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Origins, Characteristics, Evidence For, and Economic Viabilities of Conventional and Unconventional Gas Resource Bases

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GEOLOGIC CONTROLS OF DEEP NATURAL GAS RESOURCES IN THE UNITED STATES

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ABSTRACT

A strong zonation of oil and gas deposits exists in many petroleum basins, with only "dry" gas in deep-basin reservoirs and increasing amounts of oil at shallower depths. Also, both API gravity and gas-oil ratios of oil deposits decrease toward shallower depths on the basin shelves, away from the deep basin. Previously, this basinal hydrocarbon zonation has been taken as prima facie evidence that dry gas (methane) was being formed from the thermal destruction of C_{15+} hydrocarbons (oil) in the deep basin; however, (1) the persistence of C_{15+} hydrocarbons to great depths (7–10 km) and extreme maturation ranks ($R_o=5.0-7.0$ percent) in petroleum basins and (2) methane carbon-isotopic compositions in the Anadarko Basin and from aqueous-pyrolysis experiments strongly argue against the above hypothesis of deep-basin methane resulting from C_{15+} hydrocarbon thermal destruction. Instead, a model is favored wherein most deep-basin methane has simply been generated from kerogen during the C_{15+} hydrocarbon generative phase. The invariably observed basinal zonation of hydrocarbons is hypothesized to result from condensation, buoyancy, and separation-migration processes.

In the deep basin, only methane remains in the gas phase due to high fluid pressures. The C_2-C_4 hydrocarbon gases are condensed into, and behave as, a liquid phase. With continued C_{15+} hydrocarbon (and methane) generation in the deep basin, eventually all (or most) deep-basinal traps are filled to the spill point with methane, and all other fluids (oil, condensed C_2-C_4 hydrocarbon gases, and water) are displaced out of the deep basin to shallower traps on the stable shelves of petroleum basins by differential entrapment. These processes are driven by buoyancy differences within the fluids and because methane "rides over," or is found on top of, all other fluids in the deep basin.

Evidence suggests that water may have been flushed from some (many?) deep-basinal traps by methane, as hypothesized. Both carbon dioxide and hydrogen sulfide are present in abundance in some deep-basin gas reservoirs and

would have existed in those reservoirs for tens to hundreds of millions of years. Because these gases are highly soluble in water, their presence dictates that water is not in contact with such gas reservoirs. The absence of water in some deep-basinal gas reservoirs carries implications for the deep-basin gas resource base, two of the more important of which are that (1) hydrocarbon thermal-cracking reactions are promoted in these water-free environments, and (2) when water is introduced into such reservoirs during drilling and completion operations, in some cases significant reservoir damage could occur in a skin around the wellbore from the principles of two-phase-fluid flow and the Jamin effect. Such reservoir damage, if it occurs, could greatly harm gas productivities, which could lead to an underestimation of the recoverability and economic viability of certain deep-basin gas-resource bases and the condemnation of both individual wells and prospects.

As stated, it is hypothesized here that most deep-basinal gas deposits have originated from methane generation that accompanies C_{15+} hydrocarbon generation in source rocks combined with condensation-buoyancy-separation-migration processes. Carbon-isotopic values of methane and carbon dioxide in some deep-basinal gas deposits demonstrate, however, that high-rank dry-gas deposits do exist which have originated from C_{15+} hydrocarbon thermal destruction. Such deposits do appear to be unusual, however.

It is postulated that gas expulsion from the source rock, like oil expulsion, is significantly less efficient than generally perceived. It is also hypothesized that gas expulsion would be greatly facilitated by major faulting (with accompanying large-scale fracturing). Such faulting would physically disrupt source rocks (and the rocks adjacent to them) to allow gas to escape in significant volumes. Therefore, a "rule of thumb" concerning deep-gas deposits, is that large "conventional" deep-gas deposits (not tight gas, basin-centered gas, and so forth) should always be associated with major faults.

One of the hypotheses serving as a foundation for the preceding rule of thumb is that deep petroleum basins are

more of a "closed system," with regard to fluid flow and fluid expulsion from source rocks, than generally envisioned. Current petroleum geologic-geochemical thought generally models deep petroleum basins as open systems that allow efficient hydrocarbon expulsion and flow of deep-basin fluids to proceed, for the most part, unabated through geologic time. There is, however, strong evidence against this viewpoint, evidence that supports the proposition that deep basins are primarily closed systems in regard to fluid flow. If this latter viewpoint more closely approximates the natural system, then much more of the gas generated in deep basins will have been retained in the deep basins than previously perceived. This possibility carries the implication that much larger and much higher grade deep-basin gas-resource bases may exist than previously envisioned. In point of fact, monstrous in-place gas-resource bases have already been proven, such as coal-gas, tight-gas, basin-centered gas, Gulf Coast geopressured-geothermal gas, and so forth. The very existence of these various gas-resource bases validates the proposition that deep basins are much more of a closed system with regard to fluid flow than has been previously portrayed by some basinal models.

It is the principal recommendation of this paper that geologic-based engineering studies be instituted to ascertain if wider spread commercially viable production of such in-place unconventional gas-resource bases is possible. Significant production of such unconventional in-place gas (and oil) resource bases at this point may be the only avenue by which the United States can significantly curtail an increasing dependence on the Middle East for its energy needs.

INTRODUCTION

The important parameters controlling the generation of hydrocarbon gases and their accumulation must be understood to correctly assess the potential of both conventional and unconventional deep-basin gas-resource bases. Such an understanding necessitates discussion of a number of diverse geologic and geochemical topics.

A simplified model for the origin of methane in conventional gas deposits is that methane can (1) originate as biogenic methane, (2) be cogenerated with C_{15+} hydrocarbons in the source rock and move to a gas and oil or gas reservoir, (3) originate from in-reservoir thermal destruction of a deep oil deposit to a dry gas (principally methane) deposit, (4) originate from C_{15+} hydrocarbon destruction from the hydrocarbons remaining in deeply buried fine-grained rocks, (5) originate from remnant hydrocarbon-generation potential remaining on high-rank kerogen after mainstage C_{15+} hydrocarbon generation is mostly complete, or (6) originate from any combination of the above. Most deeply buried dry-gas deposits are thought to originate by in-reservoir conversion of oil to methane beginning at about vitrinite reflectance (R_o) values of 0.9 percent (Tissot and Welte, 1984). Two facts

argue strongly against this hypothesis: (1) C_{15+} hydrocarbons are thermally stable in deep-basinal situations to vitrinite reflectance values of 7.0–8.0 percent (Price, this volume), and (2) in the C_{15+} hydrocarbon destructive phase both the C_{15+} hydrocarbons and the generated methane have distinct compositional and (or) carbon isotopic overprints, rarely observed in methane of deep-basin dry-gas deposits. These two facts thus suggest that there must be another process, or processes, responsible for the origin of deep-basin gas deposits. Such possible processes are examined herein.

C_{15+} HYDROCARBON THERMAL STABILITY

It is widely accepted in petroleum geochemistry that oil in deeply buried reservoirs begins to meaningfully thermally decompose to methane at $R_o=0.9$ percent and totally decomposes to methane (or other hydrocarbon gases) by $R_o=1.35$ percent and that this process is responsible for the formation of most deep-basin dry-gas deposits. Price (1993, this volume) demonstrated, however, that C_{15+} hydrocarbons are thermally stable in nature to $R_o=7.0-8.0$ percent. The large body of data supporting Price's conclusion strongly conflicts with a hypothetical model originally proposed to explain certain observations from nature, a model that predicts the total thermal destruction of C_{15+} hydrocarbons by $R_o=1.35$ percent. Given a contradiction between a large, internally consistent body of data and a hypothetical model, I lean toward reexamination of the model. It is thus a premise herein that, based on the data of Price (1993, this volume), the generally accepted model for the formation of dry-gas deposits may be erroneous. It is also hypothesized that processes other than C_{15+} hydrocarbon thermal destruction at $R_o=1.35$ percent are responsible for the large body of convincing data, in the form of strongly delineated zonations of oil and gas versus maturation rank in petroleum basins, commonly cited as evidence to support the accepted model.

BASINAL OIL AND GAS ZONATION

A paucity of oil deposits in high-rank coarse-grained rocks is another persuasive and primary line of evidence, together with reduced hydrocarbon concentrations in fine-grained rocks containing type III organic matter at $R_o=0.9$ percent, supporting the hypothesis of C_{15+} hydrocarbon thermal instability in the vitrinite reflectance range of 0.9–1.35 percent. As discussed in Price (1991), however, this sparsity of oil deposits in high-rank rocks can be explained by two other processes.

First, during vertical oil migration and emplacement, abnormal fluid pressures of deep-basin rocks would prevent oil from entering such rocks. As such, oil would be vertically

bypassed to shallower, hydrostatically pressured rocks during compaction, oil-expulsion, and emplacement processes. Secondly, as discussed in Price (this volume), increasing amounts of methane are cogenerated with C₁₅₊ hydrocarbons through all stages of hydrocarbon generation, and significant amounts of methane are generated during the end stages of C₁₅₊ hydrocarbon generation. Also, in some cases, true high-rank methane (“dry gas”) indeed is generated at great depths in some sedimentary basins by thermal destruction of C₁₅₊ hydrocarbons (discussed following). Any methane streaming out of the deep basin from either source will displace oil from any deep-basin, high-rank reservoirs to shallower basinal depths by Gussow’s (1954) principle of differential entrapment (buoyancy). It must be stressed that water will also be displaced from deep-basin reservoirs (even before oil, because of the buoyancy differences between water and oil) by Gussow’s principle. Furthermore, methane gas has the ability to dissolve and transport water in solution (fig. 1), an ability that dramatically increases with increasing temperature. Thus, some (many?) deep-basin gas reservoirs may be expected to be water free. Any entry of gas into deep-basin oil reservoirs also causes asphaltene precipitation (“desasphalting”) from the oil onto the reservoir rock. Such asphaltenes in such a water-

free environment would undergo enhanced maturation reactions because of the lack of water in the system (Price, this volume), resulting in a pyrobitumen char.

The end result of these processes is a strong basinal segregation of hydrocarbon fluids. Oil would be in reservoirs at shallow and moderate depths on the stable shelves of petroleum basins, and dry gas would be in deep-basin reservoirs, some of which would also contain a charred pyrobitumen. Furthermore, as discussed in Price (1980a), the oil deposits would also exhibit a zonation: Both gas-oil ratios and API gravities would greatly decrease with increasing distance from the basin center. Such decreases would be due to two causes. First, with increasing distance of secondary migration, lighter fractions (including hydrocarbon gases) would be progressively lost from oils. Second, the most distant oils from the deep basin would be the oils generated first by any given source rock. Oils generated later by the same source rock would be more mature, and contain higher percentages of lighter fractions, than the first-generated oils, and would be closer to the basin deeps than the first-generated oils. The end hydrocarbon distribution (fig. 2) in a basin would clearly appear to be due to thermal destruction of oil at high maturation ranks; however, this distribution could also be explained by other processes operative in petroleum basins, including those in which fluid buoyancy plays a key role. Furthermore, the hydrocarbon distribution shown in figure 2 will independently result from these processes irrespective of any contributions from C₁₅₊ hydrocarbon thermal destruction.

The C₂-C₄ hydrocarbon gases would also be flushed by methane from the deep-basin reservoirs in some basins. Salisbury (1968) discussed the strong zonation of oil and gas in Silurian and Devonian reservoirs of the West Texas Permian Basin. He noted that methane has a very low critical temperature as compared to the other (C₂-C₄) hydrocarbon gases, and, thus, although methane is always in the gas phase under the pressure-temperature conditions of the West Texas Permian Basin deep-basin gas reservoirs, the C₂-C₄ hydrocarbon gases are condensed in the liquid phase. As such, the C₂-C₄ hydrocarbon gases in deep-basin reservoirs are subject to the same separation-migration phenomena as oil by Gussow’s (1954) principle of differential entrapment. It is important to realize that such condensation-buoyancy-driven hydrocarbon-gas migrations cause the zonation of dry gas deposits (high concentrations [98+ percent] of methane in the gas, relative to the other hydrocarbon gases) observed in many deep petroleum basins, irrespective of any contribution from the thermal destruction of C₂+ hydrocarbons. A high concentration of methane (≥98 percent) in a gas deposit by itself cannot be taken as absolute evidence of a high-rank origin for the methane. In fact, data discussed following strongly suggest that much (most?) dry gas in deep-basin reservoirs has originated from condensation-separation-migration processes, with no or little contribution from C₁₅₊ hydrocarbon thermal-destruction reactions.

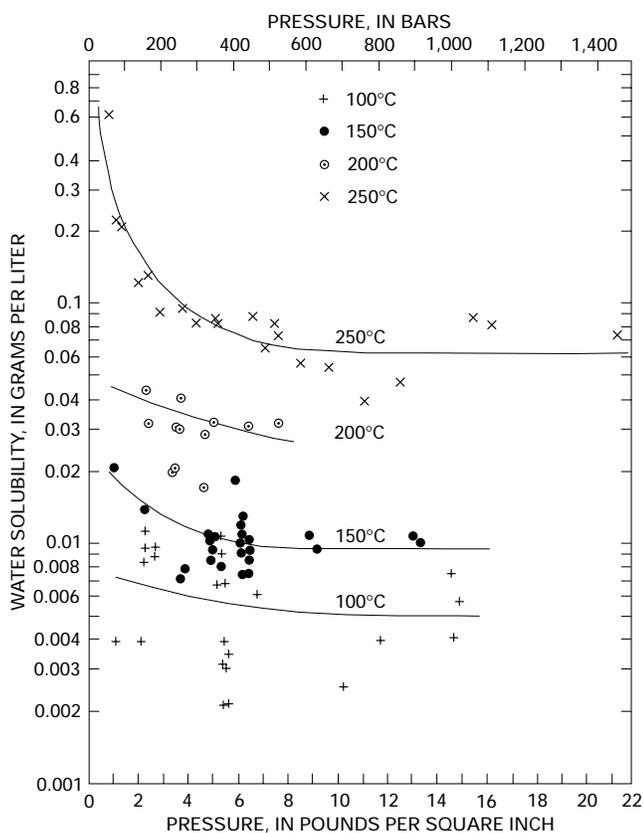


Figure 1. Solubility of water in methane at four different isotherms as a function of pressure. Data from Price and others (1983).

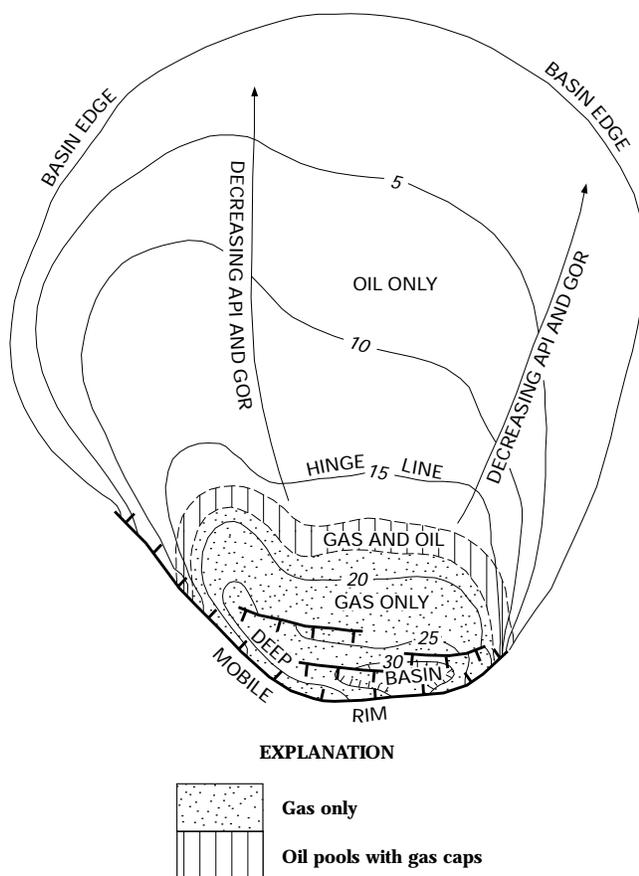


Figure 2. Plan view of a hypothetical basin showing oil and gas distribution in any one formation expected from the application of the model presented herein. Contours are total sediment thickness in thousands of feet. Faults (shown by hachured lines) dip back into the deep basin and transport hydrocarbons from this area; hydrocarbons move from the faults into carrier beds, resulting in the hydrocarbon distribution shown in the figure. The dashed boundaries signify the approximate nature of this hydrocarbon distribution. API is API oil gravity, and GOR is gas-oil ratio.

