

Correlation of Reservoired Gases Using the Carbon Isotopic Compositions of Wet Gas Components¹

Alan T. James²

ABSTRACT

The carbon isotopic compositions of the wet gas components, particularly propane, isobutane, and normal butane, have been found to be particularly valuable for correlating one reservoired gas with another. The usefulness of these components for correlation results from their carbon isotopic compositions reflecting both the nature of their source and their maturity. This source control is strongest for gases derived from the more highly structured types of kerogen (i.e., woody-coaly; type III), although the wet gas components' carbon isotopic compositions of most gases are at least partly controlled by their source for levels of maturity below the point at which thermal destruction of the wet components occurs. As a result, the wet gas components are found to provide more positive correlations than is methane alone.

Three exploration examples illustrate the use of the carbon isotopic compositions of the wet gas components for correlation: the Leduc reef trend of Alberta, Canada; the Sleipner area in the North Sea; and the Lena field, offshore Louisiana, United States. The three examples also illustrate the need to integrate geochemical interpretations with regional geology to obtain a good understanding of the hydrocarbon source.

INTRODUCTION

In an exploration effort, hydrocarbon plays can be better defined by knowing whether separate hydrocarbon occurrences in different parts of a basin, or in different parts of the geologic section, are related. In addition, an improved understanding of the distribution of oil and gas throughout

the basin can be obtained by knowing the source-to-reservoir and hydrocarbon-maturity relationships of widely distributed hydrocarbon occurrences.

In this paper, the use of the carbon isotopic compositions of wet gas components (i.e., propane, isobutane, and normal butane) for correlating both associated and nonassociated gases is demonstrated using three examples from different exploration areas. These examples illustrate the mobility of hydrocarbons in the subsurface and show the need to integrate geology and geochemistry to obtain an improved understanding of source-to-reservoir relationships for many hydrocarbon accumulations. These examples also show the application of the carbon isotopic compositions of wet gas components for determining a gas's maturity (cf. James, 1983) and for recognizing gases that have migrated from other parts of the section.

PREVIOUS GAS CORRELATION APPROACHES

Previous regional gas correlation studies in the literature have relied primarily on the use of carbon and hydrogen isotopic compositions of methane to correlate one reservoired gas to another or to its source. Selected examples of this approach include the work of Galimov et al. (1973) and Prasolov and Lobkov (1977) in the Karakum basin; Boigk et al. (1971) and Schoell (1977, 1983b) in the Molasse basin; Rice (1983) in the San Juan basin; Matavelli et al. (1983) and Colombo et al. (1966) in the Po basin; and Stahl and Carey (1975) in the Delaware basin. (For a further discussion of the use of methane in correlation, refer also to Schoell, 1983a.)

Although useful, interpretation of the detailed source and maturity relationships of an individual gas occurrence relative to another using methane alone is often tenuous. Uncertainties in such correlations result from the similarity of multiple sources found within the section, mixing of hydrocarbons from unrelated sources, secondary microbial and thermal alteration of mature hydrocarbons, and from structural complexities that may result in unrecognized migration pathways. Publications by Fuex (1977), James (1983), Sundberg and Bennett (1983), Burns et al. (1984), Galimov (1988), and Chung et al. (1988) suggested that measurement of the wet gas components' carbon isotopic compositions can help overcome many of these gas correlation difficulties.

BASIS AND CONCEPTS FOR CORRELATION

While evaluating the maturity approach described by James (1983) in a wide variety of exploration areas, it has

©Copyright 1990. The American Association of Petroleum Geologists. All rights reserved.

¹Manuscript received, March 20, 1989; revised manuscript received, March 9, 1990; final acceptance, June 25, 1990.

²Exxon Production Research Company, P. O. Box 2189, Houston, Texas 77001.

The writer thanks Exxon Production Research Company, Esso Resources Canada, Exxon Company, U.S.A., Esso Norge a.s., Statoil, and Norsk Hydro for permission to publish this paper. I am particularly pleased to acknowledge J. Allan, D. Bergslien, B. J. Burns, S. Creaney, S. Horvik, C. B. Koons, C. W. D. Milner, R. E. Metter, G. G. L. Rinaldi, and W. A. Young for their helpful suggestions during the course of this work. The writer is also indebted to the many Exxon and Esso geologists, scouts, and engineers for their aid in obtaining the samples and reviewing the interpretations presented here. The carbon isotopic analyses were performed by P. A. Gregory and N. T. Phan, and the compositional analyses by J. L. Briggs and W. F. Muzacz at Exxon Production Research Company.

been recognized by the author that the carbon isotopic compositions of the wet gas components reflect both the level of maturity at which a gas was generated as well as the nature of the gas's source. That is, the carbon isotopic compositions of the wet gas components appear to be dependent on (1) the level of maturity at which the gas was generated, (2) the carbon isotopic composition of the organic material from which the gas was derived, and (3) the extent to which the kerogen structure influences the gaseous products. As a result, the carbon isotopic compositions of wet gas components have been found to be useful for correlating one reservoir gas with another, in addition to being useful for estimating a gas's maturity. [In this paper, the maturity of a reservoir gas refers to the maturity of the source from which the bulk of the gas came, realizing that a reservoir gas represents an integration of products derived from a source during progressive burial over a range of maturities, both on and off structure (refer to James, 1983).]

The relative amount of source control vs. maturity control on the carbon isotopic compositions of the wet gas components appears to depend on the source type. Through the analysis of several hundred associated and nonassociated gases derived from a variety of source types, it has been the author's observation that the carbon isotopic compositions of the C_1 to C_4 gas components derived from the more highly structured types of kerogen (i.e., woody-coaly; type III) commonly appear to exhibit a greater degree of source control (and, hence, less maturity control) than compounds derived from the more lipid-rich, oil-prone sources (type II). For both source types, however, the carbon isotopic compositions of the wet gas components are at least partly inherited from their source for maturity levels below the point at which thermal destruction of wet gas components occurs [about level of organic matter (LOM) = 12 or $R_o = 1.5\%$] (see James, 1983; also see Hood et al., 1975, for a discussion about LOM). This source control is exhibited by the carbon isotopic compositions of propane, isobutane, and normal butane exhibiting smaller carbon isotopic separations than would be expected for gases derived from lipid-rich sources at the same level of maturity. Minor reversals in the normal progression of the carbon isotopic compositions of the higher molecular weight wet gas components are also commonly exhibited in gases derived from woody-coaly types of organic matter as a result of this source control, i.e., normal butane may be isotopically lighter than propane, with propane being lighter than isobutane. (In the usual progression, propane is the lightest, followed by isobutane, then normal butane, although the relative position of isobutane may vary depending on the nature of the source and on the maturity. This distribution, and both the source and maturity control, have also been described by James, 1983.)

The greater degree of source control exhibited by gases derived from woody-coaly sources is probably the reason for the observations made by James (1983) and by Burns et al. (1984), which suggest that gases derived from such sources often have carbon isotopic compositions that give source maturities about 1 to 2 LOM units too high when using James's (1983) maturity approach. In these instances, the carbon isotopic composition of normal butane usually has too strong of a source influence to be used in maturity estimates. In such situations, the carbon isotopic separation

of ethane and propane gives more reliable maturity estimates, even though the methane values may plot above their expected positions. This same source control is probably also one of the principal reasons for the different maturity relationships observed by Stahl (1977) and by others for the carbon isotopic compositions of methane derived from sapropelic and from humic sources. This source control is also one of the main reasons for the differences in the carbon isotopic compositions of the "natural gas plots" shown by Chung et al. (1988) for gases derived from unrelated sources. Galimov (1988) also suggested that a source control, as reflected by differences in the abundances of aromatic and lipid-rich compounds contained in humic and sapropelic sources, may result in differences in the carbon isotopic compositions of gases as well as differences in the mechanism and timing of gas generation.

As a result of the source control exhibited by the carbon isotopic compositions of the wet gas components, propane, isobutane, and normal butane have been found to be particularly useful for correlation purposes. With increasing molecular weight, the carbon isotopic compositions of these components appear to approach the carbon isotopic composition of their source, and in fact, the carbon isotopic composition of isobutane generally appears to be largely inherited from its source. Propane does exhibit a considerable amount of maturity dependence, especially when it has come from a lipid-rich, oil-prone source, but when its carbon isotopic composition is considered together with the carbon isotopic compositions of isobutane and normal butane, all three are valuable for correlation. The carbon isotopic compositions of propane, isobutane, and normal butane generally seem to be unaffected by migration. For LOMs greater than 13 where thermal destruction of wet gas and oil is significant, the carbon isotopic compositions of propane, isobutane, and normal butane become isotopically heavier, losing both their source and maturity signatures, which they obtained at the time of their formation (James, 1983). With increasing extent of thermal destruction, the carbon isotopic compositions of these components may become significantly heavier than their source (refer to James, 1983). For an additional discussion of the relationship of the carbon isotopic compositions of the higher molecular weight wet gas components to their source, see Chung et al. (1988).

EXAMPLES

Several examples illustrate the use of the carbon isotopic compositions of the wet gas components for correlating one reservoir gas with another, for estimating gas maturities, and for understanding the relationship of one accumulation to another.

Leduc Reef Trend, Alberta

The carbon isotopic and molecular compositions of associated and nonassociated gases from Upper Devonian reservoirs along the Homeglen-Rimbey-Leduc reef trend in the Western Canada basin are shown in Table 1. The locations of these accumulations are shown in Figure 1. With the

Table 1. Carbon Isotopic and Molecular Compositions of Gases from the Leduc Reef Trend, Alberta

Field	Ricineus West	Sundre	Homeglen Rimbey	Olds	Innisfail	Bonnie Glen	Leduc	Redwater
Reservoir	Leduc	Wabamun	Leduc	Wabamun	Leduc	Leduc	Leduc	Leduc
Depth (ft)	14,776–15,024	8000	7946–7952	8694–8722	8495–8522	6710	5313–5319	3173–3286
Molecular Composition (mole %)								
H ₂ S	35.86	0.89	1.14	10.68	11.87	0.36	0.00	5.42
CO ₂	6.25	1.94	0.62	4.86	3.27	1.04	0.51	9.09
N ₂	0.28	0.10	1.02	3.04	5.76	3.58	4.79	2.38
C ₁	56.76	91.75	90.32	71.51	63.89	73.41	72.07	50.10
C ₂	0.58	3.14	3.72	5.88	6.33	12.33	13.65	14.26
C ₃	0.11	1.23	1.78	2.07	3.05	5.47	6.15	10.95
iC ₄	0.02	0.29	0.29	0.31	0.51	0.87	0.62	1.92
nC ₄	0.07	0.38	0.65	0.87	1.20	1.83	1.34	3.85
iC ₅	0.00	0.12	0.19	0.26	0.43	0.37	0.21	0.83
nC ₅	0.00	0.09	0.22	0.28	0.57	0.44	0.24	0.77
C ₆₊	0.07	0.07	0.08	0.24	3.12	0.30	0.42	0.43
C ₁ /C _n	0.99	0.95	0.93	0.88	0.81	0.77	0.76	0.60
Carbon Isotopic Composition (‰, δ¹³C vs. PDB)								
Methane	-39.84	-43.67	-42.74	-42.98	-42.75	-43.32	-44.34	-50.32
Ethane	-17.77	-27.44	-30.79	-33.10	-32.49	-33.01	-34.39	-32.58
Propane	—	-27.41	-27.98	-30.22	-29.18	-28.89	-30.59	-30.98
Isobutane	—	-26.44	-28.99	-31.12	-30.04	-29.53	-30.61	-31.43
N-butane	—	-24.75	-28.56	-29.07	-28.35	-28.12	-28.92	-29.44
Interpreted LOM	Thermally cracked >13	Thermally cracked >13	12	11–12	11	10.5	10	Mixture, 11 and lower

