 4.--Relation between normalized value of Total Gasoline and Naphtha (TG+N) in unaltered crudes (as identified in fig. 3) and total dissolved solids of associated formation waters.

chemical potential on opposite sides of the membranes providing the driving force, and (3) diffusion of dissolved gases through caprocks. Combinations of these processes also operate. Identification of the responsible mechanism is based on distinctive isotopic and chemical parameters of the surface rocks and in some cases, fluids, from underlying reservoirs. The cumulative effects are these: C^{13} depleted carbonates are either O^{18} enriched or impoverished depending upon which of the three main mechanisms has been dominant at an oil field. Furthermore, they are enriched with manganese and sometimes iron. Uncemented rock is commonly bleached or tinted because of reduction of iron in iron-bearing minerals and its subsequent dissolution and loss. How these effects may come about is discussed below. Data were obtained from the following oil fields: Bisti, New Mexico; Cement, Davenport, Doyle, Fox-Graham, and Velma, Oklahoma; Garza and Jameson Reef, Texas; and Kettleman Hills, California. In addition, a suspected petroleum-related geochemical anomaly at Gunbarrel Hill, Colorado, was investigated (Donovan, Noble, and others, 1975; Roberts and others, 1976).

Isotopic Data

The unusual carbon isotopic compositions of replacement carbonate minerals and authigenic cements in sedimentary rocks resulting from the oxidation of hydrocarbons is well documented (Thode and others, 1953; Feely and Kulp, 1957; Hathaway and Degens, 1968; Davis and Bray, 1969; Mamchur, 1969; Davis and Kirkland, 1970; Kirkland and Evans, 1976). However, few investigations have been published describing the complex interrelationship between anomalous carbon and oxygen isotopic variations in carbonate minerals over oil fields (Cheney, 1964; Donovan, 1974; Donovan and others, 1974). If the precipitation of carbonate cements with unusual isotopic compositions in clastic rocks overlying oil and gas deposits results from the oxidation of hydrocarbons and other processes utilizing hydrocarbons, then their presence could in itself provide a means of locating buried hydrocarbons.

The isotopic compositions of carbonate cements from rocks cropping out over the oil fields investigated display extremely wide ranges (table 2). These data suggest that in some instances high δO^{18} values correlate with low δC^{13} values, and in other instances the opposite is true, with low δO^{18} values corresponding to low δC^{13} values. Both isotopic distributions vary in a systematic and areally mappable way (for example, Donovan, 1974, figs. 6 and 7; Donovan and others, 1974, figs. 2 and 3; Donovan, Noble, and others, 1974, plates 1 and 2). We interpret that the C^{13}/C^{12} values reflect the source of carbon, (petroleum or natural gas), and the efficiency of hydrocarbon transport into the near surface ground-water system and subsequent oxidation. In contrast, the wide-ranging O^{18}/O^{16} values are interpreted to reflect fractionation processes operating on ground and formation waters, but modified somewhat by mixing with fresh water. Fractionated water subsequently reequilibrates with authigenic cements. Two primary fractionation mechanisms appear to be natural gas-induced evaporation of ground water and micropore filtration of vertically moving formation water. Both mechanisms should also influence the TDS content of ground waters. Over some large oil fields such as Cement and Velma, Oklahoma, different processes may have operated at different localities at the same field. We find it useful, therefore to compare mean O^{18}/O^{16} values with the C^{13}/C^{12} minimum for a particular field. This "means vs. extremes" approach results in comparison of data reflecting the processes which has predominated

Table 2.--Stable isotopic values of carbonate cements in rocks cropping out over oil fields

Number of Samples	$\delta^{13}C$		$\delta^{18}O$		Mean Annual T, °C	Calculated hypothetical $\delta^{18}O$ Mil for diagenetic $CaCO_3$	
	(Range)	Mean	(Range)	Mean		SMOW/	SMOW/
Oklahoma							
Cement (replaced gypsum)	2	(-35.5 and -25.5)	(22.5 and 25.8)				
Cement (Calc. ss.)	27	(-39.2- - 5.5)	(22.5 - 36.5)	27.4	16.4	27.1	27.1
Davenport*	24	(-11.3- - 3.3)	(27.5 - 48.8)	38.5	16.3	27.1	27.1
Doyle	39	(-26.3- - 3.1)	(26.9 - 36.9)	32.5	16.8	27.3	27.3
Fox-Graham	61	(-34.2- - 2.0)	(21.6 - 37.0)	30.2	16.4	27.1	27.1
Velma	32	(-37.6- -10.9)	(21.6 - 37.9)	29.0	16.8	27.1	27.3
New Mexico							
Bisti	31	(-18.9 - 0.1)	(10.9 - 26.7)	19.6	10.0	23.3	23.3
Texas							
Jameson reef	4	(-38.0- - 0.4)	(22.9 - 28.0)	26.0***	18.3	28.1	28.1
Garza	35	(-32.0- - 6.2)	(22.6 - 36.0)	25.3	17.0	27.4	27.4
California							
Kettleman Hills N. Dome	18	(-22.1- - 4.0)	(21.9 - 30.0)	25.2	17.2	27.5	27.5
Nya & Pecten Zone fossils from Kettleman Hills (Dodd & Stanton, 1975)	35	(- 3.8 - 1.7)	(25.7 - 33.0)	30.2			
Colorado							
Gunbarrel Hill**	48	(-18.0- - 3.0)	(12.2 - 24.1)	16.0	10.1	23.3	23.3

* Dolomite
 ** Geochemical anomaly unproven by drilling
 *** 4 samples only

over an entire field. Figure 5 is a plot of δC^{13} ranges plotted at the mean δO^{18} position for nine known (and one unproven) oil fields. The range of values for typical marine, freshwater, and diagenetic carbonates are shown for comparison. A suggested envelope for our data is also sketched in.

At least one additional refinement of these data is possible. Because many of the areas of interest are considerably separated from one another geographically, the influence of present-day temperature on the O^{18}/O^{16} composition of the carbonates was considered. The theoretical O^{18}/O^{16} composition for calcite for each area was computed using the mean annual temperature for each region and the relationship between temperature and meteoric water (Dansgaard, 1964) and the O^{18}/O^{16} equilibrium constant for the water-calcite system at a given temperature (Clayton, 1961). Some mean values are close to theoretical, but many are not, suggesting fractionation processes have occurred which override the influence of temperature. To evaluate the latter, the absolute difference between mean and theoretical O^{18}/O^{16} (ΔO^{18}) was plotted against the most negative C^{13}/C^{12} value for each area (fig. 6). Absolute differences were used in order to have sufficient data to calculate a curve, but the suggestion of parity is obvious from figure 5. It is important to note that as a mean O^{18}/O^{16} value deviates from "normal," δC^{13} decreases, and the relationship holds irrespective of the sign of ΔO^{18} . One explanation of these relationships is that they reflect the efficacy of trapping mechanisms in restraining selected hydrocarbons from escaping. It is not anticipated that additional data points would necessarily fall on the curves of figure 6. Rather we suggest that figures 5 and 6 define an approximate envelope within which most additional points will fall.

Case I: Origin of O^{18} -enriched carbonates.--The Davenport field of central Oklahoma provides a good model for this case. δC^{13} values in carbonate cements from outcrops over the field range from about -5/mil to -12/mil. δO^{18} values likewise vary, but have an especially large range of 29/mil to 49/mil. The lightest carbon and heaviest oxygen values are directly over the maximum oil column thickness (Donovan and others, 1974, figs. 2 and 3).

The Davenport field is in Lincoln County, Oklahoma. The discovery well was drilled in 1924 and found oil at 1,000 m. Rapid development followed and reached a peak during 1926. The surface rocks are Pennsylvanian shale, sandstone, and thin interbedded limestones. The first productive horizon is a thin Pennsylvanian sandstone at about 730 m. The main producing horizon is a sandstone at 1,000 m. This micaceous, lenticular sandstone has varying thicknesses (10-33 m) and grades into a sandy shale or pinches out entirely along the edge of the field. Less than 20 km² are productive.

A small surface anticline exists at Davenport, but in the subsurface the producing area of the field extends beyond the limits of the structure and is controlled by the areal extent of the main producing sand. The oil produced at Davenport differs from that found in similar sands in other nearby localities because it is a paraffinic rather than mixed-base oil. The API gravity is 51° (Brandenthaler and others, 1926; Radler, 1930; White, 1941; Donovan and others, 1974). Davenport was located by surface mapping.