The proposition is easily tested if the lack of deep-basin, high-rank oil is due to buoyancy displacement by methane or to in-reservoir conversion of oil to high-rank methane. Methane gas has the capacity to dissolve C_5+ hydrocarbons in solution (Price and others, 1983). Buoyancy displacement of oil by methane would still leave small, but measurable, concentrations of C_{15+} hydrocarbons dissolved in dry-gas deposits. In-reservoir conversion of oil to high-rank methane should result, on the other hand, in the total destruction of C_{15+} hydrocarbons. Cold trapping or filtration of a pressurized gas stream from a high-rank gas deposit would isolate any C_{15+} hydrocarbons dissolved in the methane, such that they could be quantitatively and qualitatively analyzed.

In point of fact, such an investigation has already been carried out. A senior petroleum geochemist, recently retired from a major oil company, informed me of a study he helped

carry out wherein dry gases from about 20 different high-rank gas deposits from Texas and Oklahoma were analyzed by mass spectrometry for C_5+ hydrocarbons. A full suite of oil components was found in all these gases. Analysis of the biomarkers showed all entrained oils to be "normal" and only moderately mature, with one exception, which showed slight thermal stress. The principal conclusion from that study was that only one of the "high-rank" gas deposits analyzed had any possible contribution of methane from the thermal destruction of higher molecular weight hydrocarbons.

Compaction, migration, emplacement processes, and gas flushing by buoyancy differences all displace oil (and C_2-C_4 hydrocarbon gases) from the deep basin. Thus, it is unlikely that large, deep-basin, high-rank oil deposits will be routinely discovered. Isolated cases of high-rank oil do, however, exist. Stahl (1974) described oil produced at 7,300 m ($R_o=3.50$ percent) by the Lonestar Baden-1 wellbore, Anadarko Basin, Oklahoma. Horsfield and others (1992) described an oil field discovered by the Saga Petroleum 2/4-14 wellbore at 4,300 m in the North Sea, an oil field that lies beyond the postulated thermal deadline for C_{15+} hydrocarbons. Vitrinite reflectance profiles have been extrapolated from Tertiary–Upper Cretaceous rocks containing type III organic matter in the Williston Basin to deeper oil-bearing carbonate reservoir rocks (Price and others, 1986, figs. 19–21). Such extrapolations lead to the conclusion that oil is produced in reservoirs on the American side of the Williston Basin at vitrinite reflectance values significantly above 1.35 percent.

HIGH-RANK GAS COMPOSITION

Data from both nature and aqueous-pyrolysis experiments of Wenger and Price (1991) and Price and Wenger (1992) provide insight to the relative control of hydrocarbon cracking versus condensation-buoyancy-migration processes on high-rank gas composition. In the aqueous pyrolysis experiments, different "rates" of methane generation are found at experimental temperatures lower than about 320°C as compared to temperatures above 320°C (fig. 3). The rate of methane generation (slope of the curve versus temperature) decreases at the higher experimental temperatures, which are in the C_{15+} hydrocarbon thermal destructive phase. The rate is lower at higher experimental temperatures because the Phosphoria Shale kerogen has lost almost all its capacity for hydrocarbon generation, as reflected by the kerogen's low atomic hydrogen to carbon ratios (table 1). Thus, in the thermal destructive phase, any hydrogen that is used to make methane, the most hydrogen rich of all hydrocarbons, must be scavenged from previously generated products, resulting in charring (formation of pyrobitumen) during hydrocarbon thermal destruction. Figure 3 also shows that first detectable onset of thermal destruction (break in the slope of the curve at 320°C) clearly overlies the maximum in

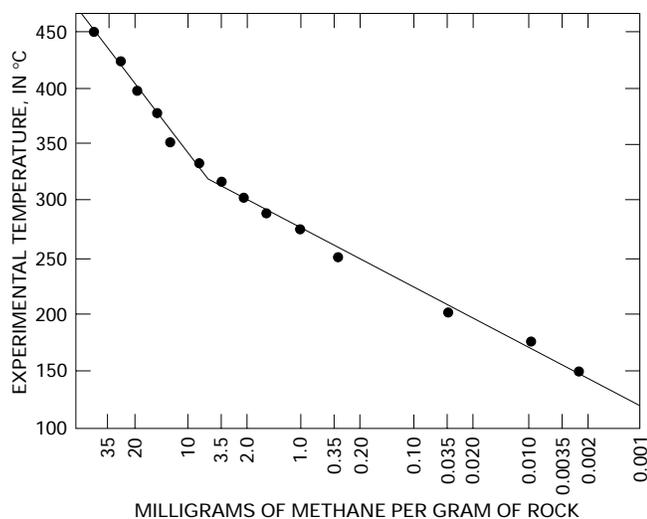


Figure 3. Methane generated, versus experimental temperature, during aqueous-pyrolysis experiments performed on the Retort Phosphatic Shale Member of the Lower Permian Phosphoria Formation.

hydrocarbon generation for the rock (Price, this volume, fig. 8) and, by 350°C, the experimental system is well into hydrocarbon thermal destruction.

In the experiments, changes in both the carbon isotopic values of methane and the gas wetness values for the generated gases accompanied C₁₅₊ hydrocarbon thermal

destruction (fig. 4). Carbon isotopic values, which progressively became slightly more negative during hydrocarbon generation, progressively became much less negative (enriched in carbon-13) during hydrocarbon thermal destruction. The hydrocarbon gases became progressively wetter (enriched in C₂-C₄ hydrocarbon gases) during hydrocarbon generation, but this trend also reversed during hydrocarbon thermal destruction, and the hydrocarbon gases progressively became enriched in methane as hydrogen was scavenged from all other entities in the system.

Rice and others (1988) provided a large data base for natural gases from different areas of the Anadarko Basin (fig. 5). Although some scatter is present, methane content in the gases clearly increases as the carbon-13 isotope increases in the methane (fig. 5), especially for fields from the central basin. This trend of hydrocarbon gases becoming both "drier" (enriched in methane) and enriched in the carbon-13 isotope with increasing rank has long been recognized (Tissot and Welte, 1984). Previously, this trend was attributed solely to thermal destruction of the C₂₊ hydrocarbons; however, if similar data from the aqueous-pyrolysis experiments of Wenger and Price (1991) and Price and Wenger (1992) on the Phosphoria Shale are plotted with the data of Rice and others (1988), the two data sets plot in distinctly different fields (fig. 6). The data do, however, trend in the same direction in the hydrocarbon thermal destructive phase of the aqueous-pyrolysis experiments (experimental temperatures $\geq 320^\circ\text{C}$).

Table 1. Geochemical data for Soxhlet-extracted rock samples of the Phosphoria Formation after aqueous pyrolysis and for kerogens isolated from those rocks.

[H/C is kerogen atomic hydrogen to carbon ratio. HI and OI are Rock-Eval hydrogen and oxygen indices, respectively, of the reacted rock. TOC is total organic carbon of the rock (in weight percent). S2 and S3 are Rock-Eval S2 and S3 pyrolysis peaks (in milligrams per gram of Soxhlet-extracted rock). Tmax is the maximum of the Rock-Eval S2 pyrolysis peak (in ∞C)]

	H/C	HI	OI	TOC	S2	S3	Tmax
RAW	1.29	451	30	21.41	96.58	6.44	418
175°C, 4.32 bars	1.23	507	21	20.12	102.06	4.21	418
200°C, 6.36 bars	1.24	481	18	20.28	97.56	3.55	418
250°C, 14.5 bars	1.16	485	14	15.39	74.66	2.13	429
275°C, 22.3 bars	1.04	330	17	15.18	50.03	2.57	433
287°C, 31.0 bars	0.67	209	12	11.45	23.98	1.35	430
287°C, 366 bars	0.99	248	13	14.83	36.72	2.00	428
287°C, 681 bars	0.99	279	15	13.76	38.37	2.07	427
287°C, 965 bars	1.19	371	22	18.52	68.62	4.08	421
300°C, 41.4 bars	0.78	165	9	11.32	18.69	1.06	437
316°C, 58.2 bars	0.63	108	8	11.66	12.64	0.92	450
333°C, 80.8 bars	0.63	69	5	12.70	8.77	0.64	463
350°C, 118 bars	0.52	25	4	15.54	3.91	0.65	582
350°C, 442 bars	0.51	27	2	15.34	4.18	0.29	575
350°C, 782 bars	0.48	29	3	14.98	4.31	0.41	578
350°C, 1077 bars	0.59	62	3	13.76	8.49	0.38	466
375°C, 132 bars	0.45	10	2	16.57	1.67	0.27	585
400°C, 144 bars	0.41	6	1	17.58	1.12	0.21	598
425°C, 160 bars	0.36	3	2	18.00	0.46	0.34	599
425°C, 551 bars	0.36	6	2	17.21	1.05	0.26	598
450°C, 190 bars	0.31	2	1	16.62	0.26	0.17	--

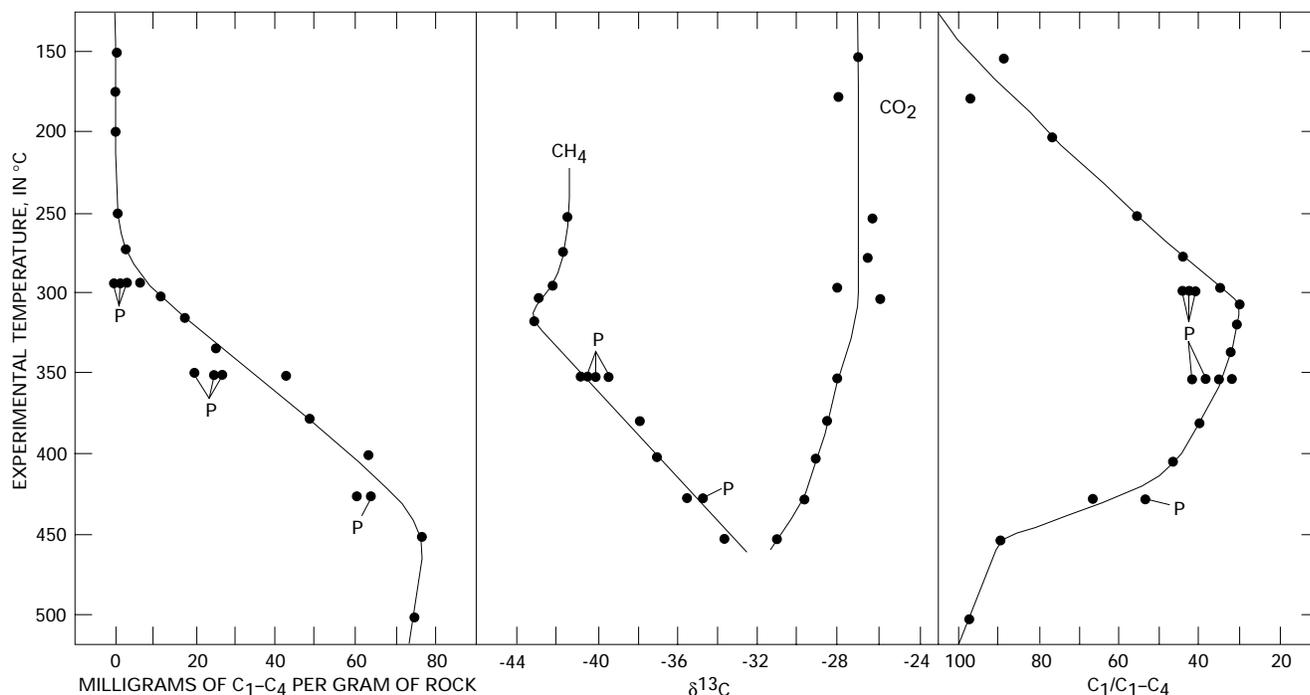


Figure 4. C₁-C₄ hydrocarbon gases generated per gram of rock (mg C₁-C₄/g RX); carbon-isotopic (δ¹³C) values for methane and carbon dioxide; and the normalized weight percent of methane to the sum of methane through the butanes (C₁/C₁-C₄) versus experimental temperature for aqueous-pyrolysis experiments performed on the Phosphoria Formation shale. P refers to data points from pressurized experiments (see Price, this volume).

It has been conclusively demonstrated that large percentages of conventional gas deposits in basins worldwide consist of significant contributions from dry (methane-rich) bacterial gases having carbon-13 isotopic values of -80 to -60 (Rice, 1980; Rice and Claypool, 1981; Mattavelli and others, 1983). Thus, methane carbon-13 isotopic variations of gas deposits in nature can be strongly influenced by the amount of biogenic gas incorporated into the deposit. Gas from the aqueous-pyrolysis experiments is, however, only thermogenic gas because no biogenic gas is in the system. This is because all of the indigenous gas, including biogenic gas, in the experimental rocks was lost from the rocks from two causes before the experiments. First, most gas from rocks is lost to the drilling mud as a result of large pressure decreases during the rock's trip up the wellbore during drilling. Second, all experimental rocks were ground to 0.015 mm and less before experiments. Also, in nature, mixing of thermogenic gases from different sources may occur during gas migration, but such mixing is not present in the aqueous-pyrolysis experiments. Even with these qualifications, however, certain insights arise from a comparison of experimental gas data and natural gas data. For example, the gas data from the aqueous-pyrolysis experiments suggest that C₂-C₄ hydrocarbon gases are thermally stable at experimental temperatures greater than those equivalent to true greenschist-facies rock metamorphism in nature (experimental temperatures ≥375°C). The aqueous-pyrolysis gas data

thus support the hypothesis that in most cases the high methane content of dry gases from nature is not necessarily related to hydrocarbon thermal stability (destruction of C₂+ hydrocarbons, discussed following). The data of Rice and others (1988), when plotted versus depth, also support this proposition (discussed following).

On a detailed scale, different paleogeothermal gradients may be present within the greater Anadarko Basin; however, vitrinite reflectance data of Cardott and Lambert (1985) demonstrate that on a gross scale maturation-rank profiles (and thus paleogeothermal gradients and paleo-heat flow) are remarkably uniform throughout the basin (fig. 7) because these data exhibit a strong correlation to increasing depth ($r=0.958$) despite the fact that the samples are from widely separated geographic locations in the basin. Furthermore, the vitrinite reflectance data of Cardott and Lambert (1985) closely parallel vitrinite reflectance versus depth data that I have gathered from the deep Bertha Rogers-1 wellbore in the Anadarko Basin. Thus, in the Anadarko Basin, on a gross scale, depth may be taken as a measure of maturation rank.