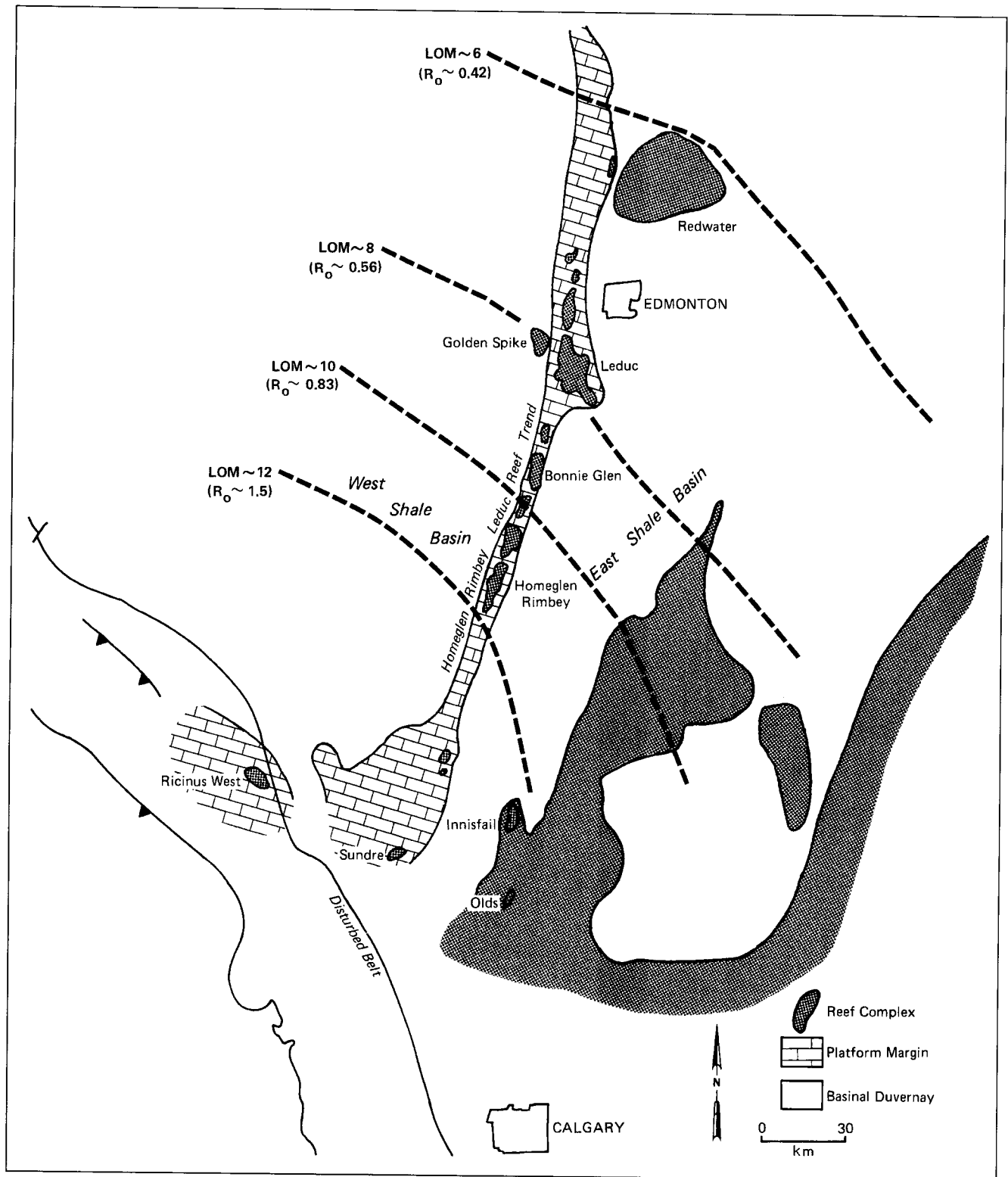


Figure 1—The Upper Devonian Homeglen-Rimbey-Leduc reef trend in the Western Canada basin. The approximate maturity of the Duvernay shale in the adjacent basins is shown by the dashed lines. Modified after Creaney (1989). R_o values are in percent.

exception of two gases (from Ricinus West and Sundre fields) that appear to have undergone significant amounts of thermal degradation at high maturities, the carbon isotopic compositions of the wet gas components shown in Table 1

are similar from one sample to the next. Overall, these gases display a carbon isotopic maturity profile similar to that described previously for west Texas (Figure 2) (compare with James, 1983, his Figure 10). [The carbon isotopic

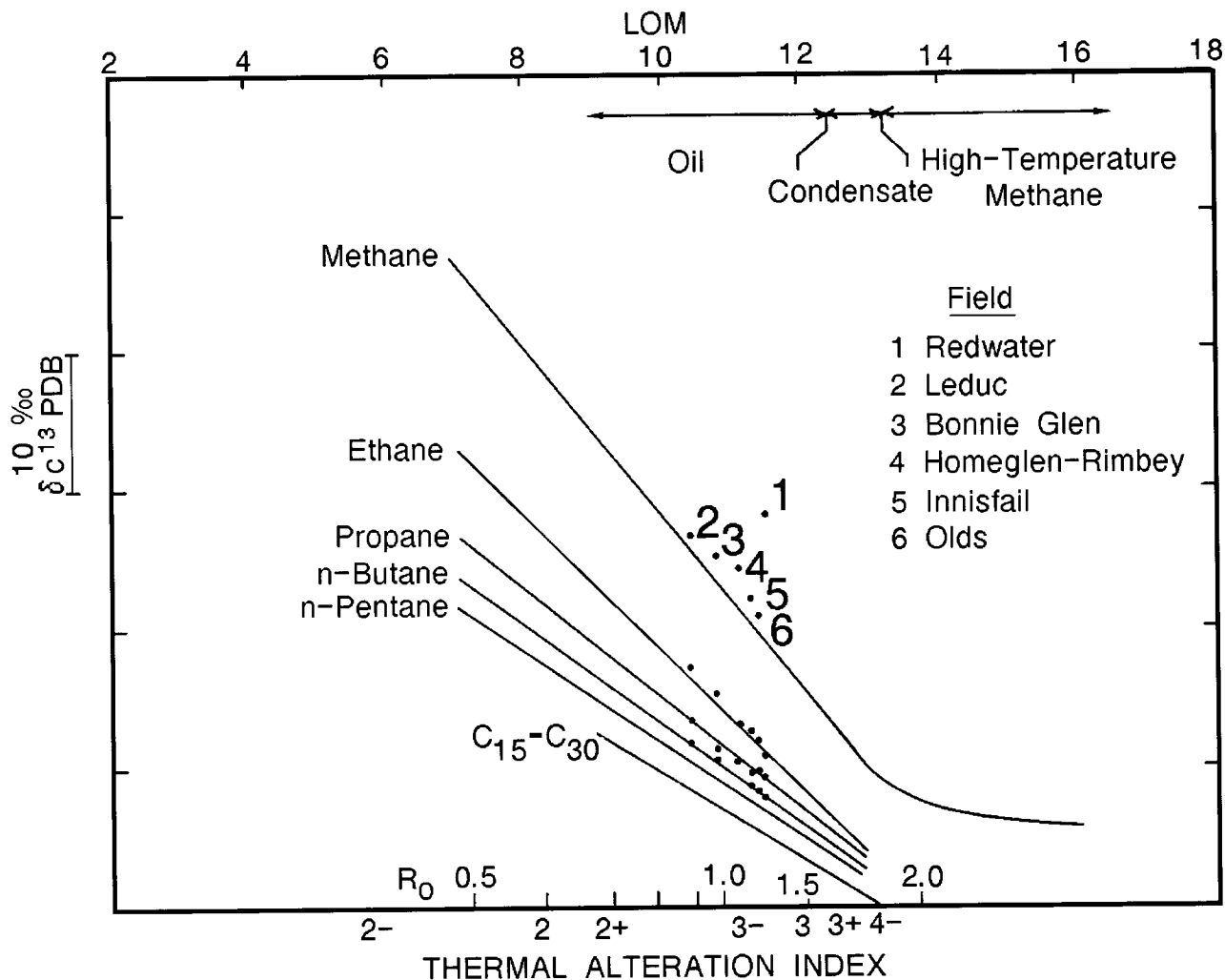


Figure 2—Associated gases from the Western Canada reef trend plotted on James's (1983) maturity diagram. The vertical axis is a sliding scale that is the algebraic difference in parts per mil between the $\delta^{13}\text{C}$ values of the natural gas components. (For more detail see James, 1983.)

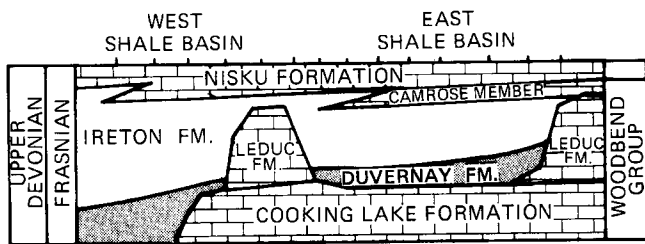


Figure 3—Generalized stratigraphic cross section showing the relationship of the basal Duvernay Formation to the Leduc reefs. From Stoakes and Creaney, 1984.

compositions of the Ricinus West and Sundre gases are isotopically heavier than the other gases listed in Table 1 as a result of their having undergone thermal degradation. They are similar to the thermally degraded gases described previously by James (1983) in west Texas, and are located within the highly thermally mature deep basin and overthrust belt.]

The similarity of the carbon isotopic compositions of the individual wet gas components from one sample to the next for gases from the Olds, Innisfail, Bonnie Glen, and Leduc fields (Table 1) suggests that all of these gases probably have been generated from the same source interval. Based on the work of Creaney (1989) and Stoakes and Creaney (1984), as well as additional unpublished work on crude oil correlation, the organic-rich Upper Devonian Duvernay Formation found in the shale basins on either side of the reef trend is believed to be the source of these hydrocarbons (Figure 3).