Salinities of formation waters at Davenport approach 200,000 ppm. This precludes dissolution and removal in solution of large quantities of liquid

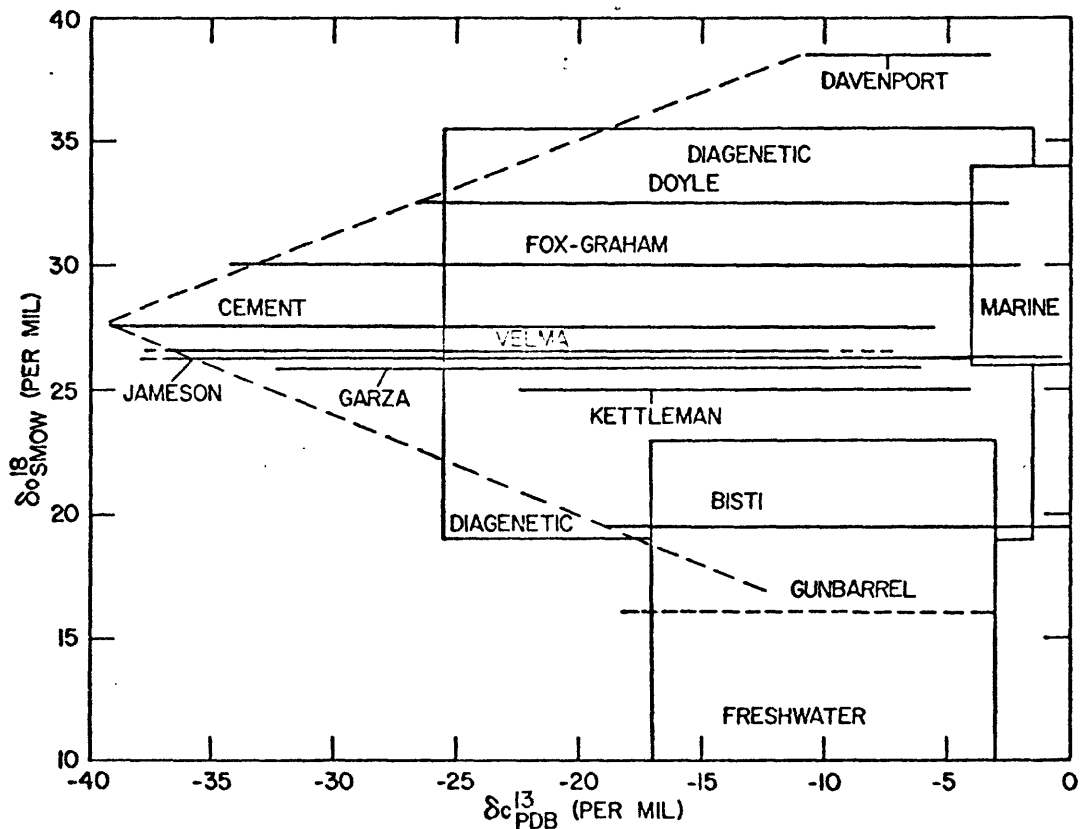


Figure 5.--Ranges of $\delta^{13}\text{C}$ from carbonate cements in outcropping sandstones from 9 known and one suspected oil accumulations plotted at the mean $\delta^{18}\text{O}$ position. Compositional limits of typical carbonates shown for comparison (Murata and others, 1969). A suggested envelope is also drawn (dashed line).

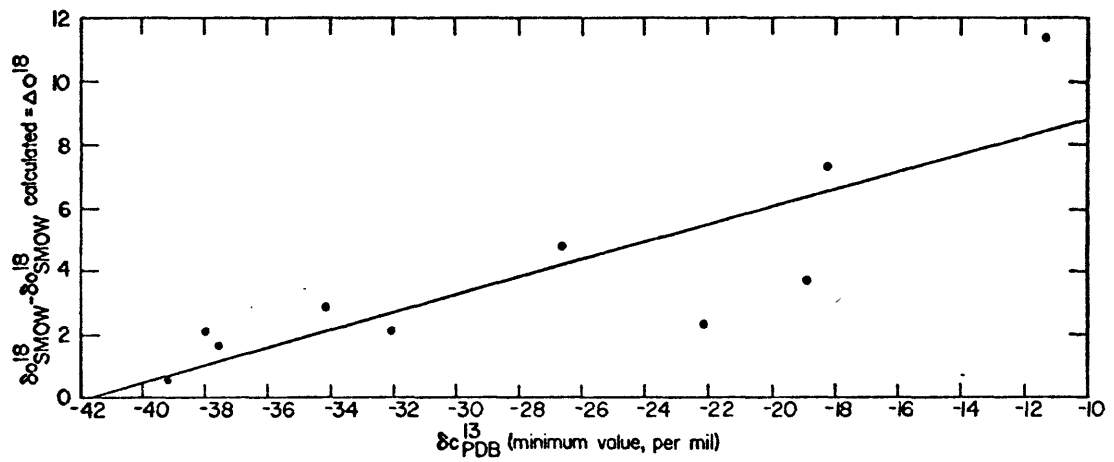


Figure 6.--Relation between the absolute difference between mean and theoretical δO^{18} (ΔO^{18}) and the most negative δC^{13} value found in carbonate cements of sandstones cropping out over oil fields.

hydrocarbons as an effective escape means. However, the petroleum there has an API gravity of 51° and is considered a condensate (Brandenthaler and others, 1926). Escape of gas by diffusion thus appears logical. Diffusion of gaseous components usually takes place through the water phase. In this mode, the driving force is provided by concentration differences of gas in the liquid rather than involving the transfer of large amounts of dissolved constituents in a moving aqueous solvent. The experiments of Pandey and others (1974) show that although a gas in the liquid-water phase has a diffusion coefficient less than in the dry gas phase, the coefficient behaves similarly to that for bulk diffusion, and does not vary with pore size. Additionally, although the effects of pressure on the dry gas diffusion coefficients are different for high and low permeability rocks, "there are no pressure effects on diffusion coefficients through water-saturated rocks when the calculations are made on the basis of water phase concentrations" (Pandey and others, 1974, p. 301). Because the kinetic theory of gases does not hold for the diffusion of gases through the liquid-water phase, their evidence that the liquid bulk diffusivity does not vary with pore-radius is of major significance in explaining leaky fine-grained caprocks.

Gas-induced evaporation of ground water, initially proposed by Mills and Wells (1919) and confirmed as thermodynamically feasible by Nisle (1941), is the suggested fractionation mechanism for the large range of δO^{18} values found in carbonate cements at Davenport. Natural gas diffusing from the underlying deposit expands as it rises and comes out of solution. As it passes through ground water, it selectively evaporates H_2O^{16} relative to H_2O^{18} owing to differences in vapor pressure of the two waters (Rayleigh distillation). The O^{18} -enriched waters subsequently equilibrate with carbonates precipitating from mineralized pore waters. Data for evaporating waters in the Sahara indicate that Rayleigh distillation can fractionate surface water sufficiently to invest carbonates with similar O^{18}/O^{16} values (Fontes and Gonfiantini, 1967).

Case II: Origin of O^{18} -depleted carbonates.--The Bisti oil field in New Mexico provides an example of O^{18} -depleted carbonate cements overlying an oil field. Bisti is in southern San Juan County, New Mexico, on the southwest flank of the San Juan basin. The discovery well was drilled on a stratigraphic target in October 1955. Several other nearby pools were later discovered and linked together into the Bisti oil field.

Gas and oil occur in Upper Cretaceous off-shore marine bar sandstones. The bars grade into a silty shale, a forebar facies grading in a basinward direction (northeast) and a sandy shale or backbar facies in a southwest direction; the sandstones provide a series of narrow permeability lenses. There also is evidence of a positive hydrodynamic gradient caused by a northeastward (downdip) flow of water coupled with a decrease in updip permeability.

Significant gas is co-produced with oil and a limited free-gas cap exists at the updip edge. The oil has an average API gravity of 39°. Solution gas is the drive mechanism. The field contains 232 wells and the estimated ultimate recovery is 56 million barrels of oil (Devlin and Tomkins, 1957; McNeal, 1961; Sabins, 1963; Tomkins, 1957).

The systematic areal variation of O^{18}/O^{16} values which are on the average less than standard or theoretically determined values for carbonate-cemented rocks over oil fields implies potent and effective fractionation processes have been at work. Fractionation in the direction of O^{18} depletion, however, is not difficult to explain. Given the constraints of the general geologic framework into which most oil fields fall and the experimental, theoretical, and empirical data now available, isotopic fractionation of vertically moving water as a result of shale micropore filtration is a plausible fractionation mechanism (Huber and others, 1956; Longworth, 1960; Devell, 1962; Eyraud and others, 1963; Graf and others, 1965; Hanshaw and Zen, 1965; Hitchon and Friedman, 1969; Coplen, 1970; Coplen and Hanshaw, 1973). Berry and Hanshaw (1960), and Hanshaw and Hill (1969) have suggested that the San Juan basin of New Mexico may exhibit shale-membrane phenomena.

Carbonate cements in outcropping Cretaceous sandstones over the Bisti field display mean O^{18}/O^{16} values indicating significant depletion in O^{18} . The distribution of δC^{13} and δO^{18} values roughly parallels the subsurface facies elements of Sabins (1963) (fig. 7). Relatively low salinity formation waters of 45,000 ppm and an overlying section of interbedded sandstone and shale support the concept of escape of hydrocarbons dissolved in water under an osmotic drive. Not only does salinity have a pronounced effect on hydrocarbon solubility, but the very fact that differences in concentration occur in formation waters on opposite sides of shale membranes indicates differences in chemical potential as a driving force which can move the water through shales in an upward (or downward) direction. Water migrating upward under the influence of chemical potential undergoes isotopic fractionation by shale micropore filtration. Coplen and Hanshaw (1973) experimentally demonstrated with distilled water and NaCl solution forced through compacted clay that the ultra-filtrate is depleted in both D and O^{18} relative to the residual solution. And, although salts are also retained in the residual solution by shales with membrane properties (McKelvey and Milne, 1962; Hanshaw, 1962; Hanshaw and Coplen, 1973), no additional isotopic fractionation due to a salt filtering mechanism was observed by Coplen and Hanshaw. Vertically moving fractionated water mixes with ground water where isotopic exchange with precipitating diagenetic salts result in O^{18} -depleted cements.