If high methane concentrations in deep-basin gas deposits in the Anadarko Basin were due to hydrocarbon thermal destruction, then both the percentage of methane in the gas deposits and the amount of the carbon-13 isotope in the methane molecules would (1) increase versus depth and (2) exhibit decreasing scatter versus depth. If, however, the high methane content of deep-basin gas deposits is principally due

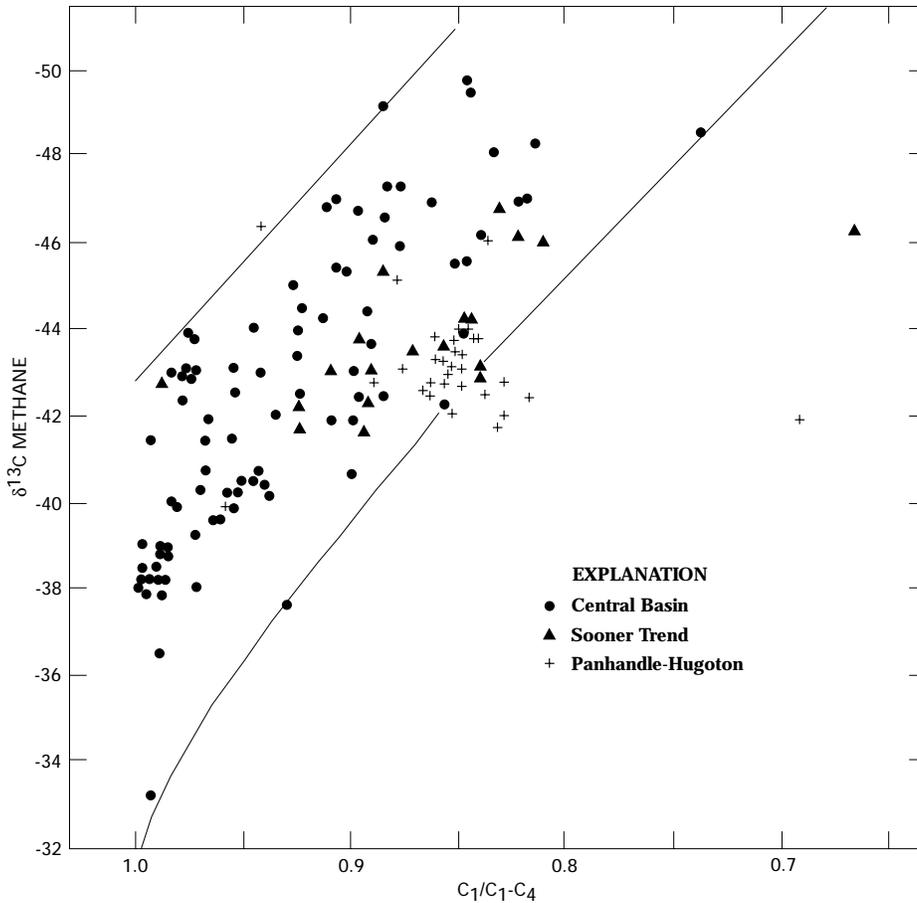


Figure 5. $\delta^{13}\text{C}$ for methane, versus volume percent ratio of methane to methane + ethane + propane + butanes (C_1/ C_1-C_4), for produced natural gases of the Anadarko Basin. Data from Rice and others (1988).

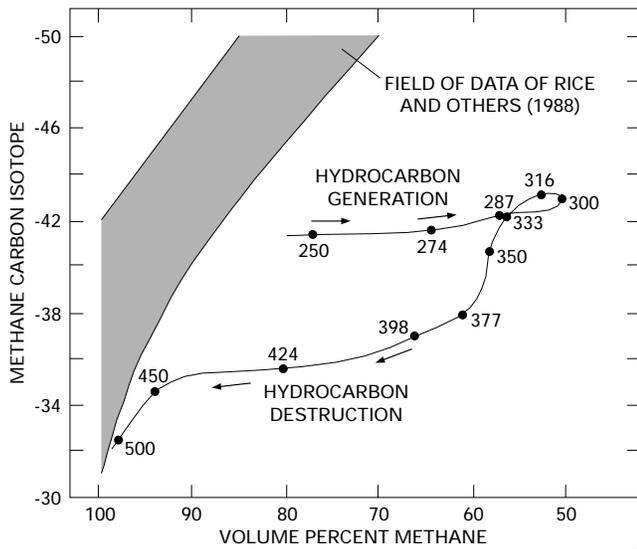


Figure 6. $\delta^{13}\text{C}$ for methane versus volume percent ratio of methane to methane+ethane+propane+butanes (C_1/ C_1-C_4) for produced natural gases of the Anadarko Basin (Rice and others, 1988) and for hydrocarbon gases generated in aqueous-pyrolysis experiments performed on the Phosphoria Formation shale. Numbers are experimental temperatures ($^{\circ}\text{C}$); arrows indicate trends in the experimental data.

to condensation-buoyancy-migration processes, then only the percentage of methane in the gas deposits would demonstrate a significant increase versus depth; methane carbon isotopes would not necessarily become heavier with increasing depth. Methane content would increase versus depth because increasing fluid pressure would cause increasing condensation of C_2+ hydrocarbon gases into a liquid-oil phase. That liquid phase could then be displaced to shallower traps by Gussow's (1954) principle of differential entrapment as more methane entered the deeper reservoir. In figure 8, at depths of 3,657 m (12,000 ft) and deeper (and especially beyond 4,270 m, 14,000 ft), there is a pronounced trend of increasing methane content in the gases whether one chooses the dashed or solid envelope. Furthermore, below 4,270 m (14,000 ft), the amount of scatter in the data significantly decreases versus depth. At 3,657 m (12,000 ft) and deeper, however, the methane $\delta^{13}\text{C}$ values exhibit significant scatter and do not demonstrate a pronounced trend of becoming less negative with increase in depth. Thus, the data of figure 8 suggest that the characteristics of high-rank gas deposits in the deep Anadarko Basin are not related solely, or perhaps even significantly, to hydrocarbon thermal destruction. Furthermore, trends in the methane compositional data of figure 8 (with the exception of a few data

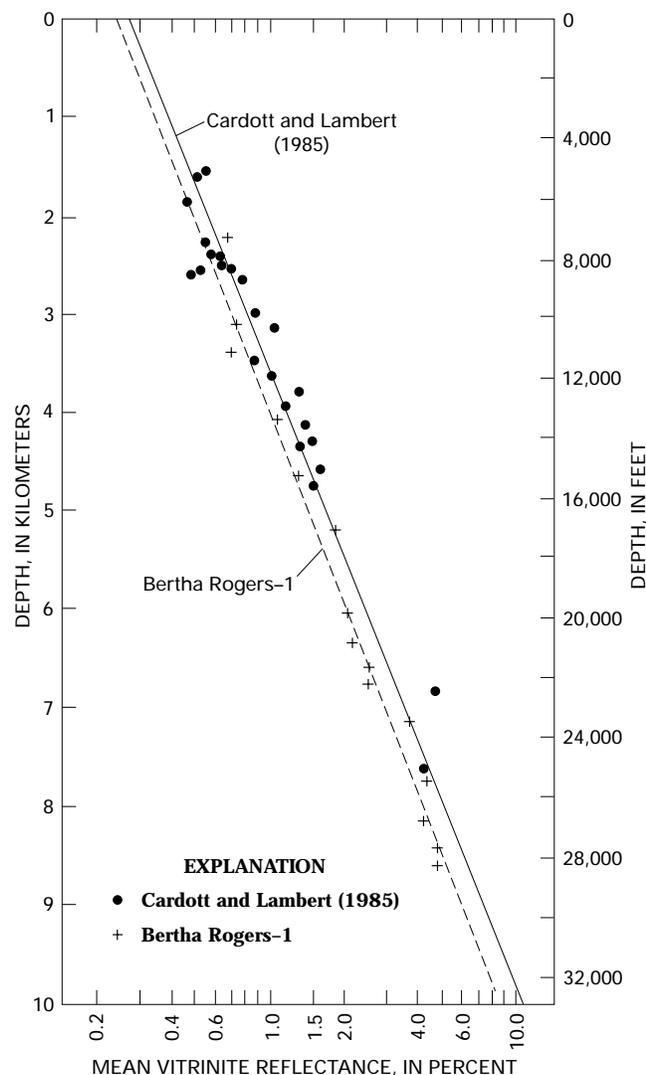


Figure 7. Vitrinite reflectance, versus depth, for the Lower Mississippian and Upper Devonian Woodford Shale for samples from Anadarko Basin (dots and solid line) from the data of Cardott and Lambert (1985). Vitrinite reflectance data from Bertha Rogers-1 (crosses and dashed line) shown for comparison. The dashed line has a correlation coefficient of $r=0.989$ to the crosses. The solid line has a correlation coefficient of $r=0.958$ to the dots.

points indicated by arrows) behave as would be expected if condensation-buoyancy-migration processes were primarily responsible for the compositional characteristics of the deeply buried high-rank gases.

The three deep sample points (indicated by arrows, fig. 8) are exceptions to the trend of increasing methane content with increasing depth and may offer some insight into the natural system. First, the elevated amounts of C_2+ hydrocarbons and moderately negative $\delta^{13}C$ values in these three samples both argue against an origin of these gases from hydrocarbon thermal destruction. Second, the model for gases of condensation, separation by buoyancy, and

migration as discussed above a priori assumes laterally continuous migration paths for the hydrocarbons. In such cases, after a trap is filled with methane, the displaced oil (including C_2+ hydrocarbons condensed in the liquid phase) would migrate to a shallower trap, updip from the original trap. If, however, the original trap becomes isolated from a lateral migration path (a closed system) and has no updip outlet, then the trap would quickly become overpressured, could not accept more fluid migration into it, and could not expel fluids from it, thus retaining abnormally high concentrations of C_2+ gases for the trap depth. If the sample set compiled by Rice and others (1988) is a valid representation of all gas deposits in the Anadarko Basin, and there is no reason to think that it is not, then by the preceding reasoning, most gas deposits in the basin would belong to laterally continuous migration paths (relatively open systems), and only a minority of gas deposits would be isolated closed systems. The deep (7,300 m, $R_o=3.50$ percent) oil deposit intersected by the Lonestar Baden-1 wellbore (Stahl, 1974) (discussed earlier) is another example of a closed or isolated trap that prevented gas flushing of reservoir C_2+ hydrocarbons.

Comparison of carbon isotopes (fig. 9) of methanes generated in aqueous-pyrolysis experiments performed on rocks containing six different types of organic matter (see Price, this volume), table 1, to the data of Rice and others (1988) (figs. 5, 8) provides further insight into the natural system. Figure 9 shows that carbon isotopic values for methane from the different rocks at a given temperature vary widely. The Eocene Green River Shale (type I organic matter), the Los Angeles Basin mid-Miocene shale, and the lignite (type IV/III organic matter) are, however, atypical source rocks. The organic matter in shale from the Mississippian-Devonian Bakken Formation, the Phosphoria Shale (except for its highly sulfur rich nature), and the Pennsylvanian Anna Shale is more representative of a typical marine source rock. In the experimental temperature range over which C_{15+} hydrocarbon generation occurs in these rocks ($250^\circ C-333^\circ C$), methane carbon isotopes range only from -43.3 to -40.0 . Methane carbon isotopic experimental data from other source rocks are necessary before more trustworthy conclusions can be drawn. As a first approximation, however, let us expand the $\delta^{13}C$ range of values for methane from these three rocks slightly from -43.4 to -40.0 to a range of -44.5 to -39.0 and take this latter range of values as representative of methane carbon isotopic values for methane generated during mainstage C_{15+} hydrocarbon generation from typical marine source rocks. These limits, when applied to the data of Rice and others (1988) (figs. 5, 8), permit several speculative hypotheses.

First, methane in figures 5 and 8 that has $\delta^{13}C$ values more negative than -44.5 either would be derived from unusual organic matter types or would be mixed with biogenic methane, and I prefer the second possibility. Schoell (1983, his fig. 1) tentatively set the range of $\delta^{13}C$ values for associated methane gas (methane cogenerated with oil) from

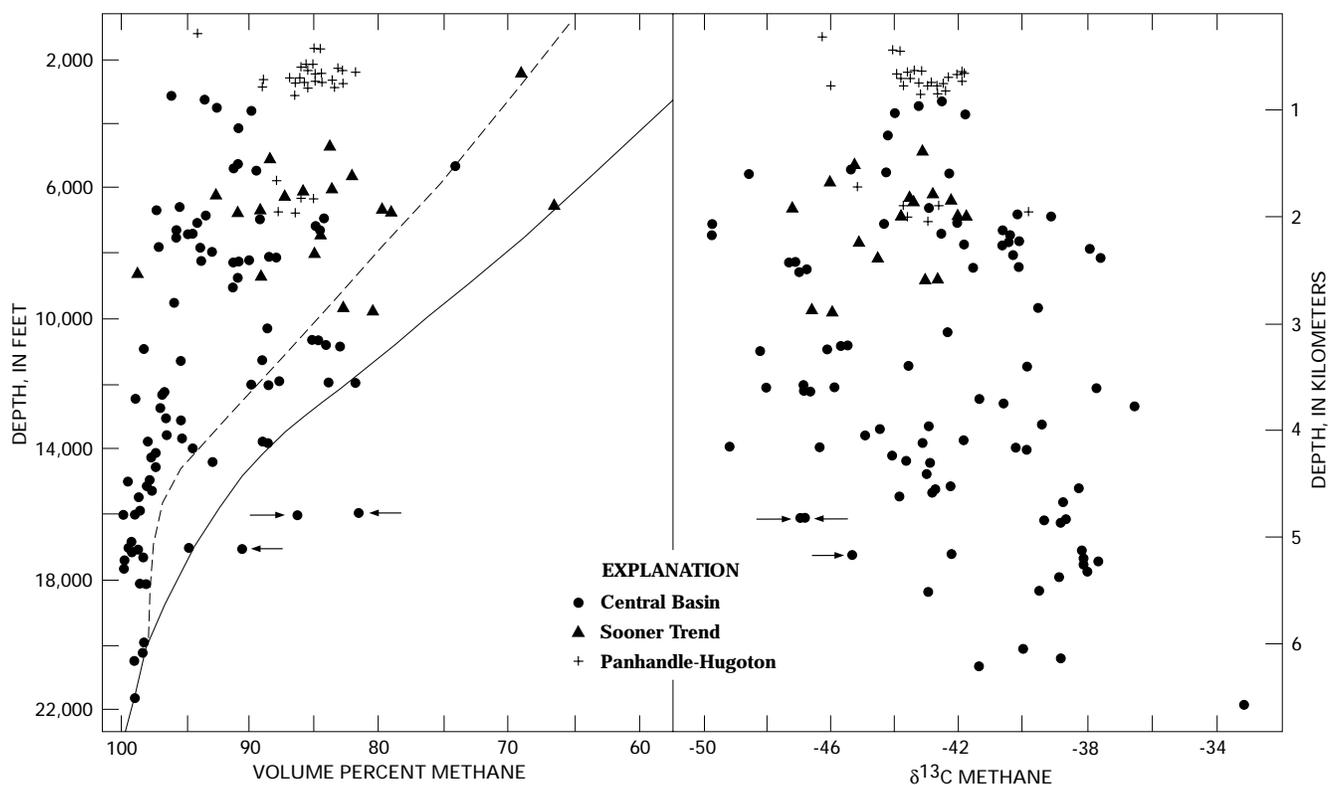


Figure 8. Volume percent methane of C_1 – C_4 hydrocarbon gases and methane carbon isotopic value ($\delta^{13}C$), versus depth, for gas deposits of Anadarko Basin. Volume percent methane values are calculated from data of Rice and others (1988). Arrows designate samples discussed in the text. Dashed and solid lines in volume percent methane plot represent arbitrary sample envelopes (discussed in text).

marine organic matter at -60 to just less than -40 in the classification scheme he proposed. The lower limit of his classification (about -40) agrees with the experimental data of this study, but there is significant disagreement with the upper limit. Schoell (1983, p. 2237) noted, however, that constraints existed to his classification and that, "Additional experimental data from pyrolysis experiments would aid the understanding of differences between associated and non-associated gas." Those "additional experimental data" are shown in figure 9.

It should be noted that biogenic methane trapped within the porosity of fine-grained rocks would have $\delta^{13}C$ values of -60 to -80 and is routinely buried to the depths where thermal methane is generated. The mixing in the source rock of -44.5 to -39.0 thermal gas and -60 to -80 biogenic gas and the migration of this mixed gas from the source rock would produce gas deposits having $\delta^{13}C$ values in the range of -60 to -45 . Thus, on the basis of the experimental data of figure 9, it is proposed that the range of $\delta^{13}C$ values for methane cogenerated with oil from marine source rocks may be much narrower (-44.5 to -39) than has previously been proposed (Kartsev and others, 1971; Stahl, 1974; Bernard and others, 1977; James, 1983, 1990; Schoell, 1983). Furthermore, there is no way to negate the possibility that methane having

$\delta^{13}C$ values of -60 to -44.5 did not derive a significant component of biogenic methane from the source rock.