When the carbon isotopic compositions of gas from the Olds, Innisfail, Homeglen-Rimbey, Bonnie Glen, and Leduc fields are plotted on James's (1983) maturity diagram, the gases appear to have been generated at LOMs of 11–12 (Figure 2). These interpreted maturities agree with the maturities of the Duvernay shale in the basins on either side of the reef trend (Figure 1), and they also agree with the interpreted maturities of the associated oils determined

Table 2. Carbon Isotopic and Molecular Composition of Upper Devonian Gas from Caprona Field, Alberta

Field	Caprona
Reservoir	Leduc Upper Devonian
Depth (ft)	5320–5329
Molecular Composition (mole %)	
H ₂ S	0.50
CO ₂	9.15
N ₂	18.19
C ₁	59.66
C ₂	7.11
C ₃	4.01
iC ₄	0.35
nC ₄	0.74
iC ₅	0.11
nC ₅	0.11
C ₆₊	0.07
C ₁ /ΣC _n	0.83
Carbon Isotopic Composition (‰, δ¹³C vs. PDB)	
Methane	–47.88
Ethane	–37.90
Propane	–35.00
Isobutane	–32.10
N-butane	–31.04
Interpreted LOM	~9–10

from C₂₉ sterane isomerization, naphthene ring distributions, and other analyses not discussed here. Although it is clear that the Homeglen-Rimbey sample fits with the other gases listed in Table 1 for LOMs in the range of 10 to 12, due to the particular wet gas carbon isotopic compositions of the Homeglen-Rimbey sample and because of its isotopic reversal of propane with respect to the butanes, the sample cannot be uniquely positioned on the maturity diagram on Figure 2. This reversal may be due to mixing from multiple facies or maturities within the same source interval. Gas chromatograms of the associated oil suggest that the sample has not undergone any alteration.

The Redwater gas listed in Table 1 is a mixture of the mature Upper Devonian gas previously described and immature (or biogenic) methane. When plotted on the maturity diagram (Figure 2), the position of the Redwater wet gas components suggests that the mature components of the gas have been generated at an LOM near 11, similar to the other Leduc gases shown in Figure 2. In contrast, the Redwater methane value plots well above its expected position, suggesting that a significant contribution of low-maturity methane (possibly of bacterial origin) is also present within the accumulation. Note that the Redwater field is located in an immature portion of the basin at an LOM of about 6 (Figure 1).

The similarity of the carbon isotopic compositions of the wet gas components at Redwater and the mature Devonian gases reservoired deeper in the basin (Table 1) suggests that all of these gases have come from the same source at about the same level of maturity. The mature gas constituents at Redwater are thought to have migrated to their present loca-

Table 3. Comparison of Devonian- and Cretaceous-Reservoired Gases within the Leduc Field, Western Canada

Reservoir	Upper Devonian Leduc Fm.	Lower Cretaceous Basal Quartz Fm.	Upper Cretaceous Cardium Fm.
Depth (ft)	5313–5319	5303–5308	3068–3074
Molecular Composition (mole %)			
H ₂ S	0.00	0.76	0.00
CO ₂	0.51	0.22	0.80
N ₂	4.79	3.17	3.41
C ₁	72.07	75.80	91.92
C ₂	13.65	12.53	2.34
C ₃	6.15	5.14	0.92
iC ₄	0.62	0.58	0.24
nC ₄	1.34	1.18	0.26
iC ₅	0.21	0.22	0.07
nC ₅	0.24	0.27	0.01
C ₆₊	0.42	0.13	0.03
C ₁ /ΣC _n	0.76	0.79	0.96
Carbon Isotopic Composition (‰, δ¹³C vs. PDB)			
Methane	–44.34	–43.82	–57.20
Ethane	–34.39	–33.29	–37.53
Propane	–30.59	–30.09	–34.34
Isobutane	–30.61	–29.82	–33.12
N-butane	–28.92	–28.50	–33.65
Interpreted LOM	10	10	~8–9, possibly mixed with bacterial methane

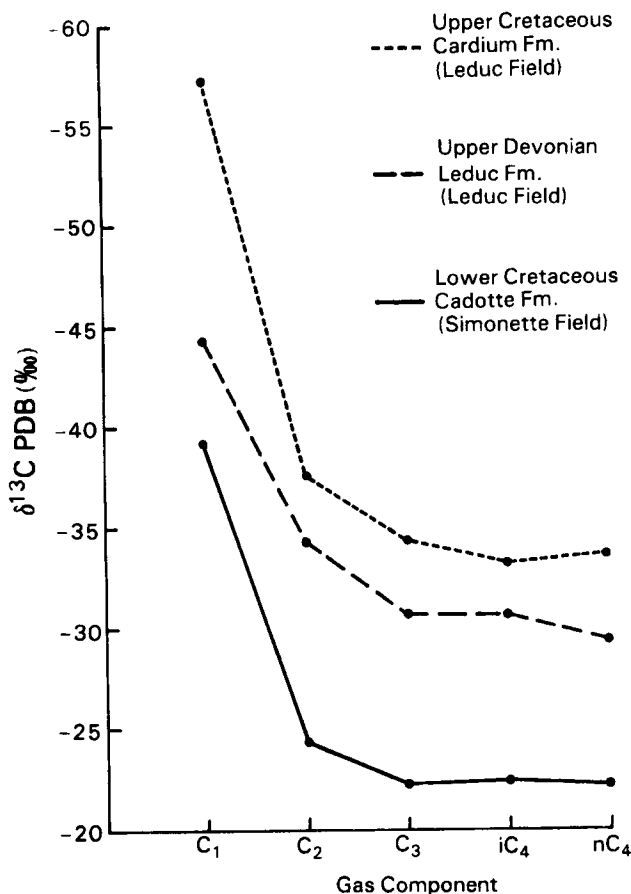


Figure 4—Comparison of Western Canada gas families.

tion from deeper in the basin and mixed with immature methane.

A comparison of the associated oil at Redwater with oils found deeper in the basin supports the interpretation made from the gases, and indicates that the oil has also originated deeper in the basin and from the same source as the other Leduc oils found along the reef trend (refer to Creaney and Allan, 1989; see also Gussow, 1955).

For comparison purposes, an example of low-maturity gas generated from the Duvernay Formation at an LOM of about 9 is shown in Table 2. This gas from the Caprona field is located south of the reef trend and is distinct from the Redwater mixture.

Due to the abundance of possible migration pathways along fractures and permeable layers, considerable movement and mixing of hydrocarbons is suspected to have occurred within the Western Canada basin. Based on the carbon isotopic compositions of wet gas components from several additional accumulations, the same mature Devonian gas previously discussed is also believed to be present in some of the overlying Lower Cretaceous reservoirs found along the eastern part of the reef trend. At the Leduc field for example, where the Lower Cretaceous unconformably overlies the Upper Devonian, associated gas from the Basal Quartz Formation reservoir (located just above the sub-Cre-

taceous unconformity) is nearly identical, both isotopically and compositionally, to the gas in the underlying Devonian Leduc Formation (Table 3). This similarity suggests that the Basal Quartz gas in this field may have migrated from the Devonian. A similar suggestion has also been made by Deroo et al. (1977) for the oils associated with these same gases. As a result, the reservoir age does not necessarily correspond with the age of the hydrocarbon source in this part of the basin. Although the depths of the two samples shown in Table 3 are similar, they are from different wells, located in different parts of the field.

To help demonstrate that the carbon isotopic compositions of the wet gas components reflect, at least in part, the isotopic compositions of their sources, gases from additional hydrocarbon sources in the Western Canada basin are shown in Figure 4 and in Tables 3 and 4. At the Leduc field, gas from the Upper Cretaceous Cardium Formation is readily distinguished from Upper Devonian Duvernay-derived gas found deeper in the section (Table 3, Figure 4). These differences are believed to result from differences in the maturity of the gases and also from differences in the isotopic compositions of their sources. To illustrate that the differences are not entirely maturity related, a comparison of the Cardium sample with low-maturity Duvernay-derived gas from the Caprona field (Table 2) shows that the carbon isotopic compositions of the butanes, as well as the molecular compositions, are distinct.

Additional Western Canada basin gases, which are distinct from both the Upper Devonian and Upper Cretaceous gases previously discussed are shown in Table 4 and in Figure 4. These gases have significantly more positive wet-gas component carbon isotopic compositions ($\delta^{13}\text{C}$ near -22 ‰) than the gases previously reported. In the deep part of the basin at Simonette and Edson fields (Table 4), these gases occur in both Mississippian and Cretaceous reservoirs. Although their source or sources are presently unknown, the significantly more positive wet-gas component carbon isotopic compositions probably result from their sources being enriched in ^{13}C relative to the others. As a result, gases derived from such sources are readily recognizable, even when they are encountered in various reservoirs within the complexly faulted and structured overthrust belt (Table 4). In this author's opinion, the source control exhibited by the wet gas carbon isotopic compositions of these gases is an alternative explanation for why the gases described by Krouse et al. (1988) in the overthrust belt have such isotopically heavy carbon isotopic compositions in contrast to the sulfate reduction process proposed by Krouse et al. (1988). Although the sulfate reduction mechanism may well occur in some accumulations, the consistent carbon isotopic compositions of the wet gas components from one sample to the next shown in Table 4 are more likely to be inherited from their source. (In fact, on Table 4 note that one of the gases, which is reservoirized in front of the overthrust belt in the deep basin, contains no hydrogen sulfide, suggesting that thermochemical sulfate reduction is unlikely to have been significant in this specific accumulation.) Additional examples of these isotopically heavy gases have also been found to have undergone fairly severe thermal destruction of their wet gas components, leaving their remaining wet gas components even more isotopically posi-

Table 4. Comparison of Western Canada Deep Basin and Overthrust Belt Gases

Location	Deep Basin		Overthrust Belt		
	Simonette	Edson	Hanson Creek	Wildcat Hills	Jumping Pound
Field	Simonette	Edson	Hanson Creek	Wildcat Hills	Jumping Pound
Reservoir	Cadotte Lower Cretaceous	Elkton Mississippian	Mississippian	Turner Valley Mississippian	Turner Valley Mississippian
Depth (ft)	7058–7109	9142–9156	11,940–12,129	6591	9799–10,139
Molecular Composition (mole %)					
H ₂ S	0.00	1.11	2.85	3.29	2.38
CO ₂	1.15	5.25	3.15	1.77	6.26
N ₂	0.18	0.70	0.10	1.16	0.13
C ₁	90.80	89.65	87.58	87.44	85.38
C ₂	5.98	2.38	4.52	3.60	4.05
C ₃	1.18	0.51	1.03	0.77	0.93
iC ₄	0.21	0.14	0.20	0.21	0.25
nC ₄	0.24	0.14	0.19	0.23	0.24
iC ₅	0.11	0.00	0.07	0.11	0.13
nC ₅	0.06	0.00	0.04	0.05	0.09
C ₆₊	0.09	0.12	0.17	1.37	0.16
C ₁ /ΣC _n	0.92	0.96	0.93	0.95	0.94
Carbon Isotopic Composition (‰, δC¹³ vs. PDB)					
Methane	-39.22	-37.30	-38.53	-39.13	-39.62
Ethane	-24.27	-23.59	-24.93	-23.52	-24.52
Propane	-22.25	-23.29	-23.93	-21.74	-22.73
Isobutane	-22.41	-22.40	-23.02	-22.77	-23.34
N-butane	-22.23	-22.42	-23.63	-21.05-	22.17
CO ₂	-3.35	-1.55	-7.56	-1.17	-2.15
Interpreted LOM	11-12	~13	~12	~12	~12

tive. Possible sources for the gases listed in Table 4 include the Lower Cretaceous (Mannville) coals as well as several additional Triassic and Jurassic units cut by the sub-Cretaceous unconformity (cf. Creaney and Allan, 1989).