Case III: Origin of carbonates with "normal" O^{18}/O^{16} ratios.--Cropping out over the Cement and Velma oil fields of southern Oklahoma are carbonate-cemented sandstones whose isotopic compositions are characteristic of this kind of relatively unrestrained leakage. These types are represented at the apex of the curves in figure 5 and are the interstitial carbonates whose average oxygen isotopic compositions are not anomalous but whose low end-member carbon isotopic contents are peculiarly depleted in C^{13} . These kinds of compositions come about by effusive leakage of hydrocarbons from reservoirs through relatively permeable, poorly compacted, fractured, and faulted roof rocks.

The Cement field is in the southeast Anadarko basin in Caddo and Grady Counties, Oklahoma. The field was discovered in 1917. The Cement structure is a northwest-southeast doubly plunging asymmetrical anticline with two distinct domes (East and West Cement). Oil and gas are produced from shallow Permian sandstones and Pennsylvanian carbonates and clastics from depths ranging from 600 to 2,100 m.

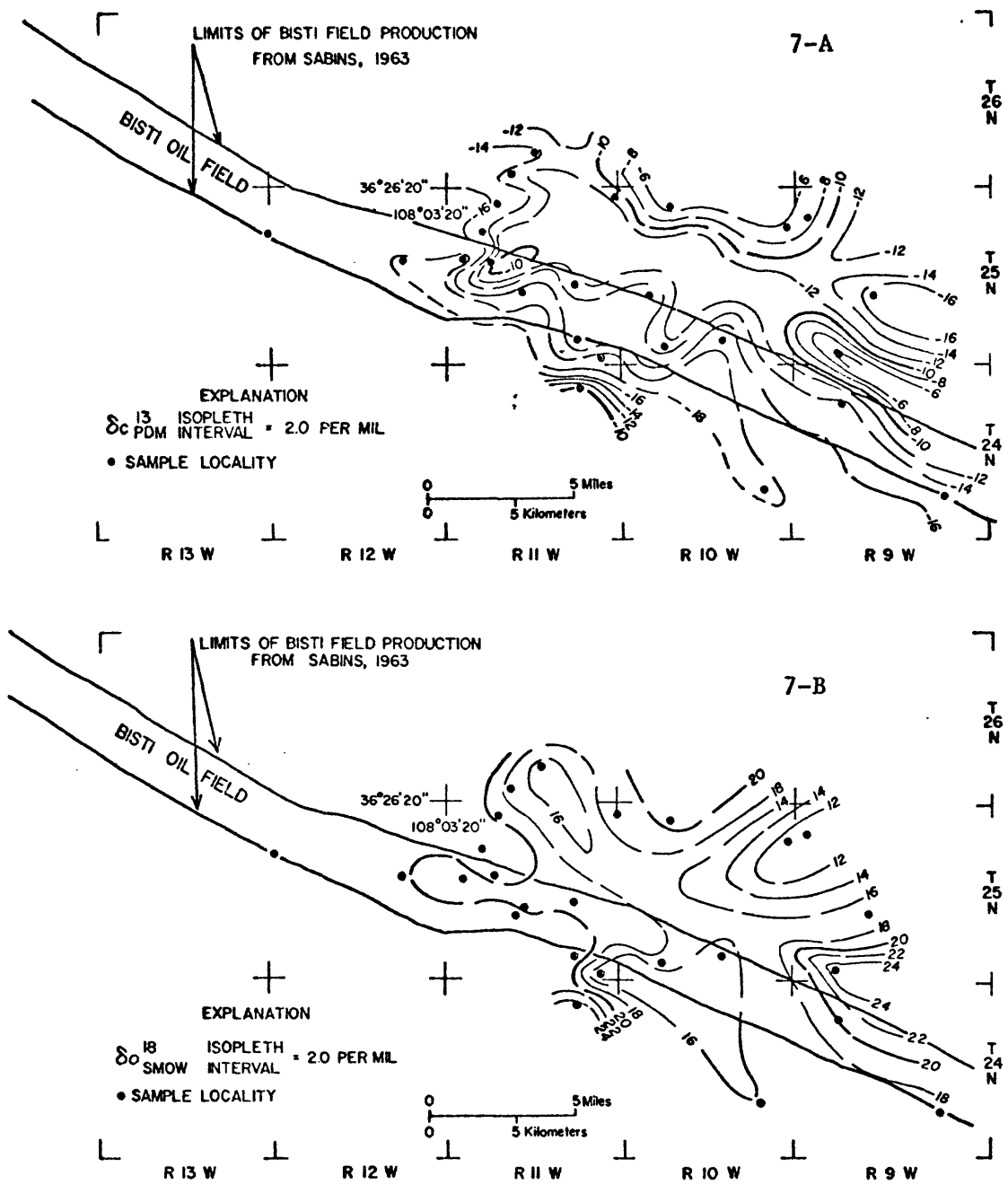


Figure 7.--Sketch maps of the variation of δC^{13} (A) and δO^{18} (B) in carbonate cements from surface sandstones cropping out over the Bisti oil field, New Mexico. Unpublished data from R. L. Noble. Isopleth interval 2/mil.

The steeper northwest flank of the anticline reflects a major reverse fault which trends parallel to the anticline. At the surface, Permian sandstones are unconformably draped over the more intensely folded and faulted pre-Permian section below.

Oils from Cement field have API gravities ranging from 10° to 36°. Approximately 7,500 hectares have been proven productive. Marked surface alterations have been known at Cement for some time; surface mapping led to the field's discovery (Reeves, 1922; Harlton, 1960; Hermann, 1961; Halbouty, 1968; Donovan, 1974).

The Velma oil field is located in Stephens County, Oklahoma. Production is from Paleozoic rocks arched in a northwest-southeast doubly plunging faulted anticline located along the axis of the Anadarko geosyncline. The field was discovered by geologic mapping in 1917 and early production of oil and gas from shallow (120-275 m) Permian sandstones. Deep development began in 1941 when a well was drilled to 2,180 m. Predominantly clastic rocks of Pennsylvanian, Mississippian, and Ordovician age are the important pre-Permian oil and gas reservoirs. Oil is produced by a combination of solution gas drive and gravity drainage. The API gravities range (in degrees) from the high 20's to the low 40's. Low gravity oils are found in the deeper sandstones and in downdip locations. Formation water salinities are highly variable and range from about 20,000 ppm to 90,000 ppm. As of 1955 the Velma field had 1,550 producing wells with about 2,750 productive hectares.

Outcropping Permian rocks (red beds) form a mildly arched blanket unconformably overlying the older, more disturbed section. A steeply inclined thrust fault traverses the central part of the anticline, but does not appear to penetrate the overlying Permian section. A prominent topographic ridge, with as much as 100 m of relief, is the result of differential cementation of sandstones at the surface along the axis of the structure (Borden, 1941; Davis, 1951; Mallory, 1948; Rutledge, 1956; Storm, 1921; Tomilson, 1952).

Evidence for effusion at Cement and Velma is direct: inspissated oil is readily observed in thin sections of surface rocks at both localities (as well as some oil staining observable in the field at Cement) and active oil seeps have been reported at Velma (Gouin, 1956).

Jameson reef and Garza are also interpreted to be mostly representative of this kind of leakage. The Jameson reef field is located in northwest Coke County, Texas. The producing structure is a Pennsylvanian reef on the east side of the Permian (Midland) basin. Production is from approximately 1,970 m deep. The reef is lenticular, approximately 3.6 km long and 1.2 km across at the widest point. Some of the reef highs have as much as 240 m of subsurface relief. The discovery well was drilled in 1946, and by 1954 the field had reached full development. The producing field covers approximately 8,300 hectares.

The reef mass is enclosed by Pennsylvanian black shales. The reef substrate is a relatively thin (114 m) limestone. The reef appears to have initially grown as two separate reefs on topographic highs, which subsequently coalesced. Surface mapping and geophysical methods led to the discovery (Ralston and Rettger, 1956; Halbouty, 1968).

The Garza oil field is located in southwest-central Garza County, Texas, along the northwest edge of the Permian basin. Earlier discoveries at nearby Justiceburg prompted drilling of the Garza discovery well on a local topographic high in 1935. Development proceeded slowly until 1945 when a pipeline outlet was provided for the field.

The structure is an anticlinal fold with several minor domes and saddles with a maximum relief of 40 m. The productive zone is an anhydrite-bearing dolomite of Permian age. Production from this dolomite is from many irregular porous lenses. The producing zone is overlain by red sandstones, shales, and interbedded anhydrite and salt which in turn are overlain by Triassic "red beds."

The reservoir contains oil and solution gas, and produces by solution drive. The average API gravity of the oil is 36° (Gardner, 1949; Bailey, 1953).