In the gas generation models of the different authors cited above, gas carbon isotopes have always been assumed to become continuously heavier (less negative) as maturation rank increased through the onset of C_{15+} hydrocarbon generation and into C_{15+} hydrocarbon thermal destruction. Four of the rocks in figure 9, however, have methane $\delta^{13}C$ values that become more negative during early generation stages, before the $\delta^{13}C$ values reverse and become less negative, as expected, with increasing experimental temperature. This trend may also have been present in the experiments with the other two rocks shown in figure 9; however, insufficient amounts of methane were recovered from the lower temperature runs of those experiments to permit carbon isotopic analyses. It would be convenient to simply dismiss these unexpected trends of figure 9 as experimental artifacts; however, as discussed in Price and Wenger (1992), these aqueous-pyrolysis experiments appear to closely mimic the natural system in all respects examined thus far. Other data, either from experiments or nature, are necessary to confirm or disprove these trends.

The lack of methane enriched in the carbon-13 isotope ($\delta^{13}C$ values of -38 to -20 in the data of Rice and others

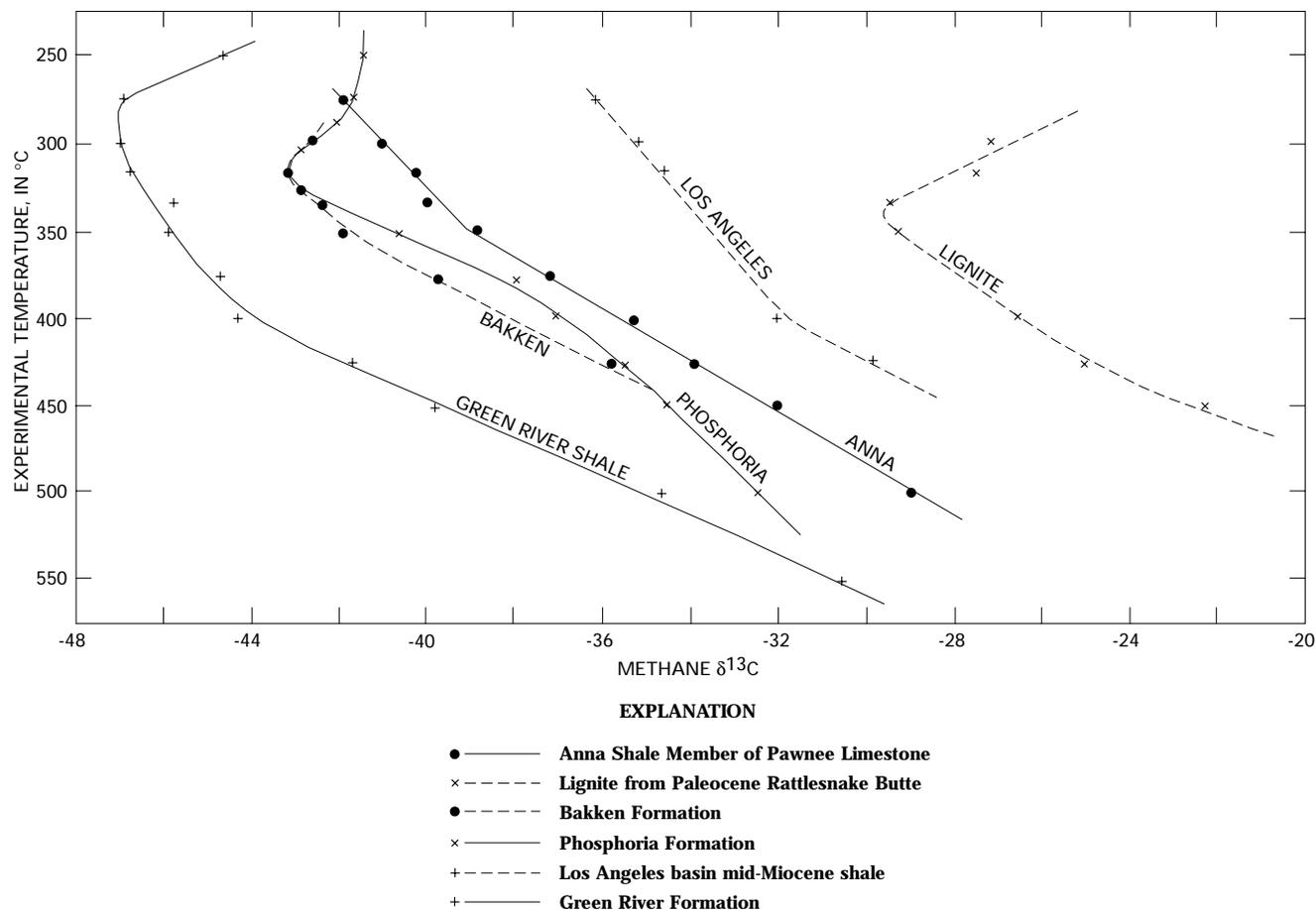


Figure 9. $\delta^{13}\text{C}$ values for methane, versus experimental temperature, for aqueous-pyrolysis experiments performed on six rocks by L.C. Price and L.M. Wenger (see Price, this volume, table 1).

[1988]) is significant. Only four gas samples have $\delta^{13}\text{C}$ methane values less negative than -38 (figs. 5, 8). Increasingly less negative $\delta^{13}\text{C}$ methane values, especially below the range -40 to -38 , have long been recognized as a product of C_{15+} hydrocarbon thermal destruction. This postulate is certainly supported by the data of figure 9. That so few gas samples have such values strongly suggests that only small percentages of the gas sample base of Rice and others (1988) could have originated from C_{15+} hydrocarbon thermal destruction. This conclusion is also supported by the moderate to measurable concentrations of C_{15+} hydrocarbons in the deepest rocks of the Bertha Rogers-1 wellbore of the Anadarko Basin (Price and others, 1981; Price, this volume, figs. 17, 23, 29). This conclusion does, however, require some qualifications.

As Schoell (1983) pointed out, not only maturity but also organic matter variations (even within one organic-matter type) can cause shifts in the $\delta^{13}\text{C}$ values of methane, as is evident in the data of figure 9. For example, at 350°C , which is in the hydrocarbon destructive phase for these aqueous-pyrolysis experiments, $\delta^{13}\text{C}$ for methane varies from -42.0 for the Bakken Shale to -38.85 for the Anna Shale. On the other hand, characteristics of the gases in the aqueous-

pyrolysis experiments (fig. 9) are mostly from reactions that took place at lower temperatures as the actual reaction temperature was approached during the experiment. For example, the "true" $\delta^{13}\text{C}$ value for methane generated at 350°C from the Bakken shale would be best determined by an experimental run at 330°C – 340°C , bleeding the generated gases off, and then running an experiment with the same vessel at 350°C . The methane generated in such an experiment would have a $\delta^{13}\text{C}$ value less negative than -42.0 . Lastly, of the three rocks (Bakken, Phosphoria, and Anna Shales) in figure 9 that were used to compare to the data of Rice and others (1988), the Anna Shale is the most appropriate. This is because the Anna Shale is from the Anadarko Basin and has likely served as a source rock for some of the oil and gas in that basin.

SYNOPSIS—PROPOSED ORIGINS OF DEEP-BASIN METHANE

For the purposes of clarity, the proposed working model of this paper for the origin of methane in deep-basin gas deposits is briefly reviewed. Most methane is believed to originate from generation from kerogen during mainstage

C₁₅₊ hydrocarbon generation. Methane carbon isotopes, from one organic matter type, so generated are expected to have a narrow (−3 to −6) range; however, the trend of carbon isotopic values versus increase in maturation rank is unclear because experimental data in the early generation stages have trends opposite from those of previously proposed models. With increasing rank, increasing amounts of methane are generated. Significant amounts of methane are generated during the middle to last stages of hydrocarbon generation.

Significant contributions of biogenic methane also are likely present in many gas deposits that otherwise have a thermogenic origin. This biogenic methane is trapped in source rocks at shallow depths and then buried to much greater depths where it mixes in situ in the source rock with newly generated thermogenic methane and is expelled from the rock as a mixed gas. This process is probably more important than the mixing of thermogenic and biogenic methane from two separate sources to form gas deposits.

By the models of this paper, very little methane is believed to originate from thermal destruction of oil in a reservoir. In some basins, true high-rank methane deposits that have originated from C₁₅₊ hydrocarbon thermal destruction do exist; however, such examples are unusual, and the methane of such deposits has distinct carbon-isotopic signatures. Furthermore, the methane of such deposits is thought mainly to have originated from thermal destruction of C₁₅₊ hydrocarbons in fine-grained rocks.

It is believed that substantial amounts of high-rank methane are generated from kerogen in fine-grained rocks at high maturation levels after mainstage C₁₅₊ hydrocarbon generation has occurred but while the kerogen still has low to moderate Rock-Eval hydrogen index values, which are remnant from higher values. The maturation levels at which this generation is envisioned to occur range from R_o=4.0 or 5.0 percent to 7.0 or 8.0 percent.

SOURCE-ROCK EXPULSION OF GASES

It is a principal hypothesis of this paper that in-reservoir thermal destruction of C₂₊ hydrocarbons (and oil) has, with some exceptions, resulted in only a small percentage of the methane in deep-basin, high-rank dry-gas deposits. Instead, most dry-gas deposits are believed to originate by processes involving hydrocarbon condensation, buoyancy, and migration that act on hydrocarbon gases produced during main-stage oil generation in source rocks, gases that are possibly mixed with biogenic methane. If this indeed is the case, then understanding expulsion of hydrocarbon gases from source rocks could aid understanding the distribution of high-rank conventional and unconventional gas deposits in deep basins more so than predictions from regional

basinal maturity trends. Indeed, site-specific prediction for deep-basin, high-rank gas deposits may even be possible. Clearly hydrocarbon gases, especially methane, are much more mobile than oil. Thus, many constraints applicable to oil expulsion do not directly apply to gas expulsion; however, some of the same rules may at least partly apply.

Previously, most petroleum geochemists, including myself, considered hydrocarbon expulsion to be a very efficient process with the result that most generated hydrocarbons (75–95 percent in organic-rich rocks) were thought to migrate from their source rocks (Price, this volume). These conclusions were drawn because of the large decrease in the hydrocarbon-generation capacity of source rocks, as reflected by decreasing Rock-Eval hydrogen index values, as a given source rock was progressively buried deeper in a basin. These hydrogen index decreases are never matched, however, by numerically equivalent increases in either Soxhlet-extractable hydrocarbons or the Rock-Eval S₁ pyrolysis peak, both of which tend to exhibit rather constant values versus depth. Thus, we petroleum geochemists, by and large, concluded that hydrocarbon expulsion is very efficient because almost all generated hydrocarbons clearly leave the source rocks. As discussed by Price and LeFever (1992), however, very little, if any, of the oil in the conventional Mississippian mid-Madison reservoirs of the Williston Basin is from the Bakken shales. This fact leads to the hypothesis that hydrocarbon expulsion is actually quite inefficient, at least in this case. Furthermore, as discussed in Price and LeFever (1992), most generated hydrocarbons probably are lost to the drilling mud during the cutting chip or core trip up the wellbore during drilling operations. Thus, the high apparent efficiencies of hydrocarbon expulsion previously called for are due in reality to efficient loss of generated hydrocarbons to drilling muds. A strong association of increasing basin richness regarding conventional oil deposits versus intensity of faulting in the hydrocarbon kitchens of deep basins was noted by Price (1994) (table 2). Price (1994) attributed this association as evidence of the absolute prerequisite that major faulting (with accompanying major fracturing) is necessary to physically disrupt organic-rich source rocks such that generated hydrocarbons can be freed for expulsion and form conventional oil deposits.

Even though gas is significantly more mobile than oil, it is possible, and perhaps probable, that significant faulting of mature and postmature source rocks is also necessary before highly efficient expulsion of generated hydrocarbon gases can occur. Thus, it is a hypothesis of this paper that a rule of thumb may exist regarding location and occurrence of deep-basin, high-rank conventional and unconventional gas deposits. Such deposits, by the models developed in this paper, should always be associated with a major fault that has disrupted mature and postmature source rocks to allow expulsion of hydrocarbon gases. Structures not associated

Table 2. Average basin productivity in millions of barrels of recoverable oil per 1,000 mi² of oil and oil-equivalent gas and total estimated ultimate recovery (EUR) in billions of barrels of oil for different major basinal structural classes.

[Examples of each class are given in parentheses. Structural intensity over and adjacent to the basin deep increases from class I through class VIII. Modified from Price (1994)]

Class	Basin type	EUR	Productivity
I	Cratonic (Williston, Paris)	14.0	16.5
II	Moderately deep to deep asymmetric cratonic basins with slight to moderate mobile rims (Uinta, Fort Worth)	25.75	80.5
III	Passive margin (Gabon, Northwest Shelf Australia)	17.0	71.5
IV	Rift/aborted rift (North Sea, West Texas Permian)	413.5	335
V	Foreland-foldbelt (Anadarko, Persian Gulf)	990.5	250
VI	Downwarps (Greater Gulf Coast, Tampico-Reforma)	170	476
VII	Deltas (Niger, Mississippi Fan)	103	818
VIII	Wrench (Los Angeles, Maracaibo)	156.5	1,126

with such faulting would be less likely to contain deep-basin, high-rank gas deposits.

It should also be noted that normal and extensional faults are much more favorable for expulsion of oil into fault zones for upward migration than high-angle compressional reverse faulting (Price, 1994). The tensional voids created along normal and extensional faults allow fluid migration along faults, whereas compressional-reverse faults restrict fluid movement because of their "tightness." The much greater mobility of gas as compared to oil may, however, cancel out some of this difference between the different fault classes.

Basinal structural styles evolve through geologic time. For example, the depocenter and southernmost margin of the Anadarko Basin, although previously an extensional wrench fault regime, later evolved into a compressional tectonic regime characterized by numerous, large, high-angle reverse faults. Migration of hydrocarbon fluids could have occurred during periods of normal or extensional faulting, and later evolution to a compressional tectonic regime may have been quite favorable for the preservation of deep-basin, high-rank gas deposits over geologic time by minimizing loss by leakage up these "tight" compressional systems.

DEEP PETROLEUM BASINS— OPEN OR CLOSED SYSTEMS?

For discussion, two opposite views can be taken regarding fluid flow in sedimentary basins. (1) The depocenters of these basins are "open systems" that allow continuous product escape from hydrocarbon generation by hydrocarbon expulsion and essentially unrestricted, or only slightly restricted, fluid flow between different stratigraphic units in basins. (2) The depocenters of these basins are closed systems in which hydrocarbon expulsion is difficult (inefficient) unless source rocks are physically disrupted by faulting or fracturing or, in uncommon cases, are bounded by a continuous laterally hydraulically transmissive unit.

Furthermore, significant fluid flow between stratigraphically separate units in a basin is greatly restricted or impossible.

As discussed preceding, most petroleum geochemists call for efficient hydrocarbon expulsion from source rocks and therefore subscribe to the first model. Furthermore, as discussed following, many investigators, including Meissner (1978) and Spencer (1987), view slight to moderate overpressures in source rocks to be proof that present-day hydrocarbon generation is taking place in such rocks. Products from such generation are thought to continuously escape through "leaky" systems to replenish either conventional deposits, or unconventional resource bases, both of which are also assumed to be losing hydrocarbons via leakage. This view is best summed by Masters (1984a, p. 25–26), who described present-day gas generation, from presumed hydrocarbon thermal destruction, occurring in the deep rocks of the paleodepocenter of the Western Canadian Basin (the disturbed belt).

West of the updip edge of the Deep Basin, the entire Mesozoic section generated gas and the deeper part of it continues today to explode gas out of the organic material. This active thermal area is called the "gas furnace."

Our understanding of the trapping conditions which created the vast and thick gas-saturated section downdip from water in the Deep Basin has been substantially enlarged. Previously, the updip seal had been tentatively ascribed to "water block" caused by lower relative permeability to gas in the high-water saturation on the updip side (Masters, 1979). Now, Welte et al. (1984), and Gies (1984) have recognized that the trap is "dynamic" in the sense that the tight sand (much of it with the permeability of a silty shale) slows down the passage of gas into the more porous, water-wet sand updip. There is not actually a seal. Gas is continually leaking out updip. But gas is still being generated fast enough that the trap stays filled. A catchy term would be to call it a "bottleneck trap." In Welte's words "the gas saturation of the rock column depends on a dynamic equilibrium between gas generation and gas losses. The low permeabilities and low porosities of the gas saturated part of the rock column are essential for the existence of this unconventional gas deposit. Migration and losses of gas seem to be mainly controlled by diffusion." The coincidence of the Deep Basin gas trap and the gas window is explained by this bottleneck concept which requires that the trap be continually fed.