Sleipner Area, North Sea

In the Sleipner area located in the Norwegian part of the North Sea, hydrocarbons are contained in a number of Triassic, Jurassic, and Paleocene reservoirs located within or overlying a series of fault blocks stepping outward onto the Norwegian shelf from the eastern side of the Viking Graben (Figures 5, 6). From the beginning of the exploration effort, the Middle Jurassic (particularly the Sleipner Formation) was thought to be the most likely source of the hydrocarbons found in the Jurassic and Triassic reservoirs. When gas was discovered in the overlying Paleocene sandstones in the eastern part of the area, its origin was unknown.

Table 5 is a summary of the carbon isotopic and molecular compositions of selected gases from the Sleipner area. The locations of these accumulations and their relative structural positions are shown in the accompanying map and cross section (Figures 5, 6). A total of 19 gases from various wells and intervals throughout the area have been analyzed. The structural and stratigraphic setting of the

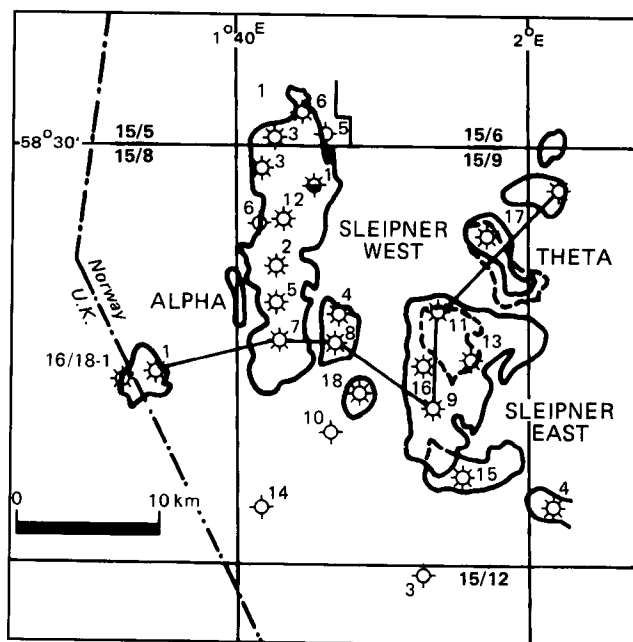


Figure 5—Sleipner area well locations, offshore Norway. Line shows the location of the eastern part of Figure 6 cross section. Note that cross section continues to the west.

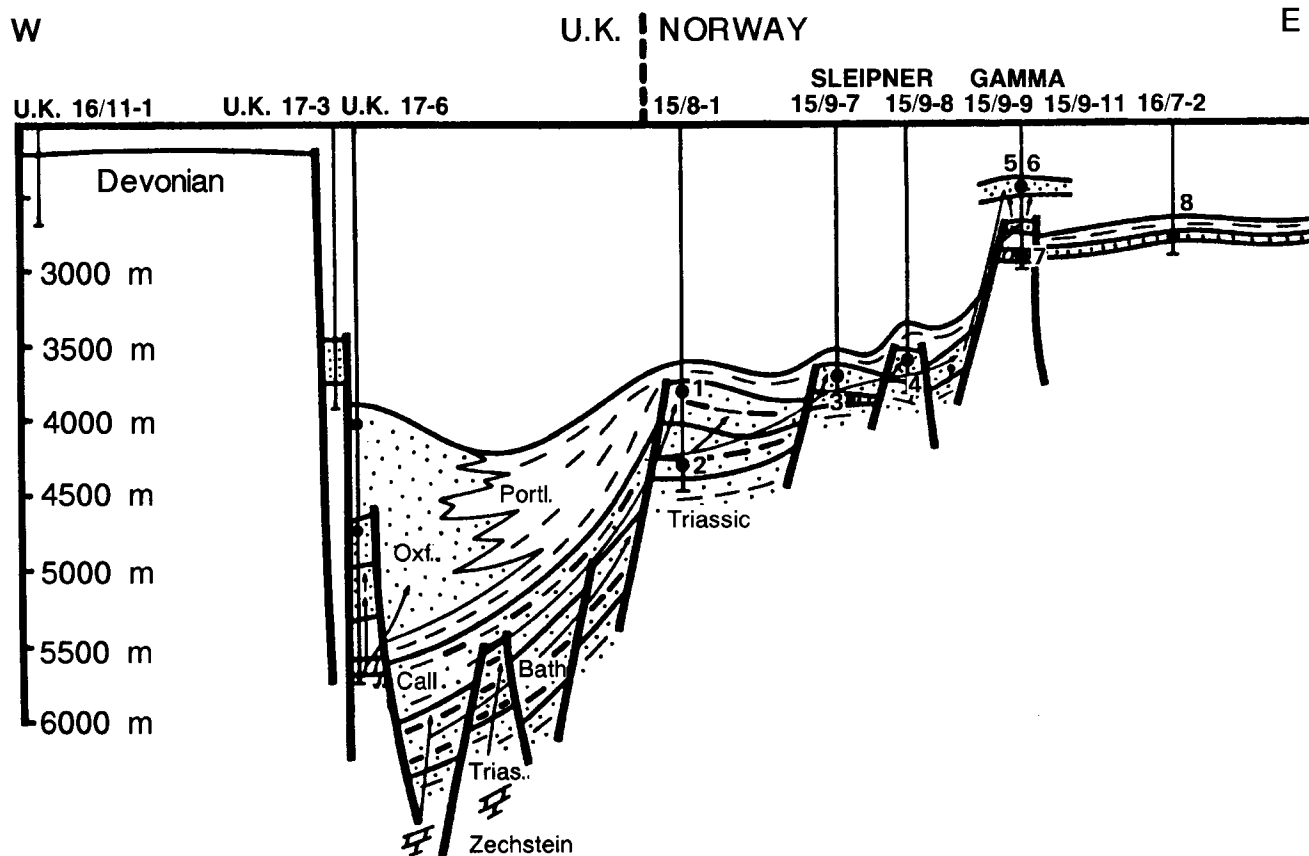


Figure 6—Generalized cross section through the Sleipner area. The single-digit sample reference numbers correspond to those in Table 5 and Figure 7. (Cross section provided by F. Mediavilla, Esso Norge a.s.) See Figure 5 for location of cross section.

Sleipner area, as well as its exploration history, has been previously described by Pegrum and Ljones (1984).

Except for having variable amounts of nonhydrocarbon gas constituents (N_2 and CO_2), all of the gases shown in Table 5 are similar to one another, both isotopically and compositionally, regardless of their reservoir age. Although the carbon isotopic compositions of methane do vary among the samples to some extent, the isotopic compositions of the wet gas components show only minor variations from sample to sample. The similarity of these gases is even more apparent when the molecular compositions of the hydrocarbon components are normalized to 100%, effectively removing the nonhydrocarbons (CO_2 , N_2) (Table 5).

When the carbon isotopic compositions of methane, ethane, and propane are plotted on James's (1983) maturity diagram using the ethane to propane separations, all of the gases cluster together indicating a source LOM of 11 to 12 (Figure 7). The carbon isotopic compositions of the normal butanes were not used in this plot because the isotopic compositions of propane and normal butane are reversed from that which would be normally expected (Table 5). Because the isotopic compositions of the wet gas components are so consistent from one sample to the next over the entire area, it is unlikely that these reversals are the result of hydrocarbon mixing from multiple sources. Rather, the reversals are thought to result from a source control superimposed on the

carbon isotopic compositions of the higher molecular weight gas components. If the gases were a result of mixing from multiple source intervals, it is unlikely that the isotopic compositions of the wet gas components (including the propane-normal butane reversals) would be so consistent from sample to sample, especially in view of the geographic and structural distributions of the samples.

Based on (1) the similarities of the carbon isotopic compositions of the wet gas components, (2) the similarity of the normalized hydrocarbon gas compositions, and (3) the clustering of the isotopic data on the maturity diagram, all of the hydrocarbon gases listed in Table 5, including those reservoirs in the Paleocene, are thought to have been generated from the same source interval at about the same level of maturity regardless of their reservoir ages.

A maturity profile from the Viking Graben onto the Norwegian shelf, based on measured thermal alteration indexes, vitrinite reflectance, and calculated maturities obtained from burial histories and time-temperature calculations (modified after Lopatin, 1971, and Hood et al., 1975), is shown in Figure 8. When compared with the interpreted maturities of the gases, the distribution of maturities in the geologic section suggests that the hydrocarbon gases reservoirs in the Sleipner area (including those in the Paleocene) were all generated from Jurassic beds deep within the Viking Graben. The hydrocarbon gases appear to have

Table 5. Summary of the Carbon Isotopic and Molecular Compositions of Sleipner Gases, Offshore Norway

Cross Section		1	2	3	4	5	6	7	8
Reference Number									
Well		15/8-1 DST 4	15/8-1 DST 1	15/9-7 DST 3	15/9-8 DST 1	15/9-9 DST 3	15/9-11 DST 2	15/9-11 DST 1	16/7-2 MFT 1
Reservoir		Hugin Fm. Mid.-Upper Jurassic	Sleipner Fm. Mid. Jurassic	Hugin Fm. Mid.-Upper Jurassic	Hugin Fm. Mid.-Upper Jurassic	Paleocene	Paleocene	Triassic or Jurassic	Paleocene
Depth (ft)		11,952-11,985	13,382-13,402	11,663-11,696	11,319-11,351	7621-7654	7979-8005	9176-9209	7588
Molecular Composition (mole %)									
H ₂ S		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂		16.65	8.89	9.50	7.79	0.29	0.23	2.98	0.15
N ₂		0.46	3.17	0.70	0.86	1.16	1.30	0.41	1.77
C ₁		68.07	65.62 (74.62)	75.65 (84.24)	75.26 (82.39)	77.47 (78.61)	75.80 (76.42)	77.67 (80.40)	78.97 (80.52)
C ₂		9.14 (11.03)	10.66 (12.12)	8.44 (9.40)	8.89 (9.73)	11.34 (11.51)	11.65 (11.75)	9.52 (9.85)	11.41 (11.63)
C ₃		4.07 (4.91)	8.60 (9.78)	4.04 (4.50)	4.76 (5.21)	6.84 (6.94)	7.88 (7.94)	6.16 (6.38)	5.72 (5.83)
iC ₄		0.43 (0.52)	1.23 (1.40)	0.50 (0.56)	0.67 (0.73)	0.91 (0.92)	1.18 (1.19)	0.80 (0.83)	0.66 (0.67)
nC ₄		0.79 (0.95)	1.29 (1.47)	0.75 (0.84)	1.05 (1.15)	1.37 (1.39)	1.81 (1.82)	1.41 (1.46)	0.95 (0.97)
iC ₅		0.14 (0.17)	0.28 (0.32)	0.17 (0.19)	0.27 (0.30)	0.27 (0.27)	0.40 (0.40)	0.31 (0.32)	0.18 (0.18)
nC ₅		0.15 (0.18)	0.17 (0.19)	0.14 (0.16)	0.24 (0.62)	0.23 (0.23)	0.33 (0.33)	0.18 (0.19)	0.12 (0.12)
C ₆₊		0.10 (0.12)	0.09 (0.10)	0.11 (0.12)	0.21 (0.23)	0.12 (0.12)	0.14 (0.14)	0.56 (0.58)	0.07 (0.07)
Carbon Isotopic Composition (‰, δ¹³C vs. PDB)									
Methane		-42.97	-44.02	-39.50	-39.48	-42.57	-42.90	-40.43	-43.89
Ethane		-28.61	-27.92	-27.44	-27.06	-27.74	-27.73	-28.14	-27.99
Propane		-26.61	-26.38	-26.02	-26.05	-26.01	-26.16	-27.16	-26.09
i-butane		-26.43	-26.73	-26.23	-26.03	-25.25	-25.52	-26.31	-26.22
n-butane		-27.61	-27.42	-26.99	-26.69	-26.68	-26.91	-28.51	-26.90
Interpreted LOM		11	11	11	11-12	11	11-12	12	11

*Values in parentheses represent hydrocarbon composition normalized to 100%.