Important factors in the effusive escape mechanism appear to be the thickness and nature of the overburden and the height of the oil column. Both Cement and Velma fields consist of relatively thick multiple oil reservoirs deformed into high amplitude faulted anticlines unconformably overlain by poorly compacted fine- to coarse-grained rocks. Their formation waters have low TDS, and especially at Cement where the water salinity decreases markedly inversely with depth. This has resulted in vertical transfer of fluids from the deeper to shallower parts of the subunconformity structure by osmotic drive as suggested previously (Donovan, 1974). The thin, poorly compacted overlying rocks were unable to restrain effusive escape of hydrocarbons accumulated in reservoirs at and near the major unconformity. Fresh waters from thermally dehydrated clays in the deeper part of the basin may have played a role in diluting the formation waters at Cement (Donovan, 1974). Once near the surface, C¹³-impoverished oxidized carbon was incorporated into pore-filling cements. Gas, released from seeping liquid hydrocarbons by depressurization where it locally induced some ground-water evaporation, can account for some high δO^{18} values at both fields.

At least two additional diagenetic processes resulting in special isotopic signatures have been interpreted to occur in rocks over oil and gas accumulations. These are the conversion of calcium sulfate to calcium carbonate by bacteria utilizing escaping hydrocarbons (Thode and others, 1953; Feely and Kulp, 1957; Davis and Kirkland, 1970; Donovan, 1974; Kirkland and Evans, 1976) and the precipitation of diagenetic pore-filling carbonates by salting out of solutes at sand-shale interfaces owing to double layer phenomena (Donovan, 1974). Both products could be useful to explorationists.

Case IV: Origin of carbonates with O^{18}/O^{16} values resulting from combined process.--Data points which fall on or near the trend line of figure 6, but between end-members, represent diagenetic carbonates whose isotopic compositions are influenced by the combined effects of the end-member processes (effusion-evaporation; effusion-micropore filtration). The relative position along the line indicates the relative importance of the end-member processes. Doyle, Fox-Graham, and Garza fields are examples.

The Doyle structure is a gentle dome about 20 km north of the major Velma field in the Anadarko basin in Carter County. Approximately 1,500 m of Permian rocks unconformably overlie the main Pennsylvanian clastic reservoirs. As with

most of the fields in this region, earliest production was from shallow Permian sandstones. In 1955 there were 186 producing wells at Doyle. A U.S. Bureau of Mines Hempel Analysis lists Doyle crude gravity from 1,787 m at 41° API. Little has been published about this field.

The gentle topography at Doyle is a surface expression of the subsurface structure. Doyle was discovered by geologic mapping in the early 1900's (Reed, 1910).

Fox-Graham was initially developed as two separate fields in Carter County, Oklahoma, a few kilometers southeast of the larger Velma structure. Discovery wells were dilled in 1915 (Fox) and 1917 (Graham). Later development extended Graham production northward, and since the mid-twenties Fox and Graham have been considered one field. The Fox structure is an irregular domal anticline of low relief separated from the elongated northwest-southeast trending Graham anticline by a deep-seated fault.

About 610 m of Permian rocks overlie the main producing zone but the earliest production was from shallow (75 m) Permian sandstones. The gently folded Permian rocks unconformably overlie a highly faulted, folded, and truncated Pennsylvanian section. Subsequent development has led to significant deeper production from Pennsylvanian sandstones as well as from pre-Pennsylvanian carbonate rocks. API gravities of the oils produced increase with depth, ranging from 19° API at 75 m to more than 40° at 1,030 m. As of 1955 there were 742 producing wells with about 800 productive hectares.

The area was explored by careful surface mapping; surface seeps were also known in the Graham area (George and Bunn, 1924; Tomilson, 1952; Tomilson and Storm, 1924).

Kettleman Hills North Dome provides another intriguing model for study. The Kettleman Hills oil field is on the west side of the San Joaquin Valley in Fresno, Kings, and Kern Counties, California. Kettleman Hills are part of the foothills of the California Coast ranges. The three domes that make up the hills extend for approximately 50 km in a northwest-southeast direction and have a width of 8-10 km. North Dome is the largest of three structures aligned en echelon (North, Middle, and South Domes). The structures are asymmetrical; the southeast limb is steepest. At North Dome, approximately 5,500 hectares have been proved productive; surface geology led to the discovery in 1928.

Miocene sandstone is the major reservoir and there are several productive zones (1,540-2,410 m). Oil is also produced from Eocene sandstone. The Miocene reservoir had a free gas cap and within the area of this cap, oil has an API gravity of 60°. Outside the gas cap area, the oil produced as an API gravity of 33° to 37°, but gravities as low as 28° are reported (Galloway, 1943; Halbouty, 1968; McAllister, 1941; Woodring and others, 1940). Formation waters decrease in salinity with decreasing depth (fig. 8).

Figures 8 and 9 display the variation with depth at North Dome of TDS and the D/H values of formation waters. The relationships between TDS vs. depth and the isotopic values vs. depth is obvious and important. Figure 10 shows the correspondence between δO^{18} and δD of formation waters at Kettleman Hills. Clayton and others (1966) have demonstrated the strong positive correlation

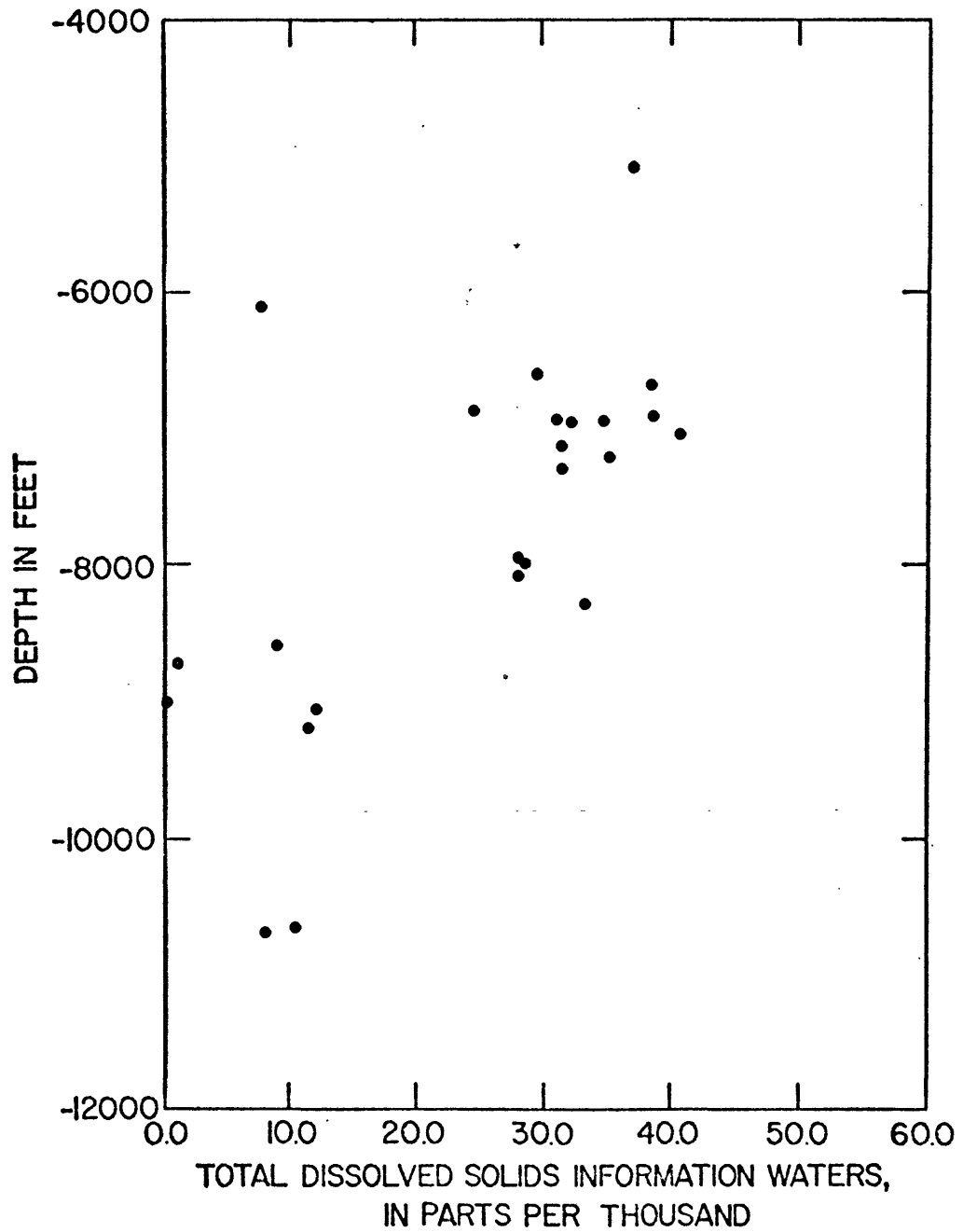


Figure 8.--Variation with depth of total dissolved solids in formation waters, Kettleman Hills, North Dome, California. Data from Kharakra and others (1973).