An alternative view, that expulsion is a very inefficient process, was recently advanced by Price and LeFever (1992) and Price (1994). The documented major loss of both

hydrocarbons and hydrocarbon gases from mature source rocks during the trip up the wellbore, the petroleum geochemistry of the Williston Basin, and data in table 2 strongly support this view. The proposal that general fluid flow is also highly restricted in the deep parts of many sedimentary basins has recently been advanced by the work of Powley (1990), Tigert and Al-Shaieb (1990), Ghaith and others (1990), and Al-Shaieb (1991). These investigators have documented “compartmentation” in basins worldwide, wherein nested compartments of rocks, whose fluids are significantly underpressured or overpressured, are in the depocenters of most petroleum basins. As noted by Powley (1990, p. 219–220),

The compartmented hydraulic systems in currently sinking basins are almost universally overpressured and are underpressured in many onshore basins undergoing erosion. The principal source of overpressures appears to be thermal expansion of confined fluids and the generation of petroleum during continued sinking, and the principal source of underpressures appears to be thermal contraction of confined fluids as buried rocks cool during continued uplift and erosion at the surface. Thus, it appears that the compartments have an amazing longevity as they undergo a continuum from overpressures through normal appearing pressures to underpressures as their host basins progress from deposition to quiescence, to basin uplift and erosion.

I agree with Powley (1990) regarding both the origins of overpressures and underpressures and their “amazing longevity” over geologic time. As noted by Dickey and Cox (1977), subnormal pressure gradients are present in the shallower rocks of all onshore United States petroleum basins. Dickey and Cox also noted that such subnormal fluid-pressure gradients can only originate from a decrease in rock burial temperature, which causes a thermal contraction of both rocks and fluids. Such a decrease in rock burial temperature in turn can only arise from (1) uplift and erosion, (2) a decrease in heat flow (and thus in the geothermal gradient), or (3) both processes. Clearly, all onshore basins have been uplifted and eroded somewhat because they are all currently above sea level. Thus, the work of Dickey and Cox (1977) supports Powley’s (1990) interpretation for the origin of subhydrostatic pressures.

Al-Shaieb (1991) discussed compartmentation in Paleozoic rocks of the deep Anadarko Basin where nested compartments of rocks having very high fluid-pressure gradients are adjacent to rock volumes having normal or only slightly overpressured fluid-pressure gradients. Pressure gradients within Lower Pennsylvanian Morrowan rocks as high as 0.987 psi/ft have been recorded. The high fluid-pressure gradients in the deep Anadarko Basin probably formed before basin evolution ceased during the Permian. Thus, it is likely that extreme fluid-pressure gradients can persist in hydraulically isolated volumes of rocks for long periods of geologic time. Such restricted fluid flow for hundreds of millions of years thus supports the concept of inefficient expulsion, as hypothesized earlier.

ABNORMAL FLUID PRESSURES

Let us return to Powley’s (1990) comment regarding the origin of overpressures from either hydrocarbon generation or the thermal expansion of confined fluids as best stated by Barker’s (1972) model of aquathermal pressuring, which is the thermal expansion of a fixed amount of fluid (usually pore water) in a fixed pore volume.

Abnormal fluid pressures first came to prominence from oil exploration in the Gulf Coast in the late 1960’s and were originally attributed to restricted compaction processes such that the sediments retained more water than they should for a given burial depth. As an aside, it should be noted that the mechanism for Gulf Coast shales retaining excess pore water in many cases likely indirectly involves hydrocarbon generation. As hydrocarbon generation proceeds, more and more hydrocarbon gas is generated, and eventually methane dissolved in shale pore waters reaches saturation levels and a gas phase (bubble) exsolves. By the principles of two-phase fluid flow (fig. 10), this gas bubble will be below the critical gas saturation level for the shale.

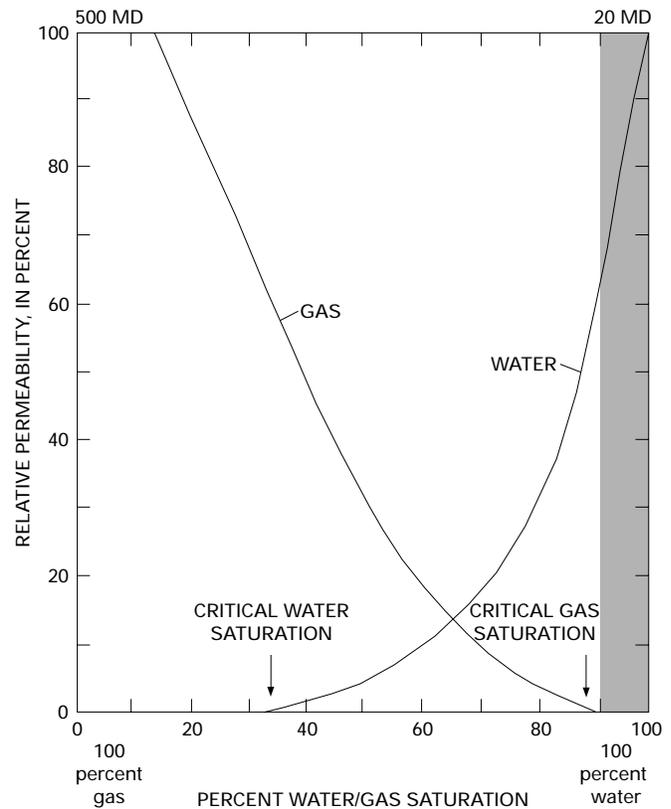


Figure 10. Relative permeabilities of gas and water. Shaded area is range of gas concentrations (below the critical-gas-saturation level) at which the Jamin effect can come into play and reduce or take to zero the relative permeability of the rock with respect to water. 500 mD (millidarcies) is gas permeability at 100 percent gas, 20 mD is water permeability at 100 percent water.

If the bubble becomes locked in a shale-pore throat, the Jamin effect (Hedberg, 1980) comes into play.

The principles of two-phase fluid flow state that where two immiscible fluid phases (here water and gas) coexist in the same matrix porosity, both fluids have critical fluid saturation levels that must be exceeded before the solid has permeability with respect to the fluid under consideration. If the concentration of the fluid under consideration is less than its critical fluid saturation level, the solid will have no permeability with respect to that fluid, which thus cannot move through the solid. If the concentrations of both fluids under consideration exceed their respective critical fluid saturation levels, then both fluids can move through the solid. Their relative permeabilities will be greatly reduced, however, with respect to what their permeabilities would be if only one fluid were in the solid alone.

The Jamin effect states that where two separate and immiscible fluid phases coexist in a rock, and one phase (gas) is below its critical fluid saturation level, a portion of that gas may be in the form of totally immobile, spherical globules that cannot be distorted and will occupy a percentage of connecting pore throats. These globules decrease, or reduce to zero, the permeability of the rock with respect to the other fluid phase (stippled area, fig. 10). Thus, if the Jamin effect is in play, shale porosity is sealed off. With further burial, we have heating of a fixed amount of water in a constant pore volume or, in other words, Barker's (1972) aquathermal pressuring.

As overpressures were discovered in other basins, these pressures were also (incorrectly in some cases) attributed to the thermal expansion of confined fluids. Exploration geologists, first Meissner (1978) and later Spencer (1987) and other investigators, noted, however, that hydrocarbon generation involves a volume increase as kerogen is degraded to various products. This proposal was verified by petroleum geochemists. For example, Ungerer and others (1983) calculated that hydrocarbon generation involves a 15 percent volume increase. Presently, however, overpressures in any organic-rich rock are almost always taken as an indication that present-day hydrocarbon generation is occurring, and this can be an erroneous assessment, in my opinion.

For example, many investigators, including Meissner (1978) and Spencer (1987), have attributed overpressures in the Bakken shales of the Williston Basin in mature basinal areas to present-day hydrocarbon generation in the shales. By this hypothesis, some of these generated hydrocarbons constantly move out of the shales to form conventional oil deposits or to be lost as seepage at the Earth's surface through geologic time. Although these interpretations are possible, I do not favor them. For one reason, no Bakken-sourced oil has as yet been found in any of the conventional mid-Madison oil deposits in the Williston Basin (Price and Le Fever, 1992), and these deposits make up 75–80 percent of the total recoverable reserves of the basin. Also, even though the Bakken shales are overpressured, all the other

units in the basin are underpressured (fig. 11), and significantly so. As discussed, a decline in rock burial temperature, which causes thermal contraction of both rocks and pore fluids, is the only mechanism that can result in basinwide subnormal fluid pressures. Low surface intercepts (0.25–0.29 percent) of 10 vitrinite reflectance profiles compiled by me throughout the North Dakota part of the Williston Basin show that there has not been significant erosion in the basin. Thus, only a decline in heat flow and hence geothermal gradients can explain the subnormal pressures observed basinwide in all units except the Bakken shales. Such declines are supported by the extreme gradients of vitrinite reflectance versus depth reported by Price and others (1986) in the type III organic matter of the Tertiary and Upper Cretaceous rocks in basinal areas where the Bakken shales are mature. Furthermore, the original four vitrinite reflectance profiles

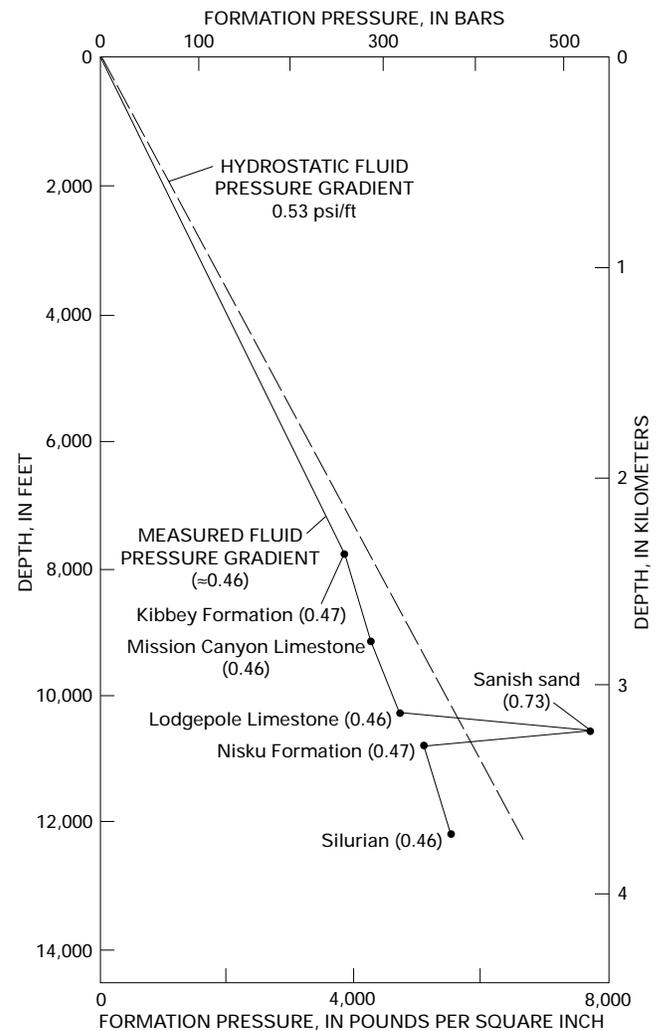


Figure 11. Formation fluid pressure, versus depth, for wells in the Antelope field, McKenzie County, North Dakota. Numbers in parentheses, fluid pressure gradient at the stratigraphic unit. Modified from Meissner (1978).

of Price and others (1986) have been corroborated by six newer, unpublished profiles. Although the Williston Basin still is quite warm, present-day geothermal gradients would have to be at least doubled to account for the observed gradients. If paleogeothermal gradients were at least halved, all ongoing hydrocarbon generation would immediately stop, by any time-temperature-dependent hydrocarbon-generation model. Although the Bakken shales are overpressured, the pressure gradients in those shales are generally lower than gradients reported by Spencer (1987) for other Rocky Mountain basins and are lower still than those in coastal or offshore petroleum basins that are clearly at their maximal geothermal gradients. It is my interpretation that the current overpressures in the Bakken shales are lower than they were before basin cooling occurred. Furthermore, I also postulate that the current overpressures have been retained in the Bakken shales through geologic time because of the model advocated herein of restricted fluid movement and inefficient source-rock expulsion in the depocenters of petroleum basins, a model supported by the investigations of Powley and co-workers. In my opinion, moderate fluid overpressures ($\leq 0.7\text{--}0.8$ psi/ft) in organic-rich rocks are not necessarily explained only by present-day hydrocarbon generation. Such pressures can also be explained as due to decayed values from much higher paleo-fluid-pressure gradients that were the result of intense hydrocarbon generation at the time of maximal heat flow in a basin. Today's moderate fluid pressures would have been retained over geologic time because of the model of (closed system) limited fluid flow in deep petroleum basins as advocated herein. Indeed, the moderate fluid pressure gradients in the Bakken shales may be taken as further evidence of the model.

ALBERTA BASIN-CENTERED GAS DEPOSIT

The basin-centered gas deposit of the Western Canadian (Alberta) Basin depocenter is another case where investigators have called for present-day hydrocarbon generation and concurrent migration through an open hydrocarbon-generation system (Gies, 1984; Masters, 1984a, b), mainly because of petroleum-geochemical studies of Welte and others (1984) in the basin. This present-day hydrocarbon generation has been proposed in spite of the fact that the gas deposit is at *subnormal pressures*. Various other investigators, including Hacquebard and Donaldson (1974), Hacquebard (1975), Magara (1986), Hutcheon and others (1980), Kalkreuth and McMechan (1988), and Tilley and others (1989), have provided evidence for, and (or) discussed, the extensive erosion that has taken place in the Western Canadian sedimentary basin. The amount of erosion increases on a trend southwestward from the Canadian plains, past the disturbed belt, into the present-day deep basin, and lastly into the ancestral deep basin (present-day Rocky Mountains). Evidence for this erosion comes from

studies of fluid inclusions, coal rank, shale and sandstone diagenesis and metamorphism, and vitrinite reflectance. Estimates of erosion range from 1,000 m of sediment or less from the Canadian plains to as much as 6,000 m of sediment from the Rocky Mountains. As an example, Hutcheon and others (1980) calculated that rocks in the Elk Valley and Mount Allan areas (southeastern British Columbia and southwestern Alberta), at present-day depths of 0–1,000 m, had paleotemperatures of 180°C–250°C.

Vitrinite-reflectance profiles from the Elsworth gas field and other areas of the present-day deep Alberta Basin have surface intercepts of $R_o=0.7\pm 0.1$ percent. In the absence of erosion, regardless of time-temperature burial history considerations, vitrinite-reflectance profiles should have surface intercepts of $R_o=0.25\text{--}0.29$ percent. Whether one uses the vitrinite-reflectance paleothermometer of Price (1983) or of Barker and Pawlewicz (1986), surface intercepts of 0.7 ± 0.1 percent imply decreases in sediment burial temperatures of at least 100°C. No current functional petroleum-geochemical model of hydrocarbon generation allows significant continued hydrocarbon generation after decreases in burial temperatures of 100°C or more.

Hydrocarbon generation, by all currently accepted petroleum-geochemical models known to me, is driven principally by increases in burial temperature, with lesser contributions from other controlling parameters (such as geologic time), depending on the model. The dominant control of burial temperature is due to the progressively stronger bonds in kerogen that must be broken by increasingly higher burial temperatures for hydrocarbon generation to proceed. Thus, burial temperature decreases of 100°C would preclude any possibility of hydrocarbon generation continuing because, once the weaker bonds are broken at a given burial temperature, the bonds cannot be rejuvenated; they have been destroyed.