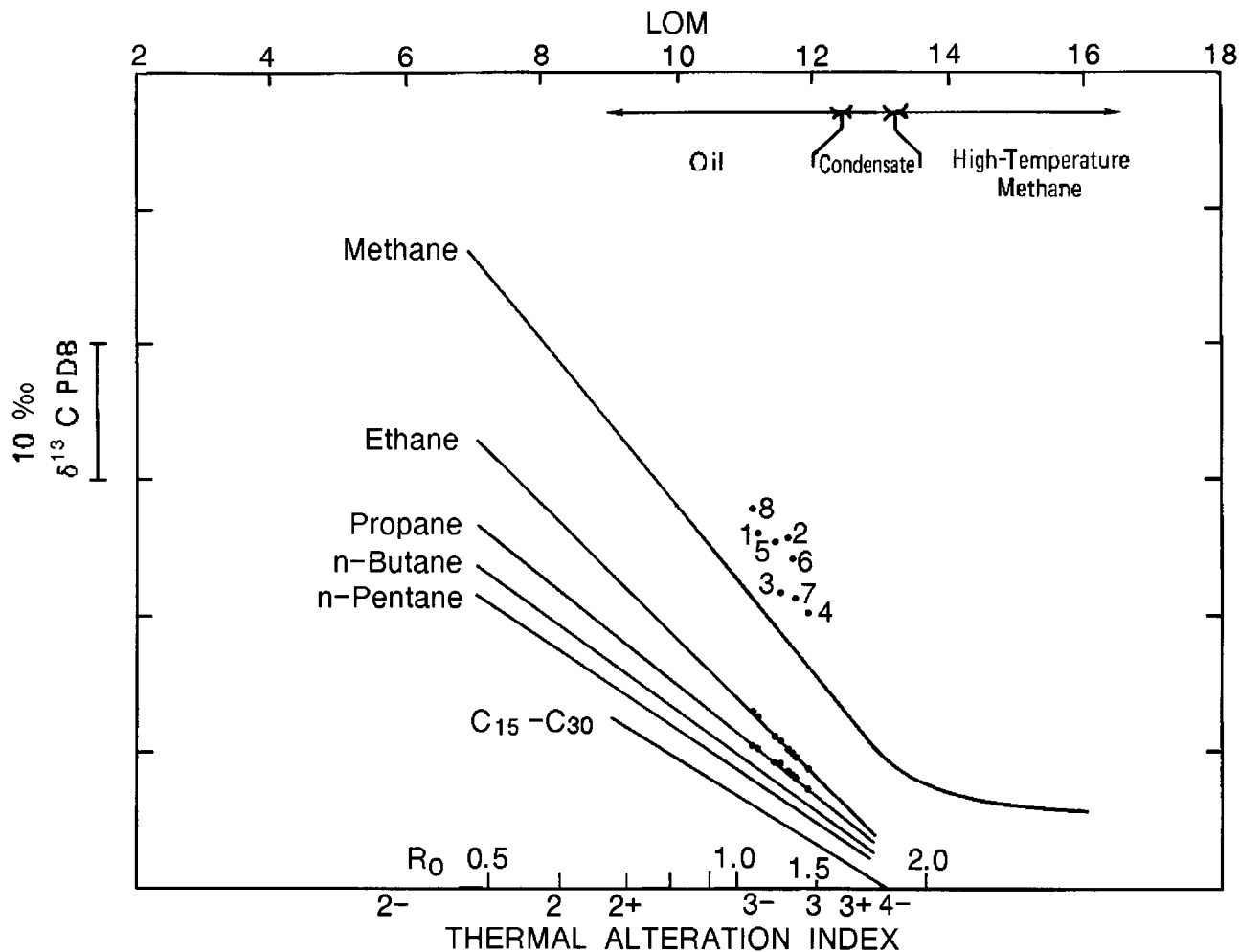


Figure 7—LOM determination of the Sleipner field gases. The sample numbers correspond to those shown in Table 5 and Figure 6.

migrated through permeable sandstones and up faults and fractures to successively shallower reservoirs in the various fault blocks, culminating in the Paleocene sandstones. As a result, similar hydrocarbon gases are found at various points along these pathways in reservoirs of different ages. The minor differences in hydrocarbon gas compositions and methane isotopic compositions are thought to result either from organic matter variations within the source or from minor mixing of hydrocarbons derived from multiple sources within the Jurassic. However, because the carbon isotopic compositions of the wet gas components are so consistent from sample to sample throughout the area, the extent of mixing from multiple hydrocarbon sources is not thought to be very great.

In the Sleipner area, the kerogen contained in the Jurassic rocks ranges from 30 to 80% structured, woody-coaly material and exhibits considerable vertical and lateral facies variations. These observations fit with the interpretations previously made concerning the source control on the variations exhibited by (1) the carbon isotopic compositions of the hydrocarbon gas components, and (2) by the differences in the molecular compositions of the hydrocarbons.

The compositional differences observed among the non-hydrocarbon gas constituents shown in Table 5 are suspected to be unrelated to the origin of the hydrocarbons. Multiple sources for the CO₂ are thought to be present. The gases containing the highest amounts of CO₂ are found deep within the section (Figure 9), either in or near the Viking Graben. This CO₂ has carbon isotopic compositions of -3 to -5‰ (Figure 10) and appears most likely to have been derived from thermal degradation of carbonates located deep within the section. Farther eastward and higher on the Norwegian shelf, the amount of CO₂ contained in the gases decreases systematically with increasing distance from the graben (Figure 11). This CO₂ is typical of that derived from normal maturation of organic matter and has δ¹³C in the range of -8 to -12‰ (Figure 10). As a consequence, the variability of CO₂ contents observed in the Sleipner gases appears to be the result of CO₂, derived from deep within the section in the Viking Graben, migrating outward to shallower reservoirs and mixing in varying proportions with hydrocarbon gases (including CO₂) derived from normal maturation of organic matter. Hence, the variations of non-hydrocarbon gas constituents found in the Sleipner gases

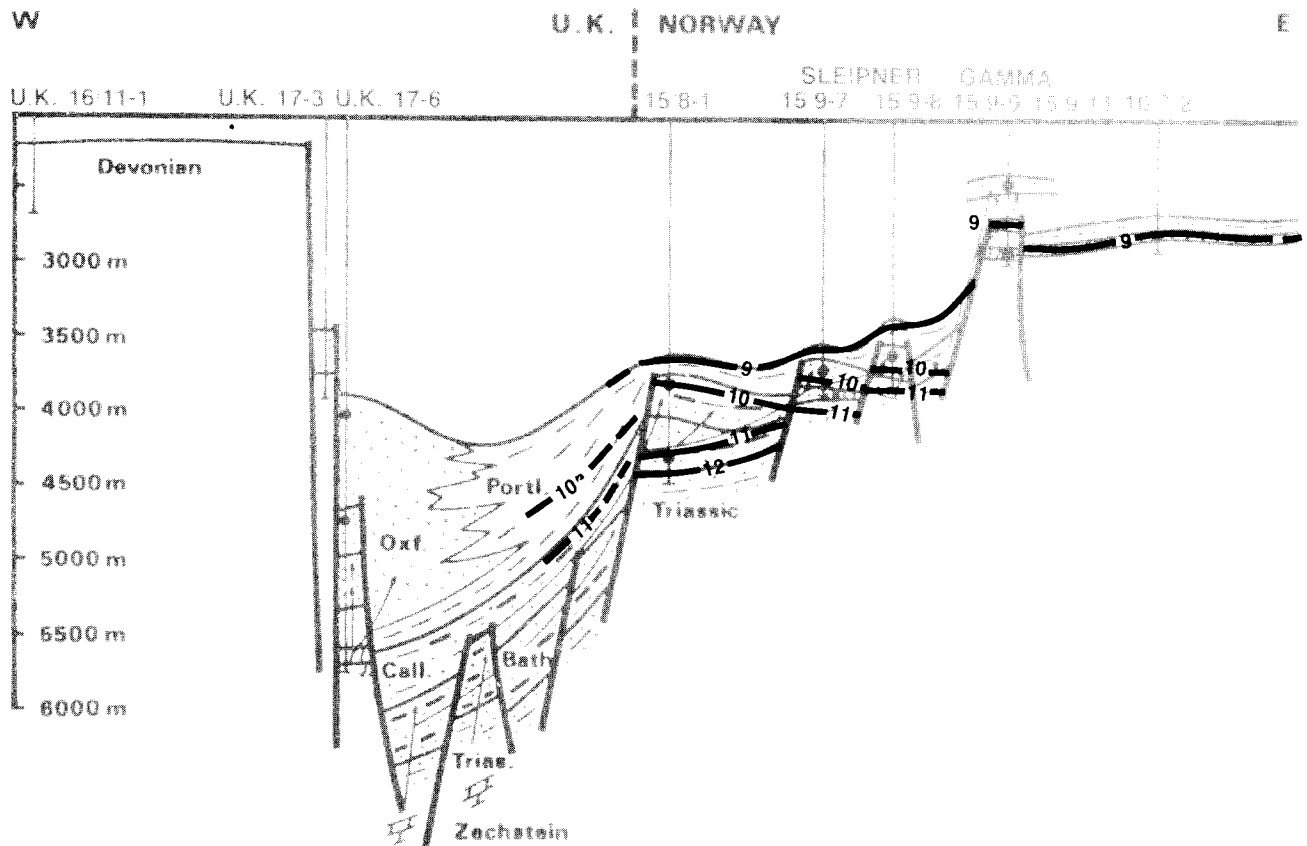


Figure 8—Sleipner area LOMs.

appear to be related more to migration, mixing, and differences in migration pathways than due to hydrocarbon source variations.

In this example, the carbon isotopic compositions of the wet gas components are shown to be valuable for allowing us to see through the variability of nonhydrocarbon gas components and for recognizing the common origin of the hydrocarbon gases. Had the Paleocene-reservoired gases not been compared in detail with the other gases, their relationship to gases contained in the older reservoirs and to a Jurassic source might have been overlooked.

Lena Field, Offshore Louisiana

Selected gases from the Lena field, offshore Louisiana (Mississippi Canyon Block 281) (Figure 12), are shown in Table 6. These gases are from stacked producing sands, which occur at depths of 4930–8613 ft (1503–2625 m) within the same fault block. The two deepest gases listed are associated with oil. All of the reservoirs are located in an immature part of the section within the Pliocene.