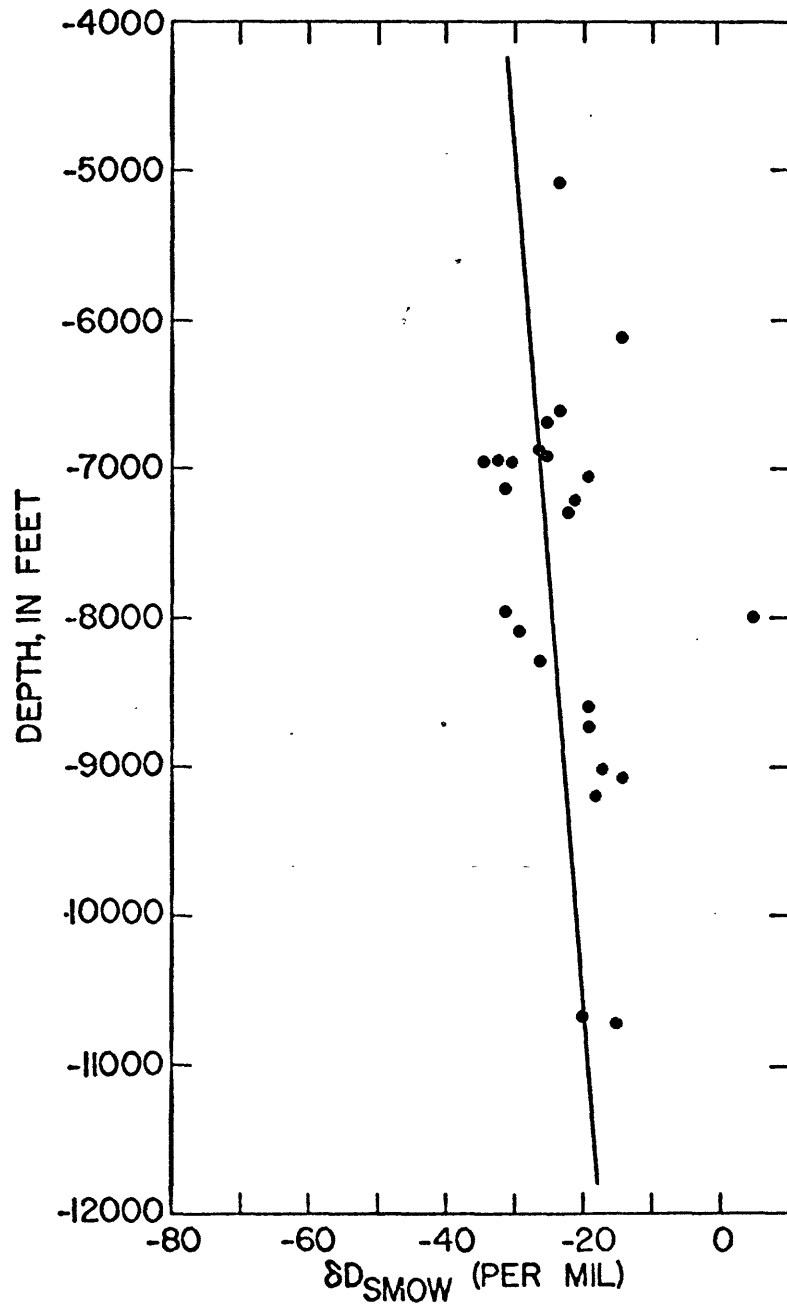


Figure 9.--Variation with depth of δD of formation waters, Kettleman Hills, North Dome, California. Data from Kharaka and others (1973).

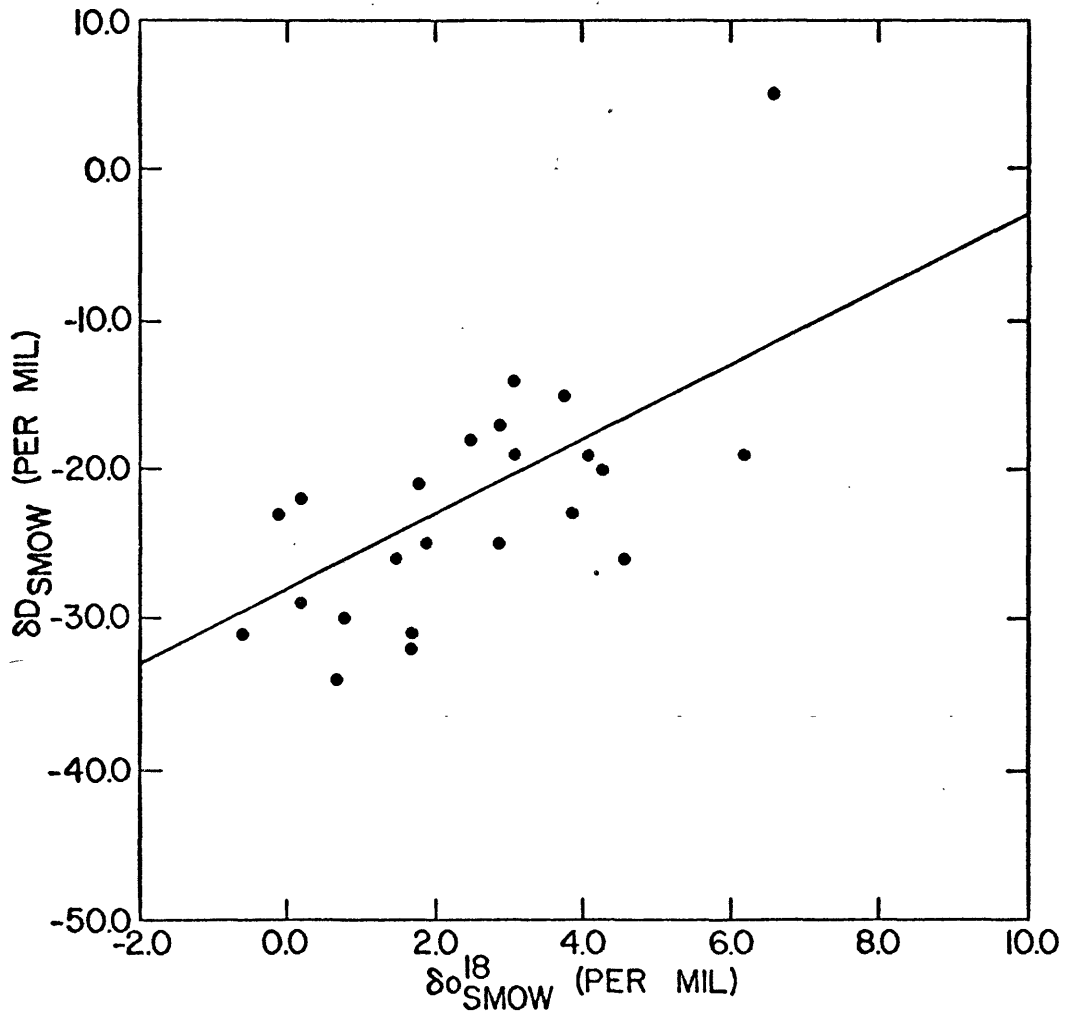


Figure 10.--Relation between δO^{18} and δD values for formation waters, Kettleman Hills, North Dome, California. Data from Kharaka and others (1973).

between δO^{18} of water and salinity; an inverse relationship is indicated by the Kettleman Hills data. The Clayton and others pioneer work also showed that the D content of formation waters is not greatly altered by exchange processes. The Kettleman Hills fluid data strongly suggest that shale micropore filtration operates there which causes a regular depletion in D and O^{18} from formation waters with decreasing depth. This process is sufficiently potent and rapid to override oxygen exchange effects between water, rocks, and dissolved solids.

The trend of decreasing salinity with increasing depth has special significance for it implies osmosis may be at work. Transfer of water from the dilute to the concentrated side of a shale membrane is also effective in transferring dissolved hydrocarbons, especially the non-polar n-alkanes. For even though the polar hydrocarbons are more soluble in water than are non-polar ones, their polarity inhibits their effective passage in solution through the shale membranes because they are filtered at the double layer along with the charged species. This accounts in part for the increased paraffinicity of crudes with decreasing depth commonly observed in fields where salinity decreases with increasing depth (fig. 11; Donovan, 1974, figs. 13 and 14).

In addition to shale micropore filtration, another driving mechanism is suggested by the southwest-northeast cross section through the Kettleman Hills region (fig. 12). The deeper Miocene reservoirs of North Dome crop out several miles to the southwest at Reef Ridge in the Kreyenhagen Hills where they are relatively steeply dipping and ideally positioned for meteoric-water recharge. Where water, under hydrodynamic pressure from recharge areas in the Kreyenhagen Hills, flows through the intervening Kettleman Plains syncline into the North Dome anticline, a vertical component of the flow vector may result. This would add a hydrodynamic driving force to the chemical driving force.