In my opinion, there are two other major flaws with the conclusion of Welte and others (1984) that present-day dry gas generation is occurring in the deep Alberta Basin. First, I am not aware of any investigators, other than Welte and others (1984), who call for significant hydrocarbon generation from underpressured rocks. Second, the very evidence that Welte and others (1984) call on to support their model of present-day methane generation and loss via updip diffusion to the surface is the evidence that conclusively demonstrates that their proposed model is flawed. Welte and others (1984) found that rocks at 2,350–2,450 m of burial, whether coal (≈ 80 percent total organic carbon) or shale (≈ 1.0 percent total organic carbon), had the same ethane concentration when normalized to rock total organic carbon ($5\text{--}6\times 10^4$ nanograms of ethane per gram rock organic carbon). They interpreted these "equal concentrations" of ethane as due to diffusion in order to support their model. Diffusion of hydrocarbon gases occurs, however, in water-saturated rock porosity and has nothing to do with the organic carbon content of the rocks in which diffusion is

occurring. If active present-day gas generation were occurring, ethane (and methane) should be diffusing from the coal into the shale because the coal has at least an 80-fold higher generation capacity for methane than the shale (80 percent versus 1.0 percent total organic carbon). Thus, active present-day gas generation and diffusion would manifest itself by equal concentrations of methane as normalized to *rock weight, or rock volume, or rock pore space*. That the coals have rock-normalized ethane concentrations some 80-fold higher than interbedded and adjacent shales demonstrates that active gas diffusion cannot possibly be taking place. Thus, no, or only small, losses of hydrocarbon gas are taking place and there is no need to call on present-day hydrocarbon generation to replace these losses.

BASINS AS EVOLVING ENTITIES

Clearly, current petroleum-geochemical thinking is more oriented toward hydrocarbon-generation models that call for present-day hydrocarbon generation coupled with leaky deep basins (efficient hydrocarbon expulsion) and not oriented toward models of limited hydrocarbon expulsion coupled with detailed consideration of a basin's geologic history as a controlling parameter of hydrocarbon generation and expulsion. I favor the latter model of hydrocarbon generation and expulsion. Basins are not constants through geologic time but instead are entities that evolve through time. Hydrocarbon generation and expulsion, and basinal fluid flow in general, are tightly linked to basinal evolutionary history, heat flow, and structuring. Maximal hydrocarbon generation, expulsion, and secondary migration occur in a basin's youthful stage when heat flow, sedimentation, and structuring are all also at a maximum. Decrease in heat flow and structural activity should lead to basinal quiescence at mature stages. With a decrease in heat flow, significant hydrocarbon generation and expulsion cease, as does meaningful fluid flow in, and out of, the deep basin. Continued significant uplift and erosion can lead to total basin destruction. If basinal uplift and erosion are halted, basinal hydrodynamic patterns can be established wherein significant meteoric water recharge in the uplift areas of basins can lead to basinwide meteoric water flow (at hydrostatic pressure), at shallow depths, driven by such recharge. If giant or supergiant oil accumulations are not breached by basinal uplift and erosion, water washing and bacterial attack driven by such meteoric water recharge may well degrade such deposits (for example, the tar sands of the Alberta Basin).

HUGE DEEP-BASIN IN-PLACE UNCONVENTIONAL GAS RESOURCE BASES

Whether or not petroleum basins (and petroleum- and gas-generating systems) are open or closed systems is more

than academic. If basins are leaky systems, then most gas generated through geologic time is bled off and eventually lost to surface leakage, and only a small fraction of the total gas generated would be left in the deep basin. If deep-petroleum basins are closed or semiclosed systems with only limited fluid flow, then much more of the gas generated by rocks in the deep basin may remain in situ. The latter case results in much larger in-place gas resources and also distinctly higher concentrations (grades) than the former (leaky) case. Whether the resource under consideration is energy, water, or heavy metals, higher grade resources are always easier to recover than lower grade resources.

A model is favored herein in which deep-basin fluid flow is limited because it occurs in closed or semiclosed systems. Organic-rich rocks that have good gas-generation potential (and the rocks adjacent to them) may retain most (50–90 percent?) of the gas that they have generated, if such rocks are not highly faulted or fractured or bounded by hydraulically transmissive units. Fine-grained rocks in the deep basin that are highly to moderately structured should retain much smaller percentages of their generated gas because many routes would be available to allow escape of the highly mobile hydrocarbon-gas molecules. If the model favored here is a reasonable representation of nature, then we may expect in-place *wet-gas* resources of the largest possible imaginable magnitudes; however, these *wet-gas* resources will be mostly in the form of nonconventional gas deposits and will not necessarily be recoverable by the present-day drilling, completion, production, and maintenance operations used to recover gas from conventional gas deposits. Examples of known, in-place, deep-basin nonconventional gas deposits are coal gas, basin-centered gas, tight gas, deep (>4,572 m, >15,000 ft) Gulf Coast geopressured-geothermal gas, and "black-shale" gas (Mississippian-Devonian black shales, Appalachian Basin). Other types or classes of deep-basin gas deposits that we have not yet recognized no doubt exist. Furthermore, some of these deposits also are in what are now shallow rocks (from uplift and erosion) but were once more deeply buried.

Based on the results of (1) the horizontal Bakken-shale drilling program in the Williston Basin, (2) ongoing detailed petroleum-geochemical analyses of all commercially produced oils in the Williston Basin, (3) the apparent high inefficiency of oil expulsion, and (4) other considerations discussed in Price and LeFever (1992), Price and LeFever proposed the possible existence of an in-place oil resource in fractured, mature, organic-rich source rocks, and the rocks adjacent to them, in many different petroleum basins of the conterminous United States in the range of tens to hundreds of trillions of barrels of oil. Clearly, much more gas than oil will escape from mature unstructured source rocks because of the much greater mobility of gas compared to oil. Indeed, as discussed in Price (1986), C_1 – C_4 thermogenic hydrocarbon gases can be detected in very low concentrations at any surface location in all petroleum-bearing basins, and even in

many petroleum-barren basins, by a variety of surface-geochemical exploration methods. Such thermogenic hydrocarbon gases at the Earth's surface both (1) result from the much greater mobility of hydrocarbon gases compared to oil and (2) result in a substantial loss of generated hydrocarbon gases through geologic time. Source rocks are certainly more chemically open systems (easier product escape) with respect to hydrocarbon gases than to oils; however, in spite of this it is probable that monstrous, nonconventional, in-place gas resources also are present in different forms in different basins. These nonconventional in-place gas resources may parallel the nonconventional oil resource proposed by Price and LeFever (1992).

Examples of such large, nonconventional, in-place gas resources are the basin-centered gas deposits of the San Juan, Denver, and Western Canadian sedimentary basins (and yet undiscovered basin-centered gas deposits in other basins); known tight-sand gas deposits in various American onshore basins; coal-gas deposits actively being exploited in different American basins, especially the San Juan Basin; and the (currently noneconomic) geopressured-geothermal gas-resource base of the Gulf Coast (and other basins). That mud-gas logging values *always* dramatically increase when mature organic-rich rocks, and the rocks immediately adjacent to them, are penetrated by the drill bit is strong evidence of the ubiquity of such gas resources. These in-place gas resource bases are present in different forms: (1) gas dissolved in the high-temperature pore water of deep-basin sands and shales; (2) free-gas bubbles in concentrations below, at, or above the critical-gas-saturation levels for the stratigraphic units in which the gas bubbles reside; (3) small noneconomic traces or pockets (shows) of free gas dispersed throughout the rocks of sedimentary basins; (4) gases absorbed in coals; and (5) gases absorbed on the kerogen of shales or dissolved in free bitumen in mature source rocks. Furthermore, the sizes of the different in-place gas resource bases are, to say the least, very large. For example, Law and others (1989) estimated that the in-place gas resource of *only* the coarse-grained rocks in the Greater Green River Basin is between 3,611 and 6,837 TCF, and Masters (1984a) estimated that the in-place gas resource in the Canadian Alberta Basin (deep basin and adjacent foothills belt) is 3,600 TCF.

Although dispersed in-place hydrocarbon gas-resource bases in all probability exist, and their size may be beyond imaginable calculations, unless at least a small fraction of a resource base can be recovered, its existence and size are only of academic interest. It is my opinion that successful (economic) recovery of such unconventional gas resources is not solely a geologic problem but depends more on the development of new drilling, stimulation, production, and maintenance techniques that are applicable to the nonclassical characteristics of the particular nonconventional gas-resource base under consideration. For example, experience with attempted economic recovery of the nonconventional oil resource of the self-sourced, fractured Bakken shales

clearly demonstrates that application of conventional drilling, completion, production, and maintenance techniques to that resource has not been successful. As another example, economic recovery of coal gas is only made possible by first producing substantial water from coals (and adjacent rocks). This greatly lowers formation fluid pressures and allows a free-gas phase to either form or increase in volume (or both). As such, the critical-gas-saturation level of the coal (fig. 10) is exceeded to a point that the permeability of the formation with respect to a free-gas phase is significantly increased. Formation of a free-gas phase allows the coal gas to flow toward the wellbore in meaningful (economic) amounts. Attempted recovery of the coal-gas resource by conventional production techniques would only lead to economic failure and a condemnation of the resource as "uneconomic." *It must be stressed that this principle also applies to other unconventional gas and oil resources.*

For example, hundreds of millions of dollars have been spent to demonstrate that geopressured-geothermal gas in the Gulf Coast *cannot be* economically produced by producing sandstone brines from moderate depths of 3,048–4,572 m (10,000–15,000 ft) and bringing those brines to the Earth's surface for extraction of dissolved methane. It was predicted (Price, 1978a, b; Paul Jones, unpublished research) that such a recovery technique would not be economic. Economic recovery of an essentially infinite geopressured-geothermal gas resource appears possible, however, in the Gulf Coast from rocks at greater depths than those being utilized by the current geopressured-geothermal research effort. Deeper rocks (1) have more immobile free gas bubbles at or below critical-gas-saturation levels for those formations; (2) have much higher concentrations of hydrocarbon gases dissolved in sandstone and shale-pore water from the higher burial temperatures and higher (abnormal) fluid pressures at depth; and (3) are much further into intense hydrocarbon (and hydrocarbon gas) generation, thus providing more gas to be recovered. Economic recovery of the deep geopressured-geothermal gas resource can likely be accomplished by production techniques similar to those used to recover the dispersed gas resource from coals: removal of sufficient volumes of deep formation waters to greatly lower fluid pressure in deep formations and therefore greatly increase free gas mobility leading to an in situ recovery, as opposed to surface extraction, of the deep Gulf Coast geopressured gas-resource base (L.C. Price and Paul Jones, unpublished research).

As a last example of the nonclassical characteristics of the nonconventional gas resources let us assume that many deep, high-rank gas deposits are in water-free reservoirs (as discussed following). If this is the case, then introduction of any water to those rocks during drilling, completion, or maintenance operations would set the principles of two-phase fluid flow and the Jamin effect into play. This, in turn, could create around the wellbore a skin effect of greatly reduced permeability with respect to gas, such that

the gas-productive capabilities immediately around the wellbore were greatly reduced or even destroyed, which in turn would destroy production economics. This could lead to a condemnation of the well and the prospect, and perhaps the play as a whole. It is thus a major recommendation of this paper that it is critical to determine (1) if some (many?) deep-basin reservoirs are water-free systems, and (2) if this is the case, whether extensive formation (skin) damage can occur around the wellbore in some water-free, deep-basin gas reservoirs as a result of introduction of water into them.

I conclude that essentially infinite, in-place, unconventional gas-resources can be proven from further geologic and geochemical research; however, evidence is sufficient that perhaps we can take these in-place hydrocarbon gas-resources as a given. Research having more potential impact would be to determine if appropriate drilling, completion, stimulation, and maintenance techniques can be developed, techniques that are applicable to the different characteristics of the different unconventional, in-place gas-resource bases. Thus, I recommend that research be instituted to determine (1) the extent of the large in-place wet-gas resources known to be present; (2) the grade (concentration) of the various gas resources; and (3) the controlling parameters of the different nonconventional gas resources. If large, high-grade, in-place gas resources do exist, and in my considered scientific opinion they do, then economic recovery of such gas resources should become a research focus. Economic recovery of such gas resources will depend on the development of nonconventional drilling, completion, stimulation, production, and maintenance techniques that are uniquely applicable to the nonclassical characteristics of each of the different gas resources.

NEED FOR RESEARCH ON UNCONVENTIONAL ENERGY RESOURCE BASES OF THE UNITED STATES

No matter which resource assessment model or published study is used, most of the large conventional American oil fields to be discovered have already been discovered, with possible exceptions of undiscovered North Slope (coastal), Santa Barbara Channel, and deep-water Gulf Coast fields. It is also well established that the Persian Gulf Basin contains the bulk of the world's conventionally producible oil. Even if another American Prudhoe Bay were discovered, it would only forestall the inevitable, an increasing dependence on the Middle East for American energy requirements. In my opinion, the only currently foreseeable chance the United States has to avoid this situation is to conduct research into the possible commercial productivities of our known, in-place nonconventional mobile gas (and oil, Price and LeFever, 1992) resources. Nonconventional gas resources—the basin-centered gas deposits of the San Juan,

Denver, and Western Canadian Basins, and coal gas from numerous basins, but especially the San Juan Basin—already make significant contributions to energy needs of the United States. There is no apparent reason why properly designed research could not delineate the appropriate techniques that must be utilized for commercial recovery of other nonconventional gas and oil resources. Such research should not be designed and carried out from a conventional mind set because exploitation of unconventional gas and oil resources will be difficult or impossible to achieve by conventional thought patterns. As Masters (1984b, p. ix) noted, discussing the basin-centered Elmworth gas field of the Western Canadian Basin,

Finding a giant Deep Basin-type gas field is technologically relatively simple, although statistically very rare. Exploiting such a field, however, calls upon some of the most advanced reservoir technology available and requires an unusual amount of coordination between the geological and engineering arms of a company. It is virtually impossible for one man to have all the skills required to analyze, measure, and produce these low-permeability, high-damage reservoirs, so a chain-link team of specialists must be available. Few companies have built, or can hold together, such teams. Perhaps the most significant contribution of this memoir, in fact, is its description of the several areas of expertise that must necessarily bond together in the exploitation of a major Deep Basin-type gas field.

It must be stressed that, with the large-scale departure of the American major oil companies from domestic onshore exploration, funding of research regarding unconventional energy resources may have to come from elsewhere, such as the Federal Government and (or) institutions such as the Gas Research Institute or American Gas Association, all of whom have a vested interest in production of gas resources of the United States.

The United States still has a strong base of domestic independent oil-exploration companies, and in reality the expertise of these companies may be America's most valuable "energy resource," although with time this base also will erode. These companies historically have been the last true onshore "wildcatters," commonly having explorationists ready to aggressively pursue new exploration concepts or plays. For example, these companies played the key role in development of the coal-gas resource (along with an independent-minded American major, Amoco oil) and also played key roles in the attempted commercial recovery of fractured-shale oil resources of the Bakken shales in the Williston Basin and from other source rocks in other basins. If research were successful into optimum recovery techniques for unconventional gas and oil resources, American independent oil companies would aggressively pursue development of those resources.

DISCUSSION

FRACTURES VERSUS POROSITY

Price (this volume) provided evidence that methane is thermally stable to depths (maturation ranks) beyond those that can be reached by current drilling technology. Thus, the

question as to the possible existence of conventional, or non-conventional, deep-basin, high-rank gas deposits partly centers on whether or not adequate porosity and permeability persist, at great depths and high ranks to hold such gas. The Tuscaloosa sandstones of the Tuscaloosa trend gas fields (Smith, 1985) are an example of abnormally high porosities and permeabilities (20–25 percent, 1–2 darcies), even though these sandstones have measured vitrinite reflectance values of 2.0–2.2 percent (Price, 1991). Furthermore, a similar example may be in the “Flex Trend” gas fields of offshore Texas. Possible controlling parameters and characteristics of deep-basin, high-rank sandstone porosities have been examined by other investigators on this project. It is unlikely, however, that our understanding of the deep-basinal processes that preserve or destroy porosity will be sufficient in the near future such that correct pre-drill, site-specific predictions can routinely be made concerning high-rank porosity preservation.