In the Lena accumulations listed in Table 6, the carbon isotopic compositions of ethane, propane, isobutane, and normal butane are nearly identical from one sample to the next, even though the methane isotopic compositions and the molecular compositions vary considerably. When plotted

on James's (1983) maturity diagram, the gases are seen to be mixtures in varying proportions of bacterial methane and mature gas, which has been generated at an LOM of about 12 (Figure 13). The similarity of the carbon isotopic compositions of the individual wet gas components from sample to sample and the similarity of the interpreted maturities suggest that the wet gases have all come from the same source. These mature, wet gases are thought to have migrated vertically along faults from deeper in the section and mixed in varying proportions with bacterial methane in the shallow section. In such mixtures, the mature gas is diluted with bacterially derived methane, leaving the isotopic compositions of ethane and higher molecular weight components unaffected. The resulting methane isotopic compositions are variable, depending on the relative proportions of the end members. With regard to specific accumulations, the Lena A-26 gas (Table 6) has the lightest methane carbon isotopic composition of the three gases listed and appears to be composed of predominately bacterial methane mixed with minor amounts of mature gas. In contrast, the Lena A-23 gas has the heaviest methane carbon isotopic composition and is the most representative of mature gas migrating from depth. The other gas listed in Table 6 exhibits an intermediate methane carbon isotopic composition and represents an intermediate mixture of the two end members.

The Lena A-23 and A-26 gases together with several additional gases from different reservoirs in other fault blocks

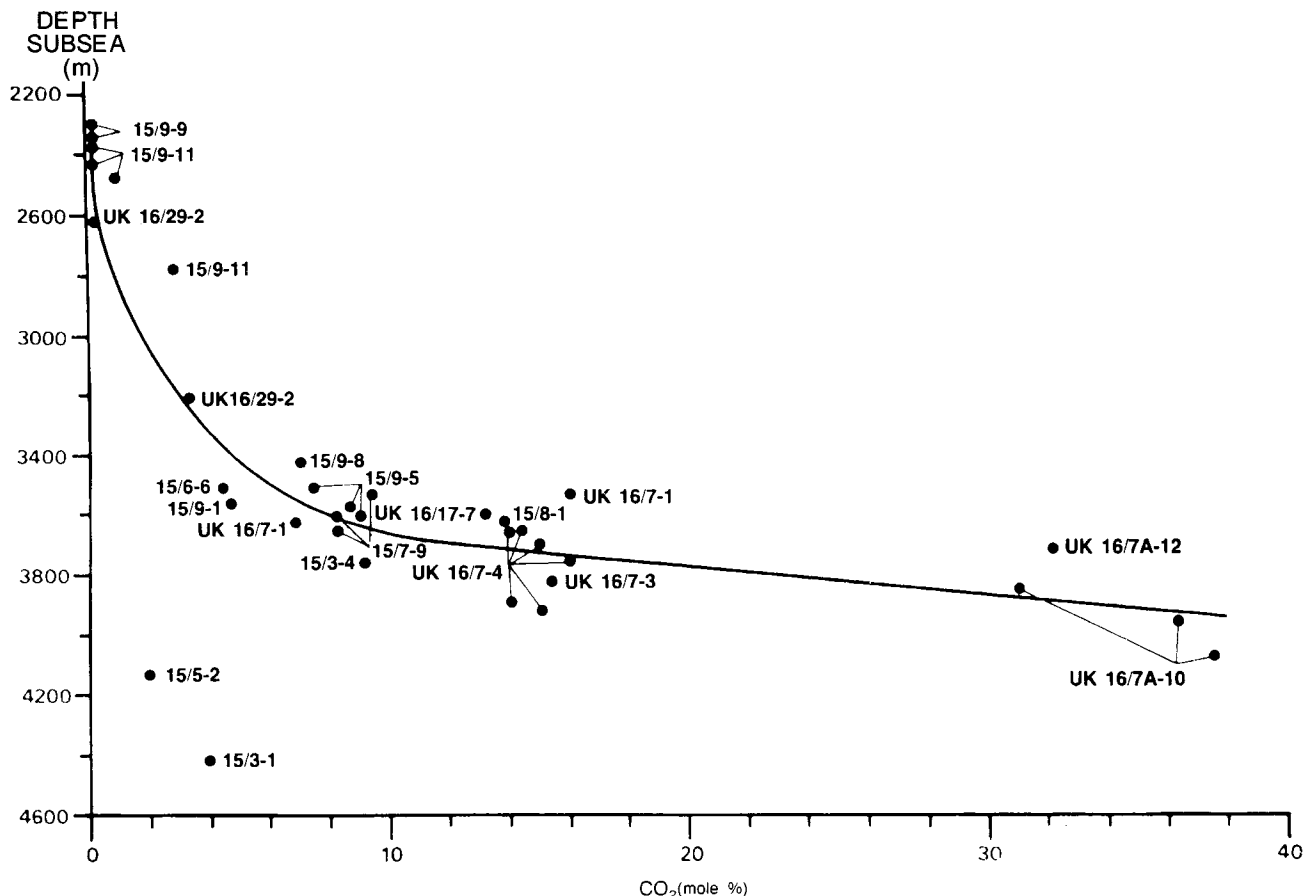


Figure 9—CO₂ content vs. reservoir depth in the greater Sleipner-Gudrun-Brae-Thelma-Maureen field area. (Provided by D. Berglein, Esso Norge a.s.)

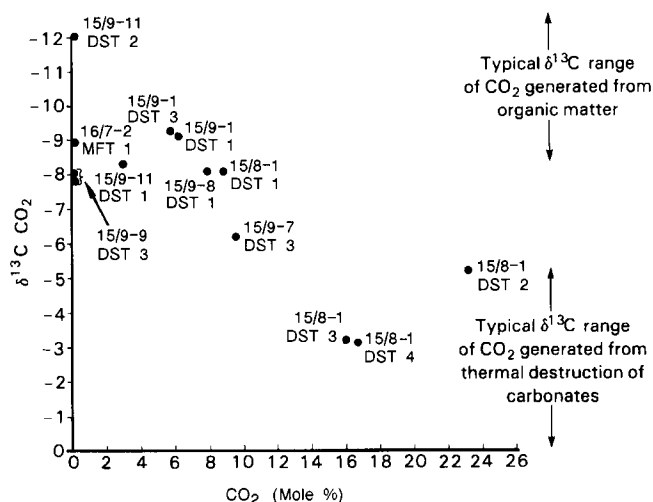


Figure 10—CO₂ in the greater Sleipner field area.

within the Lena field are shown in Figure 14. The additional gases represent a wide range of mixtures of the two end members previously described. Just as before, the carbon isotopic

compositions of the wet gas components of the additional gases show only minor variations from one reservoir to another, whereas their methane carbon isotopic compositions range considerably, from -42 to -57‰. By characterizing the gases with their wet-gas component carbon isotopic compositions, the Lena gases can be recognized easily as mixtures, with their mature gas components having a common origin. Had the gases been characterized only by the carbon isotopic compositions of methane, this relationship probably would have been missed. The gases might even have been characterized as having come from multiple sources at different maturities.

As a result of bacterial alteration, the wet gas component carbon isotopic compositions of some of the additional gases shown in Figure 14 vary somewhat from the three gases listed in Table 6. The altered gases display progressively heavier propane and n-butane carbon isotopic compositions whereas their ethane and isobutane isotopic compositions remain nearly the same as the A-23 gas (Figure 15) (see also James and Burns, 1984). Gas chromatograms of associated oils at Lena also show varying amounts of bacterial alteration, some of which are fairly severe (Figure 16), supporting the interpretation that some of the gases are altered, although the extent of alteration of the gases and oils reservoir together do not necessarily parallel each other.

No direct relationship appears to exist between the

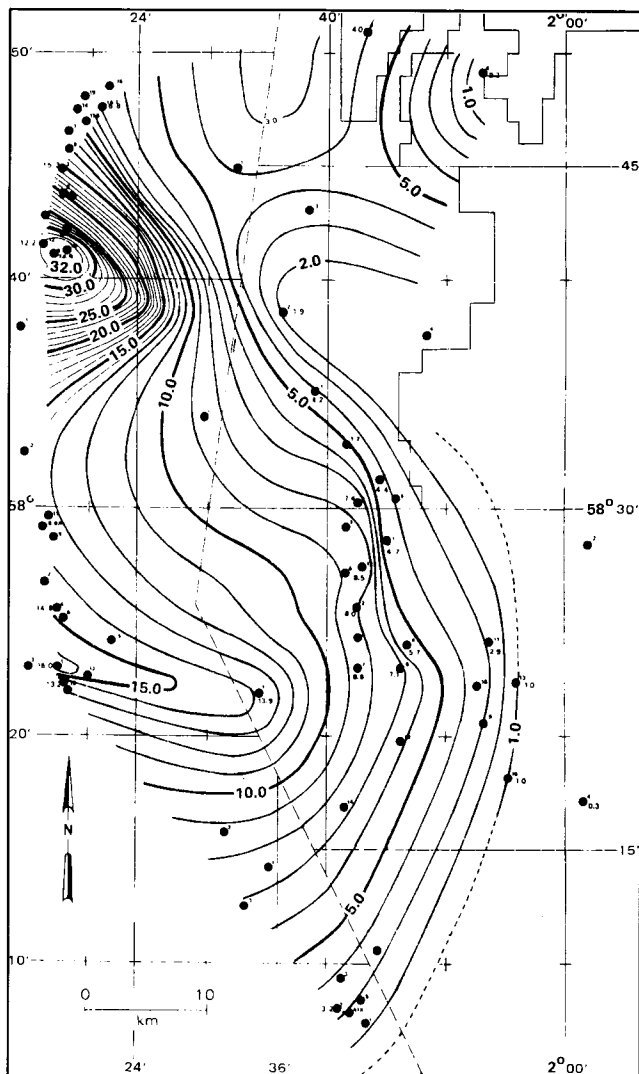


Figure 11—Distribution of CO₂ in the greater Sleipner field area (contours in mole % CO₂). (Courtesy of D. Bergslein, Esso Norge a.s.)

extent of bacterial alteration and mixing in the Lena gases, although several of the gases display the effects of both. If several gases within the area had not been available for comparison, the mixing and alteration effects of the gases would have been more difficult to recognize.

DISCUSSION

The source control exhibited by carbon isotopic compositions of the wet gas components (particularly normal and isobutane and to a lesser extent propane) make these components particularly useful for correlating one reservoir gas with another. Although no direct correlations of reservoir gases to their sources are available for the examples presented here, the inference of a source control superimposed on the carbon isotopic compositions of the wet gas

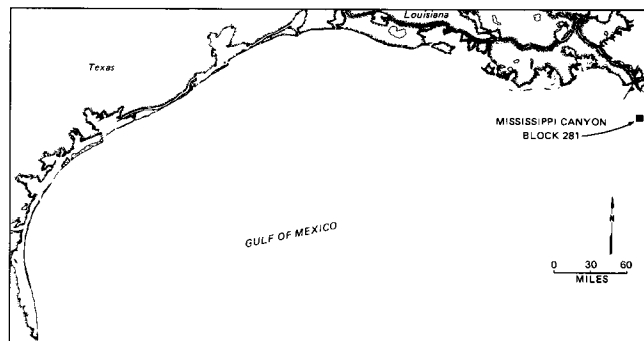


Figure 12—Location of the Lena platform, offshore Louisiana (Mississippi Canyon Block 281).

components is strong. At the Sleipner field for example, the carbon isotopic compositions of propane and normal butane are reversed from the normal order expected from a maturity influence alone. In western Canada, gases derived from three different source intervals have been differentiated by their wet gas component carbon isotopic compositions, which are at least partly source controlled.