Study of the isotopic data from Kettleman Hills North Dome rocks suggests a history of two opposing fractionation processes. The mean δO^{18} value of 25.2/mil of calcite cements is somewhat less than the theoretical value of 27.7/mil in keeping with the evidence that vertically moving waters were fractionated. Some samples taken over the anticline are O^{18} -enriched and are also depleted in C^{13} . A pronounced gravity segregation of hydrocarbons has resulted in free gas and 60° API gravity oil with gas/oil ratios as high as 80,000 ft³/barrel being restricted to the apical region of North Dome (Galloway, 1943). Thus significant amounts of gas probably have escaped the reservoirs with other fluids, and gas-induced evaporation of ground water has resulted in localized O^{18} enrichment. The isotopic data for fossil shells, from outcropping Pliocene and Pleistocene sandstones along the North Dome anticline indicates that those materials have compositions reflecting the environment in which they grew (Stanton and Dodd, 1970; Dodd and Stanton, 1975) and that they have not undergone significant isotopic exchange during diagenesis (table 2). Hence, the differences between the composition of the fossils and the pore-filling carbonates described here permits a fortuitous comparison between depositional and late diagenetic environments.

A hydrodynamic driving mechanism is also postulated for the Gunbarrel Hill region of Colorado on the east flank of the Denver basin. Here, rocks stratigraphically equivalent to local petroleum reservoirs, crop out along the Front Range of the Rocky Mountains.

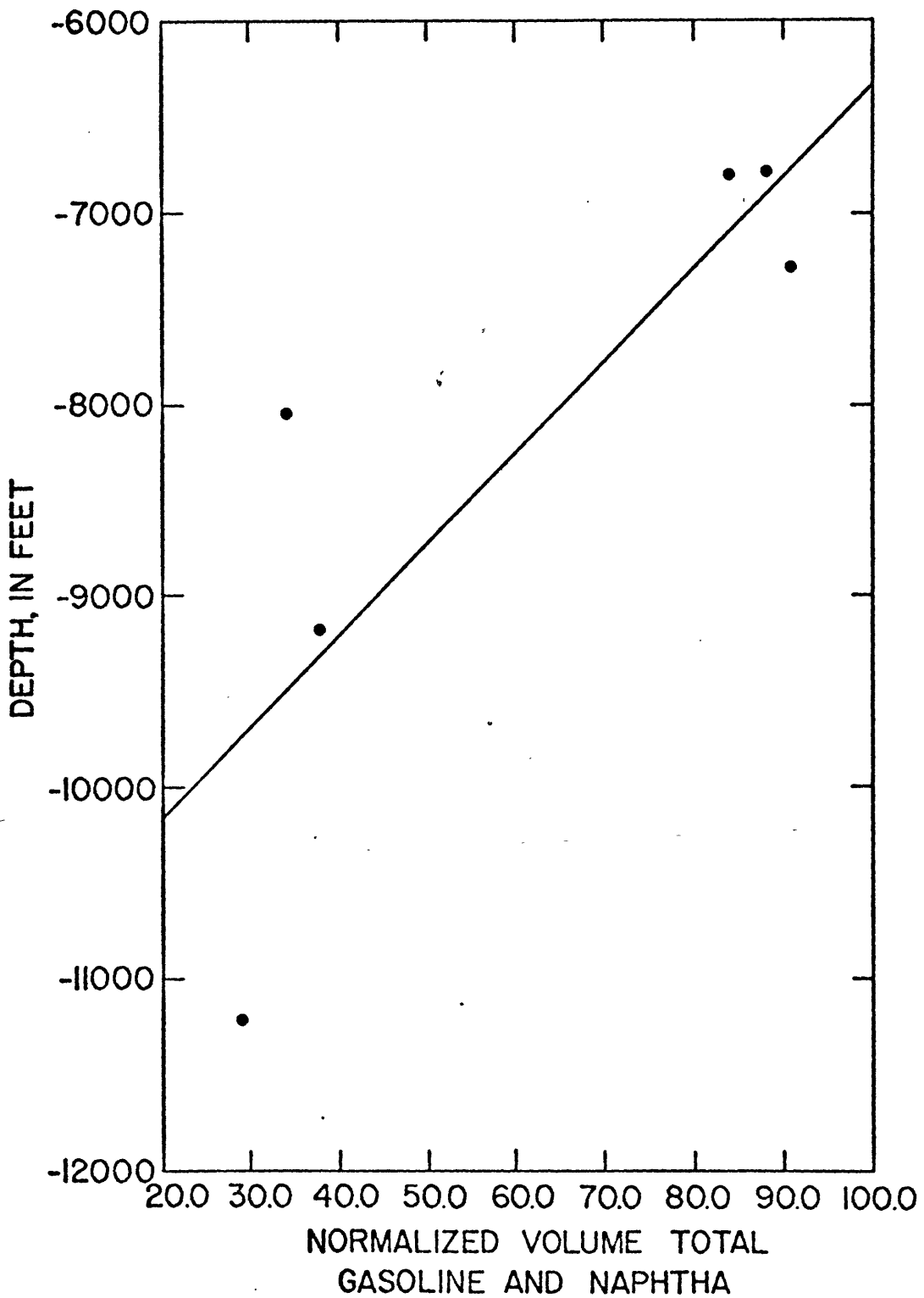


Figure 11.--Variation with depth of the normalized volume of Total Gasoline and Naphtha (TG+N) in crude oils, Kettleman Hills, North Dome, California. Data from U.S. Bureau of Mines.

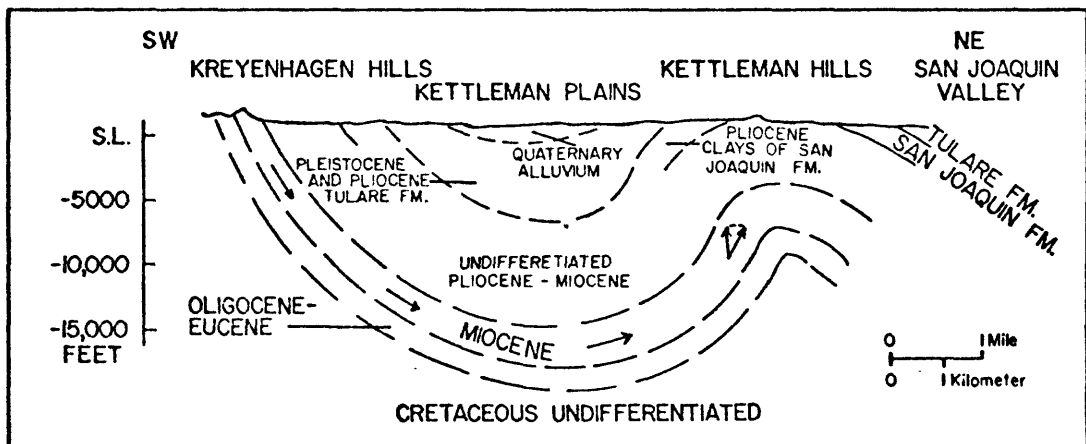


Figure 12.--Northeast-southwest cross section through Kettleman Hills, North Dome. Modified from Galloway (1943). Hypothetical flow vectors added with vertical component resolved in core of anticline.

The Gunbarrel Hill anomaly is in Boulder and Weld Counties, Colorado, on the west flank of the Denver basin. The Denver basin has long been a prolific oil and gas province. Geochemical prospecting has pinpointed several areas of color change and mineralization in the Cretaceous surface rocks, suggesting that leakage from a hydrocarbon reservoir may have taken place. Neighboring fields in the area include the Boulder oil field, the Wattenburg gas field, and the Spindle oil field. The Gunbarrel anomaly may overlie an extension of the Spindle field, a stratigraphic accumulation located a few kilometers to the east. About 20 km² are considered prospective (Donovan, Noble, and others, 1975; Roberts and others, 1976).

Gunbarrel Hill is formed by gently eastward dipping carbonate-cemented rocks. The outcropping Cretaceous sandstones are partially obscured by remnants of Pleistocene alluvial terranes. Oil and gas in nearby fields is produced from Upper and Lower Cretaceous rocks.

Ground-water recharge in this area tends to flush most reservoirs. Where oil saturations are high and where the driving force is small, the force is not sufficient to overcome relative permeability differences between oil and water. We speculate that a vertical vector component in the hydrodynamic drive of the moving dilute waters captures minute amounts of hydrocarbons by dissolution at the edge water interface and remobilizes them; bypass flow occurs around the edges of the reservoir and when the micropore filtered waters interact with precipitating carbonates at the surface, halo-shaped anomalies result which ring the vertical projection of the subsurface accumulation. In reality, such halos or aureoles are more commonly incomplete or crescent-shaped, with maximum development along the edge of the accumulation opposing the direction of subsurface flow.

Chemical Data

The weathering of iron-bearing minerals releases ferrous iron. Normally this iron is oxidized to ferric iron by oxygen dissolved in soil waters whereupon it commonly hydrolyzes and precipitates in a variety of ferric oxides. These oxides are stable in the oxidizing zone where they color sediments and rocks vivid yellows through oranges to pinks and reds. In reducing environments, however, the relatively soluble ferrous iron in the absence of oxygen remains in solution where it is available for transport. Under these conditions, continued loss of iron through dissolution and removal in water results in rocks which appear markedly "bleached" or tinted. Iron oxides from previous weathering cycles are unstable in reducing environments and, undergoing reduction, their iron is subsequently also dissolved. Hematite may be reduced to magnetite or maghemite. Additionally, in the presence of H₂S, pyrite may be precipitated. Reducing conditions in rocks over oil deposits can be caused by seeping hydrocarbons and associated compounds such as hydrogen sulfide. A qualitative measure of the intensity of reduction that has taken place in the rocks is furnished by systematic color change from dark red hues in peripherally unaltered strata to yellows and whites at central localities. This is true only for non-cemented or weakly cemented (permeable) rocks.