On the other hand, the question of porosity preservation to great depth and high ranks may be in part academic, depending on the role played by fractures, cracks, and the space between parting laminae of bedding. As noted by Price and LeFever (1992), the Bakken shales and adjacent rocks apparently contain between 100 and 250 billion barrels of generated oil, yet the porosities of those rocks range from 0 to 4 percent. It has been established that most of this Bakken-generated oil is in cracks, fractures, and parting laminae in the Bakken shales and adjacent rocks. It is possible that an analogous situation may exist with deep-basin gas, in that the bulk of the deep-basin gas may be similarly stored. All rocks are fractured to some extent, and different processes lead to the formation of fractures and cracks in rocks. For example, all onshore basins have been uplifted and cooled somewhat because they are now above sea level. Furthermore, in some of these basins heat flow has decreased greatly, such as, for example, on the northern rim of the San Juan Basin. During such cooling, thermal contraction of both rocks and pore fluids takes place, a contraction that would likely lead to development of tensional fractures in the cooling rocks. Once a deep-basin fracture or void formed by any such process, it might be quickly filled with gas, and this gas might keep the fracture open during subsequent geologic history. If deep-basin, high-rank gas is stored in significant volumes in fractures, parting laminae, and other nonclassical void volumes, rather than in rock porosity, then possible economic recovery of deep-basin, high-rank gas resources might in part hinge on geologic-engineering studies related to such nonclassical void volumes.

SIGNIFICANCE OF NONHYDROCARBON GASES

Carbon dioxide, hydrogen sulfide, and nitrogen are occasionally found in abundance in some gas fields in some basins. Furthermore, high concentrations of these

nonhydrocarbon gases have existed in some fields for long periods of geologic time. For example, such gases in deep traps of Western Canada would have been in those traps since Laramide (Cretaceous-Tertiary) deformation. Such gases in traps in the West Texas Permian and Anadarko basins would have been in those traps since at least the Permian. Both carbon dioxide and hydrogen sulfide strongly undergo association-disassociation reactions to ionic species (HS^- , HCO_3^- , CO_2^-) that are extremely soluble in water. Therefore, both CO_2 and H_2S in gas traps with a water leg would quickly be leached from the deposit and dissolved into the water phase over geologic time, probably on the order of 10,000–100,000 years. Thus, the existence of CO_2 or H_2S in traps for tens to hundreds of millions of years dictates that (1) water is neither in the trap as a mobile phase nor in contact with the trap at the edge of the gas deposit and (2) such traps are closed systems with regard to fluid migration.

The absence of water in some (and possibly many) deep-basin gas traps has two important implications. First, as discussed in Price (this volume), the absence of water allows hydrocarbon thermal-destruction reactions to occur at lower temperatures than those under which such reactions normally take place with water in the system. Thus, C_2+ hydrocarbon destruction and conversion to high-rank methane would be promoted in deep, water-free reservoirs. Second, as discussed above, when water is introduced into deep-basin, water-free gas reservoirs during drilling, completion, or maintenance operations, the productivity of the reservoir may be damaged or destroyed from a skin effect around the wellbore resulting from the principles of two-phase fluid flow and the Jamin effect.

Thermochemical-sulfate reduction has been invoked to explain both high CO_2 and H_2S concentrations in some gas deposits and also the origin of some of the high-rank gas-condensate deposits of the Alabama-Florida panhandle area (Sassen and Moore, 1988; Claypool and Mancini, 1989). Close examination of the (1) origin of the hypothesis of thermochemical-sulfate reduction, (2) evidence for the hypothesis, and (3) geographic areas where it has been invoked to be operative strongly suggests, however, that the hypothesis has little basis in fact, even though it is commonly invoked by petroleum geochemists and geologists.

The hypothesis of thermochemical-sulfate reduction was first advanced by Orr (1974), in an elegant, well-documented, and detailed discussion, to explain the presence of H_2S and CO_2 , sulfur content, and of Big Horn Basin oil sulfur isotopes, which become heavier (enriched in S^{34}) with increasing maturity. To both explain the observed variations in oil composition and support his hypothesis, Orr (1974), made three pivotal assumptions: (1) in-reservoir maturation of the oils (extensive thermal cracking of $\text{C}_{15}+$ hydrocarbons) throughout the basin at reservoir temperatures of 80°C – 120°C , (2) no or minimal water washing or bacterial degradation in the oil reservoirs of the basin, and

(3) long-distance migration of an originally uniform oil, from a source to the west, to traps completely ringing the Big Horn Basin depocenter.

Regarding Orr's (1974) first assumption, the data of this study and of Price (1993a) both strongly suggest that in-reservoir maturation of oils (thermal destruction of C_{15+} hydrocarbons) at burial temperatures of 80°C – 120°C is not possible. Furthermore, the hypothesis of widespread, low-temperature ($\geq 120^{\circ}\text{C}$) in-reservoir maturation of oil has been fully discussed and dismissed by both Phillipi (1977) and Price (1980b), the principal conclusions of those studies being as follows: (1) The extreme variations in the physical characteristics of oils with increasing depth, variations cited as evidence to support the hypothesis of in-reservoir oil maturation, are better explained by crude-oil degradation (bacterial attack and water washing). (2) No firm evidence exists for in-reservoir maturation of oil. (3) Variations in maturity characteristics in undegraded oils are better explained as due to original variations inherited from hydrocarbon generation at different maturation ranks in the source rocks or to facies variations in the source rocks rather than to in-reservoir maturation.

Orr's (1974) second assumption that crude-oil degradation is at best minimal in the Big Horn Basin is, in my opinion, erroneous. Crude-oil degradation of many Big Horn Basin oils has been documented by a different investigators, including Todd (1963). Analysis of different Big Horn Basin oils by the U.S. Geological Survey (fig. 12) demonstrates decreased concentrations of lower molecular weight hydrocarbons and n-paraffins in some oils as compared to other "normal" Big Horn Basin oils. These decreases are due to water washing and bacterial attack. The reduced concentrations of C_{15} -n-paraffins in the East Rozet and Prong Creek oils, as compared to those of normal oil from Cottonwood Creek (fig. 12), can only be due to biodegradation. Orr (1974) noted that the Pennsylvanian Tensleep Sandstone oil reservoirs in the Big Horn Basin crop out in the Big Horn Mountains where these reservoirs are subject to strong meteoric water recharge. More than 6,096 m (20,000 ft) of hydrodynamic head drives this meteoric water into the deep basin. The well-known inclined oil-water contacts in some of the Paleozoic reservoirs of the Big Horn Basin (Todd, 1963) are most probably due to the strong meteoric water flow throughout the basin. Orr's (1974) assumption of no, or only minimum, oil degradation in the Big Horn Basin simply must be considered flawed given the optimum conditions for oil degradation in the basin and the fact that oil degradation is well documented there. Thus, his subsequent assumption (Orr, 1974, p. 2297) that, "Most of the oils are black asphaltic oils classed as chemically immature" that are then cracked to lighter oils is also flawed. Although not widely recognized in 1974, it is now well known that many (most?) "immature

oils" are actually degraded oils that originally were "mature" oils.

The third assumption of long-distance migration of a "common-pool" compositionally uniform oil to the traps in the Big Horn Basin strongly contradicts actual oil distribution in the basin. As discussed in Price (1980a), Gussow (1954) and Partridge (1958) both noted that only the anticlines immediately adjacent to the depocenter of the Big Horn Basin contain oil. Anticlines nearer the mountains and removed from the depocenter, both in easterly and westerly directions, are oil barren, yet all the basinal anticlines have equivalent geologic histories. A west-to-east long-distance migration of oil would dictate that the westernmost anticlines removed from the basin deep be oil bearing, which they are not. On the other hand, a local origin of oil from the Big Horn Basin deep (Price, 1980c) would dictate that the oil be primarily in the anticlines ringing and immediately adjacent to the basin deep, which is the case.

Thus, although Orr (1974) elegantly presented his hypothesis of thermochemical-sulfate reduction using the Big Horn Basin as a model, he put unrealistic constraints on the Big Horn Basin to fit the requirements of his model. These constraints contradict known geologic and petroleum-geochemical features in this basin. Thus, in my opinion, the original type model (the Big Horn Basin) for thermochemical-sulfate reduction is, in point of fact, highly flawed.

Orr (1974) specifically detailed reaction schemes and expected products for thermochemical sulfate reduction; however, later investigations invoking the mechanism call for reaction schemes and products that are antithetic to Orr's (1974) original scheme. Furthermore, different investigators (Sassen and Moore, 1988; and Claypool and Mancini, 1989) working in the same geographic area have drawn different conclusions from both each other and Orr (1974) regarding the mechanism and its reaction products. For example, the sulfur-bearing hydrocarbons that Orr (1974) detailed as the reaction products from thermochemical-sulfate reduction are low-maturity compounds—mercaptans, thiaalkanes, cyclothiaalkanes, and thiophenes. As Orr (1974, p. 2315) noted, "A major conclusion from this type of mechanism is that the organic-sulfur compounds in a high-temperature reservoir are not predominantly the thermally stable compounds which have survived the original oil." Also, he (p. 2316) noted that the enrichments in S^{34} and C^{13} that he observed in the Big Horn Basin oils would be due to different processes and that only increases in S^{34} would be due to thermochemical sulfate reduction, "The most likely mechanism for S^{34} enrichment requires sulfate, but sulfate availability presumably would have no direct effect on C^{13} enrichment."

Claypool and Mancini (1989, p. 920) called on thermochemical-sulfate reduction to explain the gas and gas-condensate compositions that they observed in Jurassic

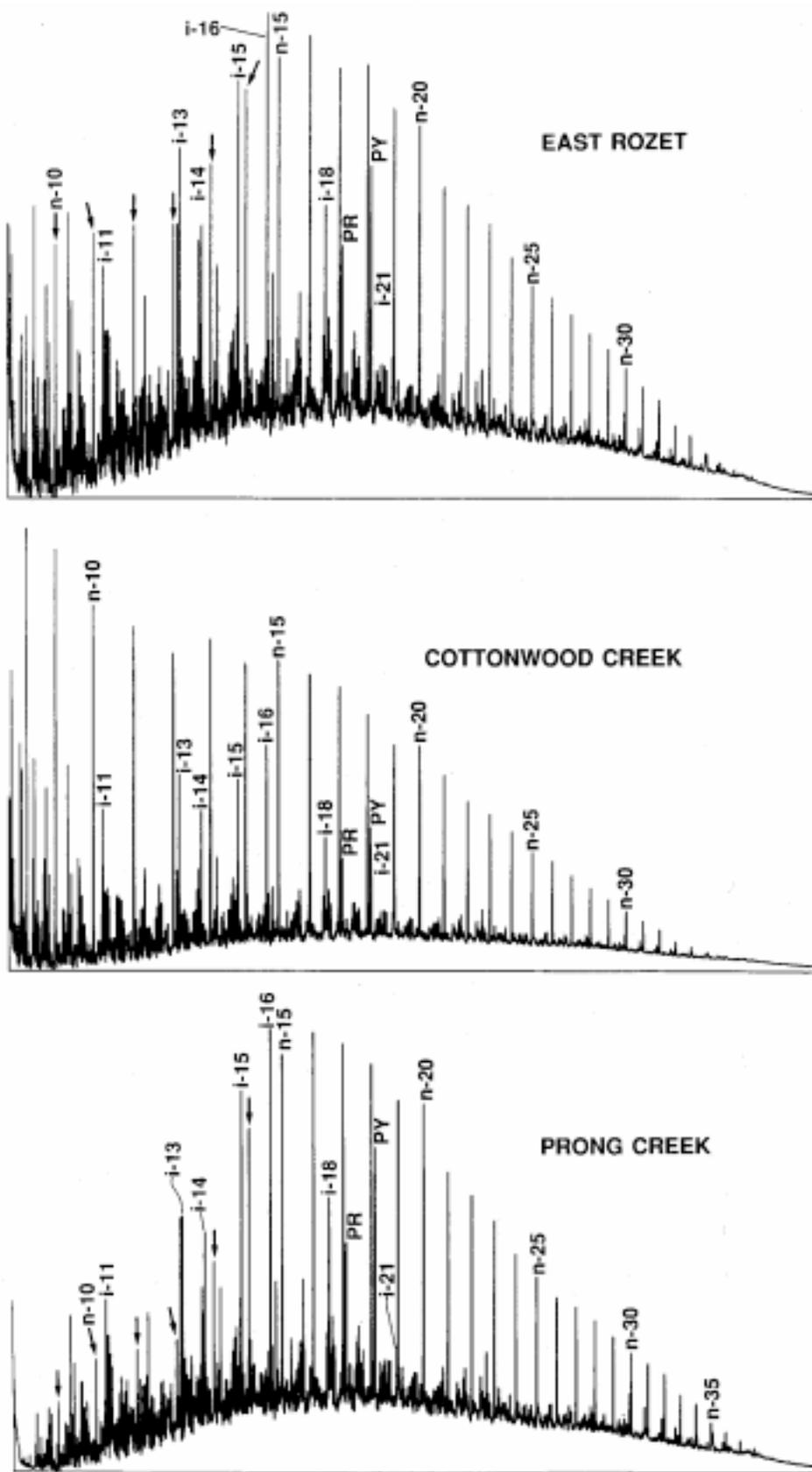


Figure 12. C₈+ saturated hydrocarbon gas chromatograms for three oils from Big Horn Basin. PR is pristane; PY is phytane; other isoprenoid hydrocarbons are labeled by i- and their respective carbon number; every fifth n-paraffin is labeled by n- and its respective carbon number. Other n-paraffins are labeled, by arrows if necessary.

Smackover production of southwestern Alabama, "The products of the oxidation reactions, coupled with the reduction of sulfate, include CO₂, aromatic hydrocarbons, and thiophenes (Orr, 1974)." Two facts should be noted. (1) Orr (1974) did not call for aromatic hydrocarbons as products of thermochemical-sulfate reduction. (2) The full suite of samples that Claypool and Mancini (1989) described exist and have been analyzed at the U.S. Geological Survey. No thiophenes (or thiaalkanes, or cyclothiaalkanes, or mercaptans) are present in any of these samples. In fact, the highest rank samples that Claypool and Mancini (1989) described as products of thermochemical sulfate reduction contain only methyl-, dimethyl-, and trimethyl- benzothiophenes and dibenzothiophenes as sulfur-bearing compounds. These compounds are, in point of fact, the most thermally stable sulfur-bearing compounds (see Price, this volume, fig. 27). Thus, the compositions of the sulfur-rich gas condensates of southern Alabama fall far outside of the original constraints proposed by Orr (1974).

Claypool and Mancini (1989) noted a significant decrease in the ratio of C₁₅₊ saturated to aromatic hydrocarbons and noticeably heavier carbon isotopes (less negative δ¹³C values) in the saturated hydrocarbons of their highest rank gas condensates. They attributed the decrease in the saturated to aromatic ratio to preferential destruction of saturated hydrocarbons and called for a preferential destruction of n-paraffins relative to all other saturated-hydrocarbon compound classes. This latter conclusion was based, however, on a Flomaton field saturated-hydrocarbon gas chromatogram (their fig. 10) resulting from inefficient silica gel-alumina column chromatography. The Claypool and Mancini (1988) Flomaton saturated hydrocarbon fraction actually had high contents of coeluted aromatic hydrocarbons and sulfur-bearing aromatic hydrocarbons. In reality, Flomaton field saturated hydrocarbons (and saturated hydrocarbons from all other high-maturity condensates of the southeastern United States; see Price, this volume, fig. 22 and accompanying discussion), if isolated by properly performed silica gel-alumina chromatography, are actually n-paraffin rich because most of the other saturated hydrocarbons have been destroyed. Although a significant part of Claypool and Mancini's (1989) "evidence" for thermochemical-sulfate reduction in the gas condensates of southwestern Alabama arose from the perception by those authors of the unusual character of the Flomaton field saturated hydrocarbons, the "unusual Flomaton characteristics" are only a laboratory artifact, and the Flomaton field saturated hydrocarbons are in reality quite similar to those from other gas condensates studied by Claypool and Mancini (1989) such as Perdido, Chunchula, Chatom, Copeland, and Big Escambia Creek.

A study by Sassen and Moore (1988) in the same area, and using some of the same samples as that of Claypool and Mancini (1989), reached significantly different conclusions than those of Claypool and Mancini (1989). Sassen and

Moore (1988) believed that their data indicated that aromatic hydrocarbons were destroyed preferentially to saturated hydrocarbons with increasing maturation. Furthermore, within the saturated hydrocarbons, the n-paraffins were interpreted as the most thermally stable compound group. It should be noted that the two studies reported on four of the same samples and reported significantly different percentages of C₁₅₊ saturated (and aromatic) hydrocarbons making up the C₁₅₊ fraction. These differences are most likely due to nonstandard laboratory techniques between the two laboratories in which the analyses were carried out. Thus, any conclusions regarding changes in saturated or aromatic hydrocarbon abundances in the gas condensates and oils examined by either study is tenuous.