Limitations of the use of the wet gas component carbon isotopic compositions for correlation purposes do exist however. Thermal destruction at high maturities causes the wet gas components to lose their source and maturity characteristics inherited at the time of their formation. This process may be so extensive that the carbon isotopic compositions of the affected components can be dramatically changed (refer to James, 1983). At more moderate maturities where the destruction process appears to start, i.e., LOMs in the range of 12 to 13 (just past the range of generation of most liquids), the effects are subtle and are more difficult to recognize. For example, where propane and the higher molecular weight components are partly degraded, it may not be readily apparent that the gas has undergone thermal degradation. In such instances, the sample could be incorrectly placed at too low of a maturity on James's (1983) maturity diagram, e.g., at LOMs of 8 to 9 instead of 12 to 14. Reliable butane data usually allow such secondary alteration phenomena to be recognized and frequently help to reduce the interpretational problems.

Bacterial alteration of gas can also cause the wet gas components to lose their original carbon isotopic compositions that they obtained at the time of their formation (James and Burns, 1984). The process can dramatically alter the carbon isotopic compositions of propane and the butanes, removing all of their original source character. If subtle bacterial alteration is present and not recognized (or even if more extensive alteration is not recognized), miscorrelations and misinterpretations of the gas's maturity can result.

A significant effort to obtain a reliable sample representative of the subsurface accumulation is required for very wet gases and when liquid hydrocarbons are present in the reservoir or in the well stream. Errors of up to 4‰ in the $\delta^{13}\text{C}$ of the wet gas components (especially the butanes) can result from sampling procedures alone if inadequate methods are employed either at the well site or in the laboratory.

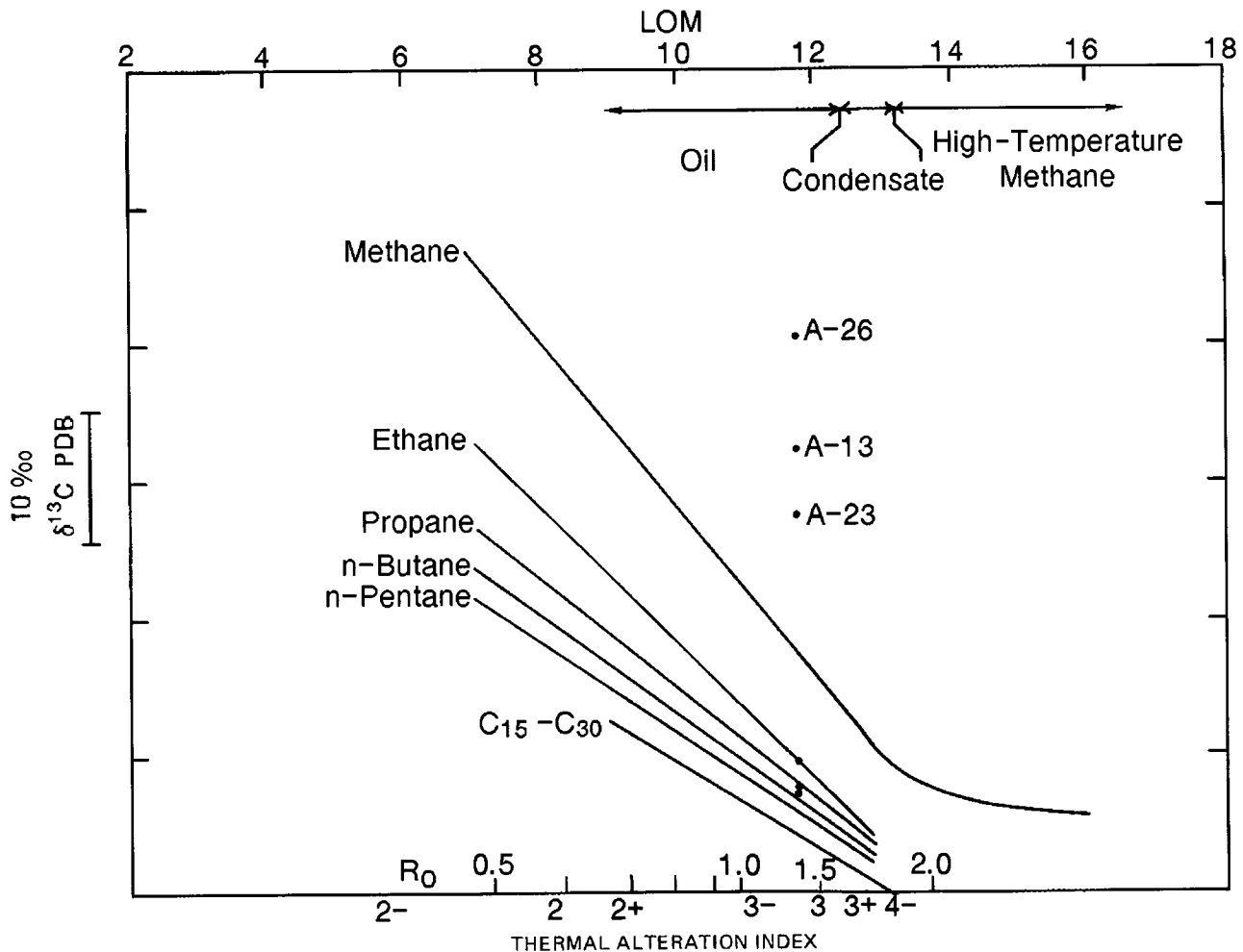


Figure 13—LOM determination of the Lena field gases. The ethane, propane, and normal butane carbon isotopic compositions of the gases are so similar from one sample to the next that the gases plot on top of each other.

We use evacuated cylinders to obtain several hundred or several thousand psi gas and fluid samples representative of flow streams and subsurface accumulations, and do not allow the cylinders to be purged or depleted. We found that many published sampling methods give unreliable butane and propane isotopic data, especially for wet gases associated with liquid hydrocarbons due to pressure, volume, and temperature phase effects. In general, sampling procedures that allow flow through a sample cylinder or allow the cylinder to be purged often provide unreliable results.

CONCLUSIONS

Use of the carbon isotopic compositions of the wet gas components for correlating one reservoir gas with another and for estimating a gas's maturity has distinct advantages over using methane alone: more positive correlations generally can be made. These components also allow bacterial alteration, mixing from multiple sources, and thermal destruction to be more easily recognized. Specifically, the carbon isotopic compositions of propane, isobutane, and normal butane gen-

erally are the most valuable because of the source control they exhibit, although ethane is also helpful. When geochemical interpretations based on the wet gas components are combined with interpretations made on the associated liquids, the result is particularly powerful. Overall, use of the wet gas components for correlation generally outweighs the difficulty of obtaining representative samples of the accumulations.

Through the application of the correlation approach described here, it has been recognized in many sedimentary basins that hydrocarbons have migrated significant distances from their source, either vertically or laterally, depending on the stratigraphic and structural relationships within the area. As a result, the age of a reservoir frequently does not correspond with the age of the hydrocarbon source. In many areas, hydrocarbon mixtures from multiple sources (or source facies) are also common.

The three exploration examples presented here illustrate the necessity of integrating geochemical interpretations with a good understanding of the regional and detailed geology if a true understanding of the hydrocarbon source and level of maturity are to be attained for many hydrocarbon accumulations.

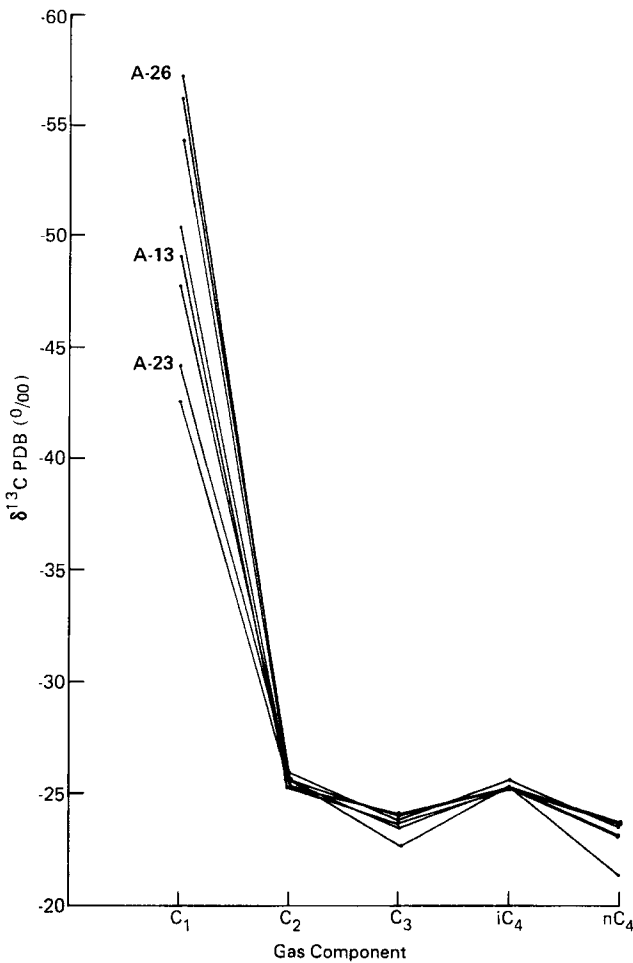


Figure 14—The carbon isotopic compositions of several gas mixtures in the Lena field.

REFERENCES CITED

- Boigk, H., W. Stahl, and R. Teichmüller, 1971, Oberkarbon im untergrund von Nordwestdeutschland—inkohlung und erdgas: Fortschritte in der Geologie von Rheinland und Westfalen, v. 19, p. 101–108.
- Burns, B. J., A. T. James, and J. K. Emmett, 1984, The use of gas isotopics in determining the source of some Gippsland basin oils: APEA Journal, v. 24, p. 217–221.
- Chung, H. M., J. R. Gormly, and R. M. Squires, 1988, Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotopic distribution, in M. Schoell, ed. Origin of methane in the earth, Chemical Geology, v. 71, p. 97–103.
- Colombo, U., F. Gazzarini, R. Gonfiantini, G. Sironi, and E. Tongiorgi, 1966, Measurements of C^{13}/C^{12} isotopic ratios on Italian natural gases and their geochemical interpretation, in G. D. Hobson and M. C. Lewis, eds., Advances in organic geochemistry, 1964: Oxford, Pergamon Press, p. 279–292.
- Creaney, S., 1989, The reaction of organic material to progressive geological heating, in N. D. Naeser and T. H. McCulloh, eds., Thermal history of sedimentary basins, 1989: New York, Springer-Verlag, p. 37–52.
- Creaney, S., and J. Allan, 1989, Hydrocarbon generation and migration in the Western Canada basin, in J. Brooks, ed., Classic petroleum provinces, Geological Society of London, p. 189–202.
- Deroo, G., T. G. Powell, B. Tissot, and R. G. McCrossan, 1977, The origin and migration of petroleum in the Western Canada sedimentary basin, Alberta: Geological Survey of Canada Bulletin 262, 136 p.