Carbonate cements which strongly impregnate rocks result from relatively rapid and intensive processes of precipitation and tend to be collectors of both iron and manganese in ionic substitution; effective chemical separation of

elements such as iron and manganese owing to slight differences in redox potential and solubility is precluded.

Manganese's chemical nature is similar to iron's and it is mobilized in a similar fashion. Over some oil fields carbonate cements are enriched in both manganese and iron whereas over others, the cements display decreased iron content with increased manganese (figs. 13 and 14). Slow increase in pH result in dissolved iron compounds reaching solubility limits before manganese compounds; rapid changes result in co-precipitation. Manganese precipitates as carbonate (or as we suggest here, substituted for other cations in other carbonates if only small amounts are present) as the ground water slowly increases pH or if the environment is or becomes reducing. Thus separation from iron is due to differences in solubility and oxidation potential (Krauskopf, 1957). We have implied in the discussion of O^{18}/O^{16} fractionations that large fractionations may indicate rapid processes whereas small fractionations may come about slowly. A plot of Log Mn/Fe vs. δO^{18} for the weakly cemented rocks at Gunbarrel Hill suggests that the separation processes may have operated there, albeit, inefficiently (fig. 14). However, we caution against too much reliance upon such plots as figures 13 and 14, as the mapped distribution pattern of such variations is equally or more important.

Laboratory measurements on carbonate cemented rocks before and after acid digestion indicate that the great preponderance (>90%) of manganese is incorporated in the carbonate lattice. Figure 15 suggests that manganese is concentrated in cements resulting from both the micropore filtration and gas-induced evaporation end-member processes because manganese appears to increase as the O^{18}/O^{16} ratio increases or decreases from a δO^{18} minimum of about 20-25 per mil. A total of 207 data points from oil field areas tabulated in tables 2 and 3 as well as a few spot samples from two additional Oklahoma fields not tabulated were used (Carter-Knox and Cruce). Figure 16 is a map of the carbonate-held manganese within the carbonate-cemented areas at Cement field. Manganese concentrations range through an order of magnitude in a systematically mappable way. Background values in non-carbonate cemented rocks average only a few hundred ppm. Figure 17 shows the manganese concentrations in soils overlying the field; the values tend to be lower and the isopleth pattern is broader and more attenuated in soils than in bedrock, but the presence of high manganese values at crestal localities persists. Similar relationships may hold for other elements but they have not been worked out by us at this writing.

SUMMARY

This paper describes some mechanisms whereby hydrocarbons may escape entrapment, migrate to the surface, react chemically with dissolved constituents in ground waters, and leave residual evidence in surface rocks and soils. The mechanisms include escape of hydrocarbons by effusion, solution, and diffusion. Meteoric water and its cycle play an important role in the overall processes and especially in mobilizing the more soluble light ends of crude oil. Gas-induced evaporation of ground water and micropore filtration of vertically moving formation water can cause isotopic fractionations, evidence of which is retained in pore-filling carbonate cements. Iron and manganese, mobilized in reducing environments caused by the presence of seeping hydrocarbons or their associated compounds, appear to be systematically concentrated in carbonate cements in rough proportion to the intensity of microseepage as interpreted

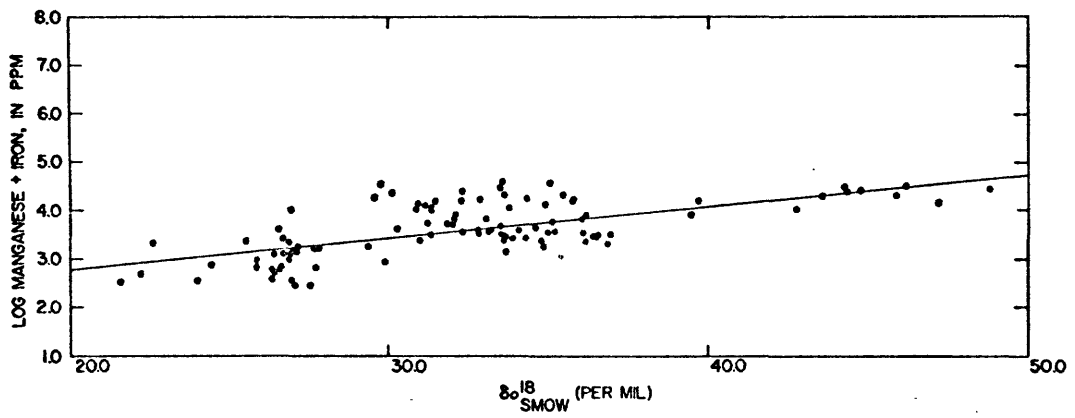


Figure 13.--Relation between iron and manganese and δ^{18} for carbonate cements in sandstones cropping out over Fox-Graham, Doyle, and Davenport oil fields, Oklahoma.

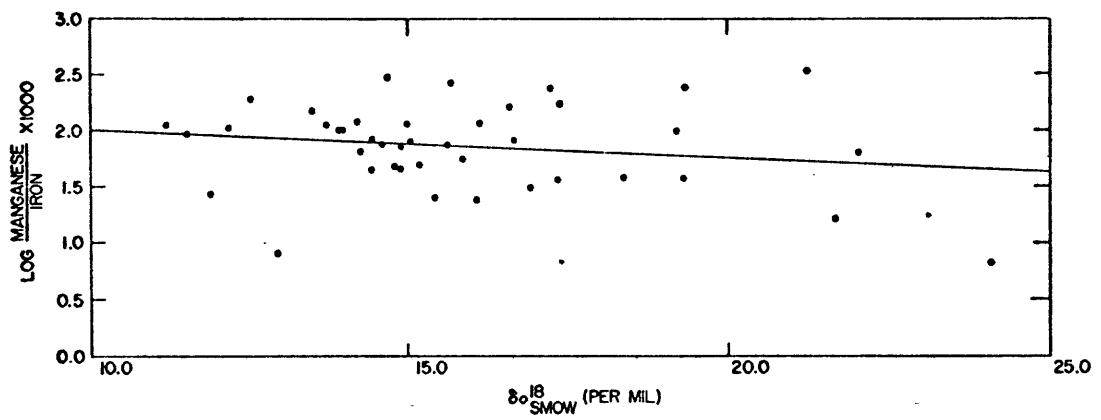


Figure 14.--Relation between total Mn/Fe and δ^{18} for calcite-cemented sandstones, Gunbarrel Hill, Colorado. Data from Donovan, Noble, and others (1975).

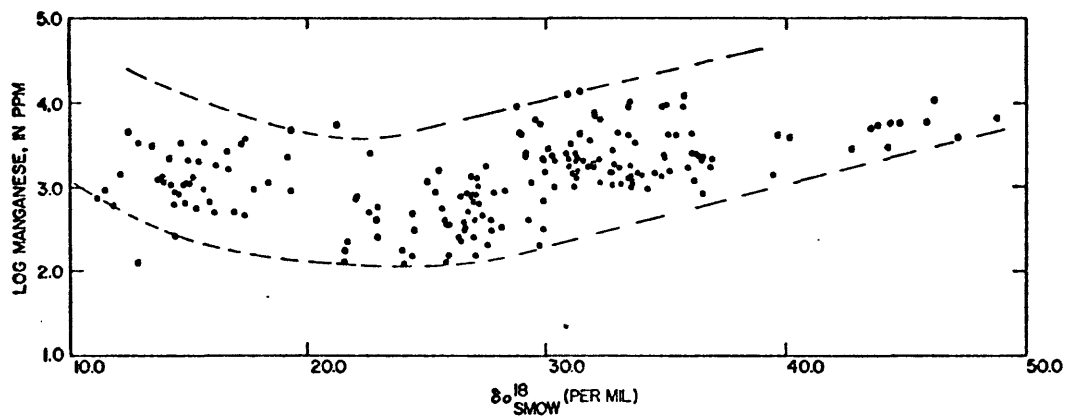


Figure 15.--Relation between manganese and δ^{18} for 207 outcropping carbonate cemented sandstones from various oil field areas. Ninety-nine percent of all points lie within dashed lines.