Thermochemical-sulfate reduction and in-reservoir thermal cracking of C₁₅₊ hydrocarbons were proposed, and have been invoked, to explain high concentrations of CO₂ and H₂S in reservoir gases, heavier sulfur isotopes, and heavier carbon isotopes in the saturated hydrocarbons, all relative to increasing maturation rank. All these features can, however, be explained by other processes. For example, in Lewan's (1983) hydrous-pyrolysis experiments on the Mississippian-Devonian Woodford Shale, the saturated hydrocarbons of the generated expelled oil became isotopically heavier (less negative δ¹³C values) with increasing experimental temperatures. This feature was also observed in the aqueous-pyrolysis experiments of Wenger and Price (1991) and Price and Wenger (1992). Obviously all maturity indices of oils, generated either in laboratory experiments or from source rocks in nature, increase in maturity with increase in maturation rank, from either increasing experimental or burial temperatures. Thus, sulfur in oil also will become isotopically heavier with increasing source-rock maturation rank, and thermochemical-sulfate reduction is not needed to explain this feature.

A strong argument against the widespread existence of thermochemical-sulfate reduction, as it has been proposed, is the presence of the principal products, CO₂ and H₂S, from the proposed reaction. As stated above, CO₂ and H₂S are both extremely soluble in water. Therefore, their high concentrations in gas reservoirs for any length of geologic time dictate that the reservoir in which they reside be either a closed hydrogeologic system, in which no water movement or diffusion through water can occur, or water free, or both. Thermochemical-sulfate reduction, on the other hand, requires an outside source of the SO₄⁼ ion to be transported, via water, into the hydrocarbon reservoir in an open hydrogeologic system. Therefore, because of the need for an open system, if thermochemical-sulfate reduction were occurring, CO₂ and H₂S could not possibly accumulate as reaction products in high concentrations. In point of fact, the very presence of these species in high concentrations dictates that thermochemical sulfate reduction cannot be responsible for their origin.

With some exceptions, gas reservoirs that contain high concentrations of H₂S and (or) especially CO₂ are most usually at high maturation ranks in basin deeps. This fact suggests that high concentrations of either or both CO₂ and H₂S could be related to processes that occur in deep basins at high maturation ranks. For example, a review by Petroleum Information Corporation (1984) discussed both CO₂ release in sedimentary basins from volcanic intrusions into sedimentary rocks and CO₂ generation from volcanic, plutonic, or metamorphic intrusions or processes on carbonate rocks. Also, Le Tran (1972) demonstrated that high concentrations of H₂S were generated at elevated maturation ranks from the sulfur-rich organic matter in the fine-grained rocks of the carbonate sequences of the southern Aquitaine Basin, France (fig. 13). It should be noted that the present-day burial depths and temperatures shown in figure 13 are not maximal for this area of the Aquitaine Basin. As summarized in Price (1983, p. 19–21), the southern Aquitaine Basin has been affected by a major orogeny, igneous intrusion, metamorphism, a highly elevated paleo-heat flow and subsequent significant erosion. The North Pyrenean fault (1) is a major crustal feature with more than 10,000 m of throw, (2) is thought to be a paleo-plate suture, (3) has been overthrust into the southern Aquitaine Basin, and (4) and is 5–10 km from the well that Le Tran (1972) studied in the giant Lacq gas field. Coustau and others (1969) carried out a detailed organic and inorganic geochemical study on the sediments of the southern Aquitaine Basin and found that paleotemperatures in this part of the basin were much higher than present-day burial temperatures. Coustau and others (1969, p. 84) concluded that Jurassic source rocks there had previously been exposed to temperatures as high as 300°C and stated, “This early and very accentuated thermic evolution is, in our opinion, the most determining factor of the exclusive presence of gaseous hydrocarbons in the deep fields of the south of the Lacq Basin, in front of the Pyrenean chain.”

Le Tran (1972) noted that (as of 1971) all known gas deposits with high concentrations of H₂S are in carbonate sequences, the southern Aquitaine Basin and Upper Jurassic Smackover Formation (southeastern United States) being the most well-known examples. As discussed in Price (this volume), the latter area also has been subjected to extreme paleo-heat flows. Le Tran (1972) concluded that most of the H₂S in gas deposits having high H₂S concentrations originated from generation processes in fine-grained organic-rich rocks of carbonate sequences when such rocks were exposed to extreme maturation ranks. I concur completely with this hypothesis.

DATA OF WEISMAN

Weisman (1971) examined isotopic compositions of methane and carbon dioxide from the Sacramento Valley and West Texas Permian–Val Verde Basin gas fields, all of

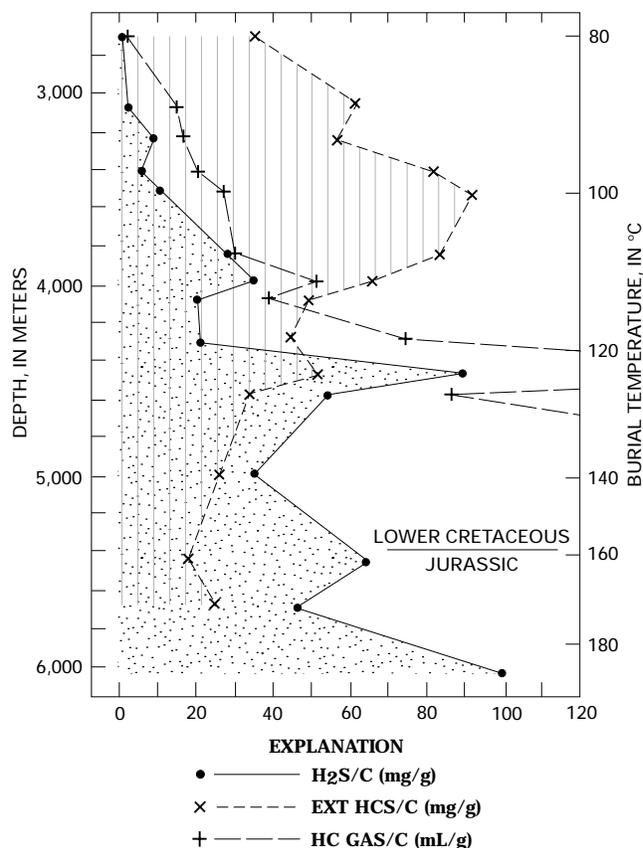


Figure 13. Increase in H₂S sorbed on sediments in the southern Aquitaine Basin, France (stippled pattern). H₂S/C is amount of sorbed H₂S in milligrams per gram of organic carbon in the sediments; EXT HCS/C is milligrams of extractable bitumen per gram of organic carbon and is shown by the field of parallel lines; and HC GAS/C is milliliters of hydrocarbon gas per gram of organic carbon. All three variables are plotted versus present-day burial depth and present-day burial temperature. The boundary between Jurassic and Lower Cretaceous sediments is also shown. Modified from LeTran (1972).

which have been affected by igneous or volcanic activity. He recorded data that support his hypothesis that at very high temperatures (500°C–1,200°C) carbon dioxide and methane equilibrate to each other (fig. 14) with respect to the carbon-13 isotope. His hypothesis is supported by data from aqueous-pyrolysis experiments (fig. 4), wherein at temperatures lower than those considered by Weisman (1971) values for both methane and carbon dioxide trend toward one another with increase in temperature. This feature could be due, however, to a strong control by the original organic matter and (or) by thermal decrepitation of calcite in the experimental rocks.

By measuring δ¹³C values in associated methane and carbon dioxide and employing his δ¹³C thermometer, Weisman (1971) documented strong increases in estimated paleotemperatures of gas fields toward intrusive plutonic

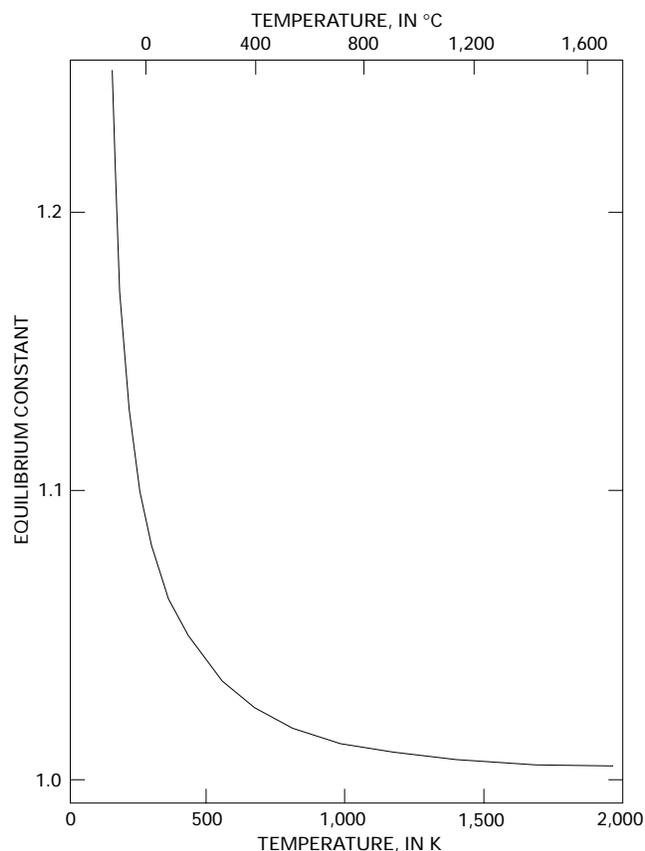


Figure 14. Equilibrium constant for exchange of carbon-13 isotope between methane and carbon dioxide. Modified from Weisman (1971).

and intrusive and extrusive volcanic features in the Sacramento and West Texas Permian–Val Verde basins. He also found strong vertical and lateral zonations of methane $\delta^{13}\text{C}$ values within several of the fields he studied. He noted, as well, a strong zonation of increasing carbon dioxide concentrations in the Cambrian–Ordovician Ellenburger Limestone of the West Texas Permian Basin gas fields toward the south and southwest that he attributed to deep-seated igneous activity.

This observed trend in CO_2 concentrations agrees with the model (discussed preceding) put forth by Petroleum Information Corporation (1984) in which the CO_2 in some deep-basin gas deposits is linked to deep-seated volcanic or plutonic activity. The methane $\delta^{13}\text{C}$ values that Weisman (1971) measured in several gas fields strongly suggest a methane origin from C_{15+} hydrocarbon thermal destruction ($\delta^{13}\text{C}$ for methane of -35 at Puckett and -28 at Brown-Bassett in West Texas). In addition, Stahl and Carey (1975) and Schoell (1980) reported $\delta^{13}\text{C}$ values of -38.0 to -35.1 for methane from deep gas deposits of the Delaware–Val Verde basins. If the extreme paleotemperatures calculated by Weisman (1971) are valid, then the gas in the fields he

studied is true high-rank methane that originated at least in part from C_2+ hydrocarbon thermal destruction. Methane having even heavier carbon isotopes has been reported by Jenden and others (1989) for gas deposits in the Sacramento Valley Basin.

CONCLUSIONS

1. Evidence for deep-basin high-rank ($R_o=0.9$ – 1.35 percent) hydrocarbon destruction classically has been attributed to the lack of deep-basin oil deposits and to strong basinal hydrocarbon zonations in which dry gas is only in the deep basin and oil is on the shelves and both gas to oil ratios and API gravities decrease with decreasing burial. These hydrocarbon distributions also result, however, from (a) secondary migration of the first-generated (most immature) oils furthest from the generation sites in basin depocenters; (b) emplacement processes during secondary migration (oil emplaced mostly at shallow depths during vertical migration); and (c) condensation, buoyancy, migration, and flushing processes (Gussow's [1954] principle of differential entrapment) that sweep away oil, water, and the C_2 – C_4 hydrocarbon gases from the deep basin resulting in only dry-gas (methane-rich) gas deposits remaining in the deep basin.

2. Carbon-isotopic compositions of methane from aqueous-pyrolysis experiments and from gas deposits from nature strongly suggest that most of the methane in gas deposits originates from kerogen during, and at the last stages of, mainstage C_{15+} hydrocarbon generation. Mixing of this methane cogenerated with C_{15+} hydrocarbons with biogenic methane trapped in source rocks at depth also occurs. With some exceptions, only minor methane is generated by the thermal destruction of C_{15+} hydrocarbons in fine-grained rocks and even less is generated by thermal destruction of oil in the reservoir. Some gas deposits show by methane-isotopic, compositional, and geologic evidence that they have a high-temperature (400° – $1,200^\circ\text{C}$?) origin involving C_{15+} hydrocarbon thermal destruction; however, such gas deposits are unusual. It is hypothesized that most high-rank, deep-basin, dry-gas deposits are made up mostly of methane co-generated with C_{15+} hydrocarbons and originate from condensation and buoyancy processes and differential entrapment (Gussow, 1954). These processes are believed to lead to an expulsion of all, or most, C_2+ hydrocarbons (and water) from deep-basin gas traps.

3. Support for this model of the origin for dry-gas deposits is as follows: C_{15+} hydrocarbons in fine-grained rocks are thermally stable to $R_o=7.0$ – 8.0 percent; oil of only moderate biomarker maturity is entrained, in solution, in deep, high-rank, dry-gas deposits in small concentrations; and a few high-rank oil deposits have been found.

4. It is hypothesized that gas expulsion from source rocks, similar to oil expulsion, is much more inefficient than

generally perceived, and thus it is believed that intense faulting and fracturing are necessary to physically disrupt source rocks so that significant expulsion of gases can occur. Thus, conventional deep-basin gas deposits should almost always be associated with major faulting. Normal and extensional faulting is most favorable for migration because of voids along the fault zones. Later evolution to compressional (high-angle reverse) faulting (such as in the Anadarko Basin in southern Oklahoma) is favorable for preservation of deep-basin gas deposits over geologic time.

5. Very large, in-place, nonconventional gas-resource bases have been proven, among which are basin-centered gas, coal gas, tight gas, black-shale gas, and Gulf Coast geopressured-geothermal gas. It is hypothesized that the existence of such unconventional gas-resource bases is primarily due to, and is direct evidence of, highly restricted (closed-system) fluid flow and inefficient hydrocarbon expulsion in deep sedimentary basins. Much of the rock volume of deep sedimentary basins is perceived to be an essentially closed system with respect to significant fluid flow once basinal evolution goes beyond the youthful stage to the mature stage and geothermal gradients decline. It is further hypothesized that these different nonconventional gas-resource bases may be both larger and of a higher grade than previously believed.

6. Additional geologic-geochemical studies to document the extent, grade, and characteristics of nonconventional gas resources would be useful. Geologic-based engineering studies to determine the appropriate techniques applicable to the nonclassical characteristics of each of these different gas resources would assist in economic recovery of these resources.

7. Cracks, fractures, parting laminae, and other such voids in deep-basin rocks may provide significant storage capacity and thus help to offset a general trend of decreasing porosity with increase in maturation rank (depth) in deep petroleum basins.

8. Both CO₂ and H₂S are quickly (10⁴–10⁵ years) leached out of water-bearing deep-basin gas deposits because of their high aqueous solubilities. Thus, the presence of either of these two gases in deep-basin gas deposits dictates that such gas deposits contain no water and are closed systems with regard to fluid migration. The probability of water-free, deep-basin gas reservoirs has strong implications for enhanced thermal destruction of C₁₅+ hydrocarbons and possible formation (skin) damage around the wellbore during drilling, completion, and stimulation operations.

9. Although the hypothesis of thermochemical sulfate reduction has been proposed to explain high concentrations of carbon dioxide and (or) hydrogen sulfide in some high-rank gas deposits, the hypothesis may be overstated. High concentrations of these nonhydrocarbon gases are believed instead to result from various high-rank processes that take place in deep petroleum basins, including plutonic activity,

volcanic intrusive and extrusive activity, and the tendency of carbonate-facies source rocks to generate significant amounts of hydrogen sulfide at very high maturation ranks.

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