Table 6. Carbon Isotopic and Molecular Compositions of Selected Gases from Stacked Producing Intervals, Lena Field, Offshore Louisiana

Well	A-23	A-13	A-26
Reservoir Sand	B-50	B-40	B-5
True Vertical Depth (ft)	8411–8631	7971–8079	4930–4996
Molecular Composition (mole %)			
H ₂ S	tr*	0.00	0.00
CO ₂	0.27	0.32	0.21
N ₂	0.27	0.05	0.55
C ₁	95.18	94.90	97.49
C ₂	2.85	2.61	1.12
C ₃	0.83	1.05	0.35
iC ₄	0.18	0.29	0.09
nC ₄	0.19	0.32	0.09
iC ₅	0.07	0.17	0.04
nC ₅	0.04	0.08	0.02
C ₆₊	0.12	0.21	0.04
Carbon Isotopic Composition (‰, δ¹³C vs. PDB)			
Methane	-44.05	-48.99	-57.16
Ethane	-25.80	-25.14	-25.61
Propane	-23.74	-23.40	-23.69
Isobutane	-25.66	-25.29	-25.00
N-butane	-23.53	-23.31	-23.02
CO ₂	-11.57	-8.20	-11.83

*tr = trace.

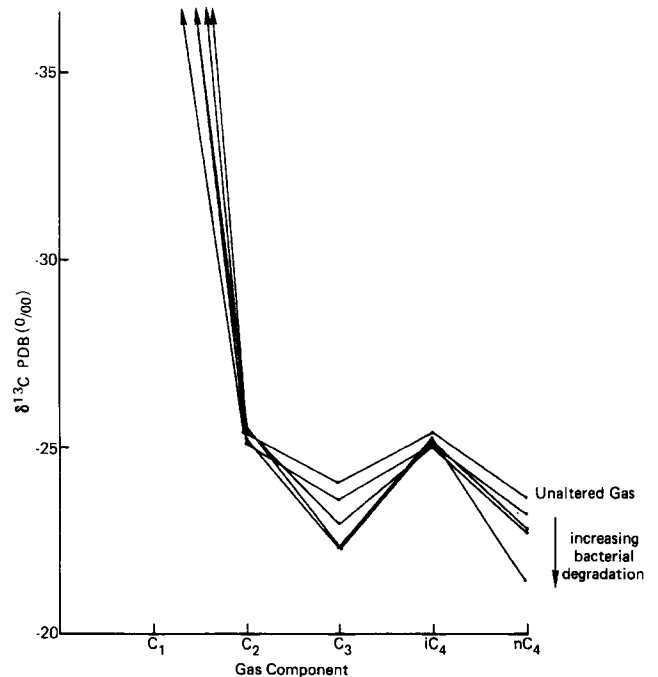


Figure 15—Lena field gases showing the effects of bacterial alteration.

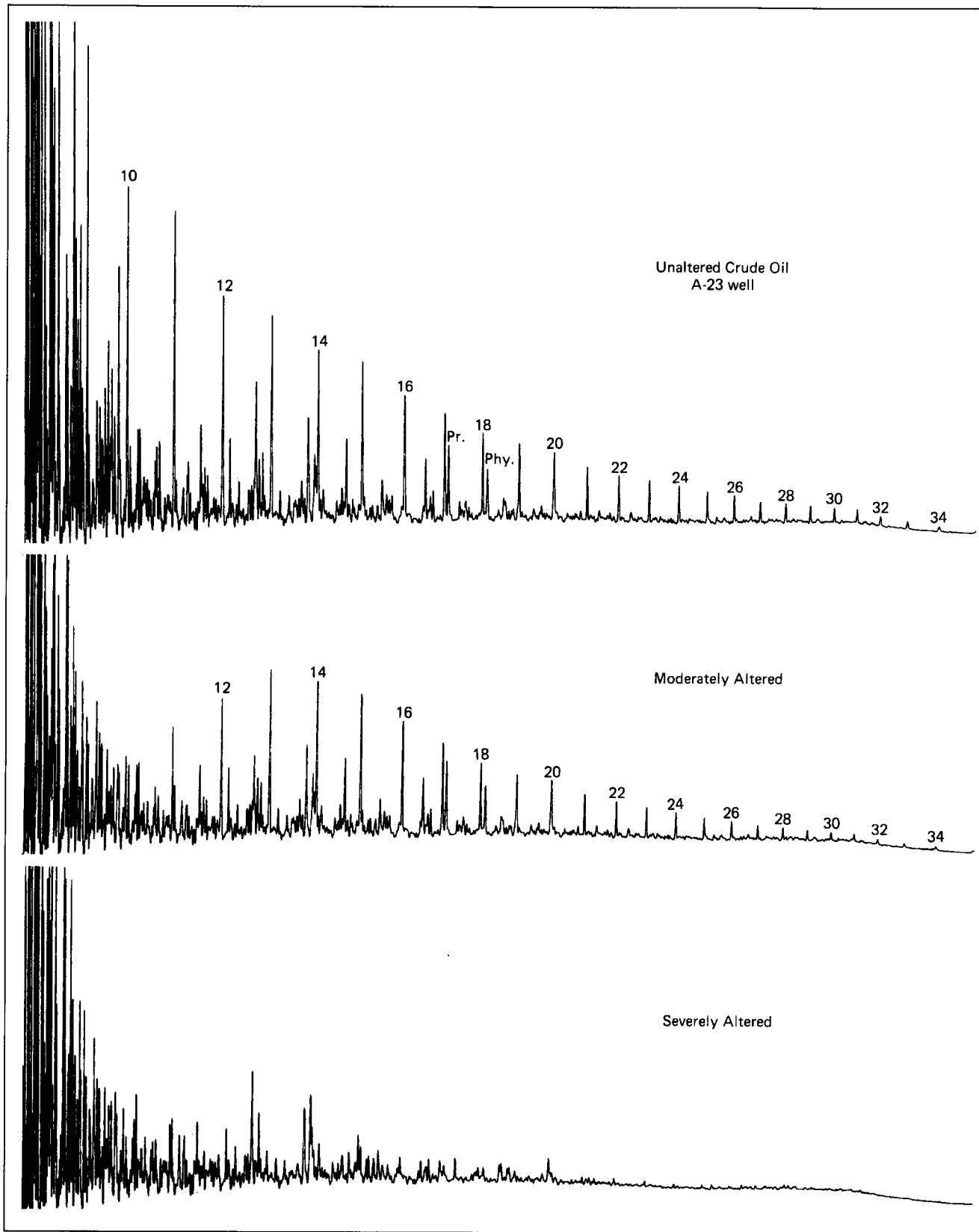


Figure 16—Whole-oil capillary gas chromatograms from the Lena field displaying a range of bacterial alteration. The location of the normal paraffins are indicated by their carbon numbers.

- Fuex, A. N., 1977, The use of stable carbon isotopics in hydrocarbon exploration: *Journal of Geochemical Exploration*, v. 7, p. 155–188.
- Galimov, E. M., 1988, Sources and mechanisms of formation of gaseous hydrocarbons in sedimentary rocks: in M. Schoell, ed. *Origin of methane of the earth*, *Chemical Geology* v. 71, p. 77–95.
- Galimov, E. M., G. I. Teplinskiy, Z. A. Tabassaranskiy, and E. Y. Gavrilov, 1973, On the conditions of formation of gas deposits in the eastern part of the Turan plate as revealed by the carbon isotopic composition of the gases: *Geochemistry International*, v. 10, p. 1259–1271.
- Gussow, W. C., 1955, Time of migration of oil and gas: *AAPG Bulletin*, v. 39, p. 547–574.
- Hood, A., C. C. M. Gutzjahr, and R. L. Heacock, 1975, Organic metamorphism and the generation of petroleum: *AAPG Bulletin*, v. 59, p. 986–996.
- James, A. T., 1983, Correlation of natural gas by use of carbon isotopic distribution between hydrocarbon components: *AAPG Bulletin*, v. 67, p. 1176–1191.
- James, A. T., and B. J. Burns, 1984, Microbial alteration of subsurface natural gas accumulations: *AAPG Bulletin*, v. 68, p. 957–960.
- Krouse, H. R., C. R. Viau, L. S. Eliuk, A. Ueda, and S. Halas, 1988, Chemical and isotopic evidence of thermochemical sulfate reduction by light hydrocarbon gases in deep carbonate reservoirs: *Nature*, v. 333, p. 415–419.
- Lopatin, N. V., 1971, Temperature and geologic time as factors in coalification: *Akademiya Nauk SSSR Izvestiya, Seriya Geologicheskaya*, no. 3, p. 95–106.
- Mattavelli, L., T. Ricchiuto, D. Grignani, and M. Schoell, 1983, Geochemistry and habitat of natural gases in Po basin, northern Italy: *AAPG Bulletin*, v. 67, p. 2239–2254.
- Pegrum, R. M., and T. E. Ljones, 1984, 15/9 gamma gas field offshore Norway, new trap type for North Sea basin with regional structural implications: *AAPG Bulletin*, v. 68, p. 874–902.
- Prasolov, E. M., and V. A. Lobkov, 1977, On the conditions of methane formation and migration (according to isotopic composition of carbon): *Geokhimiya*, no. 1, p. 122–135.
- Rice, D. D., 1983, Relation of natural gas composition to thermal maturity and source rock type in San Juan basin, northwestern New Mexico and southwestern Colorado: *AAPG Bulletin*, v. 67, p. 1199–1218.
- Schoell, M., 1977, Natural gases in the south German Molasse basin—application of D/H and $^{13}\text{C}/^{12}\text{C}$ isotopic analyses to deduce their origin: *Erdoel-Erdgas Zeitschrift*, v. 93, p. 311–322.
- Schoell, M., 1983a, Genetic characterization of natural gases: *AAPG Bulletin*, v. 67, p. 2225–2238.
- Schoell, M., 1983b, Isotopic techniques for tracing migration of gases in sedimentary basins: *Journal of the Geological Society of London*, v. 140, p. 415–522.
- Stahl, W. J., 1977, Carbon and nitrogen isotopics in hydrocarbon research and exploration: *Chemical Geology*, v. 20, p. 121–149.
- Stahl, W., and B. D. Cary, Jr., 1975, Source-rock identification by isotopic analysis of natural gases from fields in the Val Verde and Delaware basins, west Texas: *Chemical Geology*, v. 16, p. 257–267.
- Stoakes, F. A., and S. Creaney, 1984, Sedimentology of a carbonate source rock: Duvernay formation of central Alberta, in L. Eliuk, ed., *Carbonates in subsurface and outcrop*: Canadian Society of Petroleum Geologists Core Conference Proceedings, p. 132–147.
- Sundberg, K. R., and C. R. Bennett, 1983, Carbon isotopic paleothermometry of natural gas: in M. Bjorøy, ed., *Advances in organic geochemistry*, 1981: Chichester, John Wiley, p. 769–774.