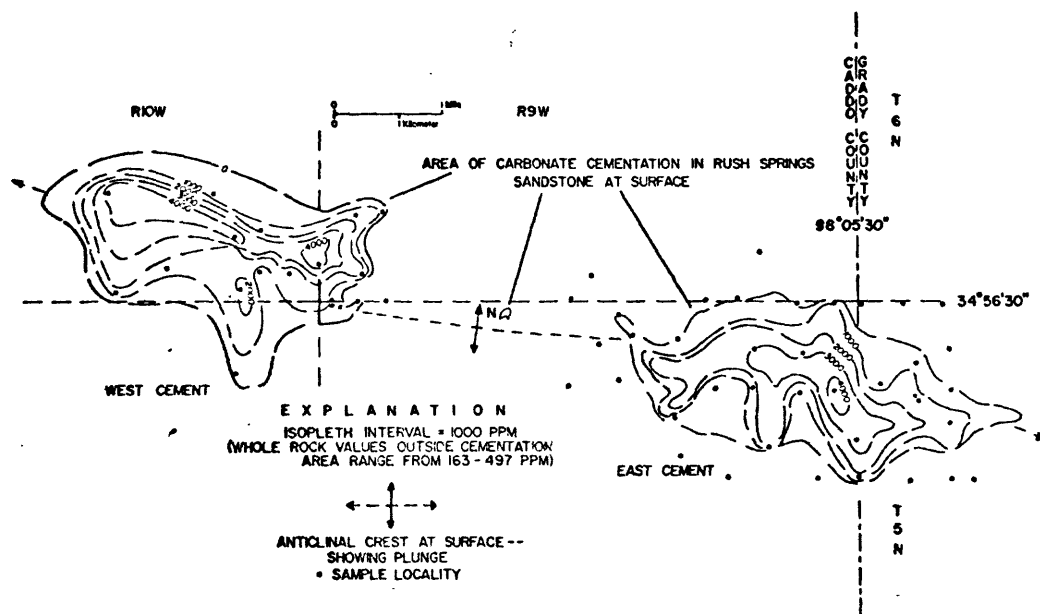


Figure 16.--Variation of manganese held in carbonate cements of outcropping sandstones, Cement oil field, Oklahoma. Isopleth interval 1,000 ppm.

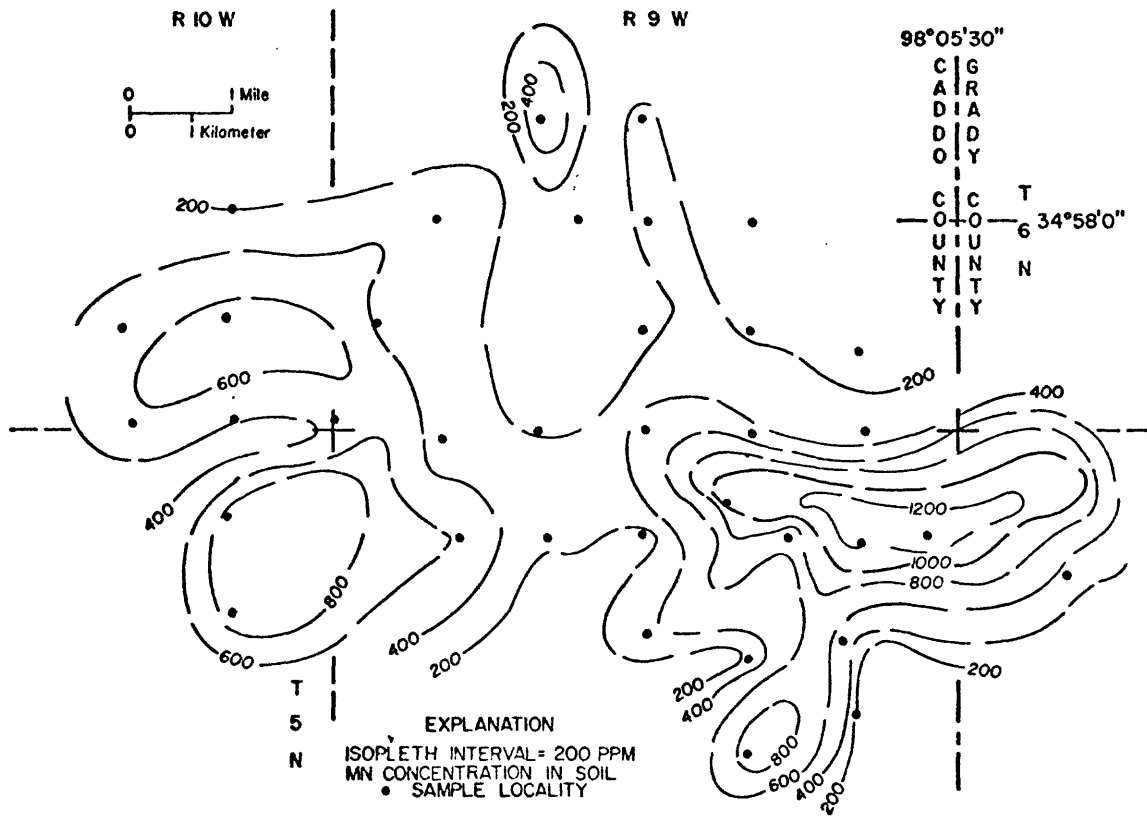


Figure 17.--Variation of manganese concentration in soils, Cement oil field, Oklahoma. Isopleth interval 200 ppm.

Table 3.--Summary of iron and manganese data for surface materials at various Oklahoma oil fields*

	Number of samples		Soil	Iron range in ppm	Manganese range in ppm
	Carbonate cements	Non-cemented whole rock			
Cement	67	11		3,600-10,500** 3,632-14,000	83-4,568
Davenport	22		19	6,540-28,480	206-1,336
Doyle	33			175-18,750	1,370-10,430
Fox-Graham	57			75-27,000	300-2,800
Velma	12 34			150-29,000	150-13,500
					125-7,000

* Cement and Davenport analyses by X-ray fluorescence; others by atomic absorption. See Appendix II.

** Corrected from Donovan, 1974, table 1.

from oxygen isotopic fractionation of ground waters. We stress here, also, that the full impact of microbial processes cannot be evaluated from the field data alone.

The model is schematic; obviously the real mechanisms are infinitely more complex and interactive, but the concepts proposed can serve as a geochemical basis for prospecting for oil and gas deposits. Certain chemical properties of surface rocks are strongly influenced by petroleum microseepage and can be investigated by both ground geophysical and remote measurement. These include such things as iron content, the iron's oxidation state, and carbonate mineralization. For example, detailed gravimetric surveys could isolate near surface variations in mass arising from localized late diagenetic mineralization (Elkins, 1951, p. 48-49; Ralston and Rettger, 1956; McCulloh, 1969). In addition, such mineralization conceivably could result in telluric current anomalies (Yungul and others, 1973). The spectral reflectivity of rocks is greatly influenced by the amount of iron present and its oxidation state (Hunt and Salisbury, 1970; Hunt and others, 1971; Goetz, 1975) which in turn suggest orbital and airborne multispectral imaging and image enhancement techniques. Manganese contributes to the natural luminescence of calcites in a systematic way, enabling airborne fluorometric measurement and anomalous distributions of other elements in soils are amenable to rapid airborne sampling (Donovan, Barringer, and others, 1975). Preliminary work by us suggests that the near surface reduction of hematite to magnetite may be sufficient over some oil fields to enable detection by aeromagnetic methods. Remote sensing techniques are especially attractive because they are cost effective (Craib, 1972); Maxim and Cullen, 1977).

ISOTOPIC AND CHEMICAL ANALYSES

Isotopic Data

Calcareous samples were collected from outcrops over oil fields. In general, the limited distribution of outcrops governs sampling locations and density. In the laboratory, samples were split, crushed to powder, then X-rayed to determine the proportions of calcite versus dolomite in the porefilling cements or replacement materials. Powdered samples were placed in reaction flasks with 100 percent H_3PO_4 at $25^\circ C$ for at least four hours and isotopic measurements were made on the CO_2 evolved with a Nier type of mass-spectrometer. The isotopic analyses are reported here in the δ terminology:

$$\delta = \frac{R_{(sample)} - R_{(standard)}}{R_{(standard)}} \times 1,000,$$

where $R = \text{Ratio} = C^{13}/C^{12}$ or O^{18}/O^{16} . Our standards are the Chicago PDB standard for carbon and Standard Mean Ocean Water (SMOW) for oxygen. The analytical procedures are those of McCrea (1950), Craig (1957), and Epstein, Graf, and Degens (1964). The δ values are reported to $-0.1/\text{mil}$ (2δ), and the dolomite analyses are corrected for the acid fractionation factor (Sharma and Clayton, 1965).

Isotopic ranges and means are tabulated in table 2 and the data are also displayed in a series of plots (figs. 5, 6, 9, and 10) and maps (fig. 7).

Allen and Matthews (1977), concerned with small ranges in isotopic values, have questioned the "resolving power" of plotting "typical" limestone ranges (fig. 5). However, we suggest that Murata and others (1969) boundaries of typical limestone ranges, encompassing many points from over the world, emphasize the abnormal nature of our materials.

Chemical Data

Iron and manganese contents of samples were measured either by X-ray fluorescence (XRF) in the laboratory using the analytical technique described by Adler (1966) with a Picker X-ray unit or by atomic absorption spectrophotometry (AA) in a mobile field laboratory using analytical techniques described by the Perkin-Elmer Corporation (1973). The latter unit used is Perkin-Elmer Model 360. The X-ray analyses are considered accurate to ± 10 percent and the atomic absorption data are considered accurate to ± 1.0 percent. Whole rock analyses on finely powdered samples were made with XRF techniques, and AA techniques were employed on diluted residual solutions following complete HCl acid digestion of weighed and powdered carbonate-cemented samples. All analytical data are reported in parts per million (ppm).

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