

Laboratory Simulation of Petroleum Formation

Hydrous Pyrolysis

M. D. LEWAN

1. Introduction	419	6. Effects of Reactor Wall Composition	430
2. Definition of Hydrous Pyrolysis	419	7. Consideration of Experimental Artifacts	435
3. Significance of Expelled Oil	421	8. Conclusions	439
4. Comparison of Pyrolysate Yields	425	References	440
5. Utility of Rock Samples	428		

1. Introduction

The importance of water in laboratory experiments designed to simulate natural processes is well documented in the studies of granite melts (Goranson, 1931, 1932; Tuttle and Bowen, 1958), metamorphic reactions (Winkler, 1974, p. 15; Rumble *et al.*, 1982; Ferry, 1983), and coal formation (Berl and Schmidt, 1932; Schuhmacher *et al.*, 1960). Industrial processes also benefit from the presence of water as demonstrated in oil shale retorting (Gavin, 1922, p. 181), conversion of coal to oil (Fischer, 1925, p. 180), heavy oil upgrading (McCollum and Quick, 1976a, b), and conversion of organic refuse to oil (Appell *et al.*, 1971, 1975). Prior to 1979, organic geochemists inadvertently ignored these observations and the ubiquity of water in sedimentary basins when considering the natural process of petroleum generation. A notable exception is the work reported by Jurg and Eisma in 1964. Noting differences in the thermal decomposition of behenic acid in the presence and absence of liquid water, these investigators suggested that water played an important role in petroleum generation. Although a subsequent study in 1969 by Brooks and Smith employed water in laboratory simulations of petroleum generation from coals, laboratory experiments over the next decade did not consider the role of water in petroleum generation (e.g., Tissot *et al.*, 1974; Larter *et al.*, 1977; Harwood, 1977).

In 1979, Lewan *et al.* reported that heating organic-rich rocks in the presence of liquid water resulted in the generation and expulsion of an oil-like pyrolysate. The expelled pyrolysate in this type of experiment was a free-flowing oil that accumulated on the water surface above the submerged rock. Physically, chemically, and isotopically, the expelled oil pyrolysate was similar to natural crude oils. This experimental approach was referred to as hydrous pyrolysis (Lewan *et al.*, 1979) and has been shown to provide useful information on primary migration, stages and kinetics of petroleum generation, and thermal maturity indices (Lewan, 1983, 1985, 1987; Winters *et al.*, 1983; Lewan *et al.*, 1986). The following discussion elaborates on these attributes within the context of methodology employed in hydrous pyrolysis experimentation.

2. Definition of Hydrous Pyrolysis

Hydrothermal experiments involve the heating of samples in the presence of water irrespective of whether it occurs in the form of a vapor, liquid, or fluid phase. Hydrous pyrolysis is a hydrothermal experiment, but more specifically its definition requires that the heated samples be in contact with liquid water (Lewan *et al.*, 1979) and not in contact with water vapor or supercritical water fluid. Exclu-

M. D. LEWAN • Amoco Production Company, Research Center, Tulsa, Oklahoma 74102. Present address: U.S. Geological Survey, Denver, Colorado 80225.

Organic Geochemistry, edited by Michael H. Engel and Stephen A. Macko. Plenum Press, New York, 1993.

sion of these other water phases from the definition is based on their absence under normal burial diagenesis conditions and their different chemical reactivities relative to liquid water. Water vapor in the subsurface is limited to shallow geothermal vent areas, and its reactivity with organic and inorganic components in rocks is less than that of liquid water. Supercritical water fluid is limited to subsurface regimes in excess of greenschist metamorphic conditions, and its reactivity with organic and inorganic components in rocks may be significantly greater than that of liquid water.

Water in hydrous pyrolysis experiments typically occurs in the liquid and vapor phases (e.g., Lewan, 1985), unless pressure regulators are employed to maintain only a liquid phase (e.g., Monthioux *et al.*, 1985). It is important in two-phase water systems to optimize the amount of water used for a specific reactor volume to ensure the sample is submerged in the liquid phase. The volume of liquid water in a reactor at an experimental temperature depends on the amount of thermal expansion of the liquid phase and the amount of water needed to generate the required vapor pressure in the remaining gas space of the reactor. Specific volumes of water in the liquid (γ_l^T) and vapor (γ_v^T) phases at experimental temperatures (T) are critical to these volume determinations and are available in the *ASME Steam Tables* (ASME, 1979). Using these specific volumes, the volume of liquid water (V_l^T) at an experimental temperature in a given reactor volume (V_r) may be determined by the expression

$$V_l^T = \frac{(M_w^0 \gamma_v^T - V_r) \gamma_l^T}{\gamma_v^T - \gamma_l^T}$$

where M_w^0 is the mass of liquid water added to the reactor at room temperature.

This volume of liquid water may be expressed as a percentage of the reactor volume [i.e., $(V_l^T \times 10^2)/V_r$]. Several of these percentages are shown graphically as a series of lines in Fig. 1 for an experimental temperature of 330°C. Experimental conditions plotting on or above the zero-volume percentage line represent experiments with only water vapor in the reactor, which does not constitute hydrous pyrolysis conditions. Below this line, hydrous pyrolysis conditions exist provided the amount of liquid water present is sufficient to cover the heated sample. It is helpful in this determination to have an estimate of the sample density from which its volume may be approximated. The optimum condition at room temperature for a loaded reactor is a water surface several centimeters above

the submerged sample. This makes collection of expelled oil from the water surface, after an experiment has been cooled to room temperature, more manageable without the interference of emergent sample in the expelled-oil layer.

Another consideration in loading a reactor is not to add too much water. If thermal expansion of the added water exceeds the available volume of the reactor at an experimental temperature, a dangerous condition will occur in which the reactor may violently rupture. Although commercially available reactors are usually equipped with a safety rupture disk, it is a good practice never to allow the total volume of sample plus expanded water to exceed 85 vol. % of the reactor at an experimental temperature. Pressures that develop within the remaining gas space are predominantly the result of the water vapor, which increases with temperature as shown by the vapor-liquid line in Fig. 2. The pressures in most hydrous pyrolysis experiments usually exceed these vapor pressures because of additional gases generated from the pyrolyzed sample. If a constant gas pressure is desired over a range of experimental temperatures, an inert gas such as helium may be added to the gas space in the appropriate amounts to compensate for lower vapor pressures at lower temperatures.

The definition of hydrous pyrolysis also specifies that water at experimental temperatures within a reactor is not in the supercritical fluid phase. This prerequisite is based on the exceptionally high solubilities organic substances have in supercritical fluid water (Deshpande *et al.*, 1984; Houser *et al.*, 1986; Amestica and Wolf, 1986) and the absence of this phase in the subsurface under the conditions in which petroleum generation occurs. Experiments using distilled water are limited to temperatures below the critical point of 374°C. As shown in Fig. 2, this critical-point temperature may be raised with the addition of NaCl to the water. While NaCl solutions provide subcritical temperatures as high as 700°C (Sourirajan and Kennedy, 1962), they are also highly corrosive, and care must be taken in selecting an appropriate reactor-wall composition.

Figure 2 also shows that the critical-point temperature of water may be lowered with the addition of CO₂. Supercritical fluid water may occur at temperatures below 300°C in experiments that generate high CO₂ concentrations relative to the amount of water present in the reactor. An example of this is the experiments conducted by Monthioux *et al.* (1985), in which high CO₂ concentrations were generated from pyrolyzed coals at high pressures in the presence of small quantities of added water. Calculations based

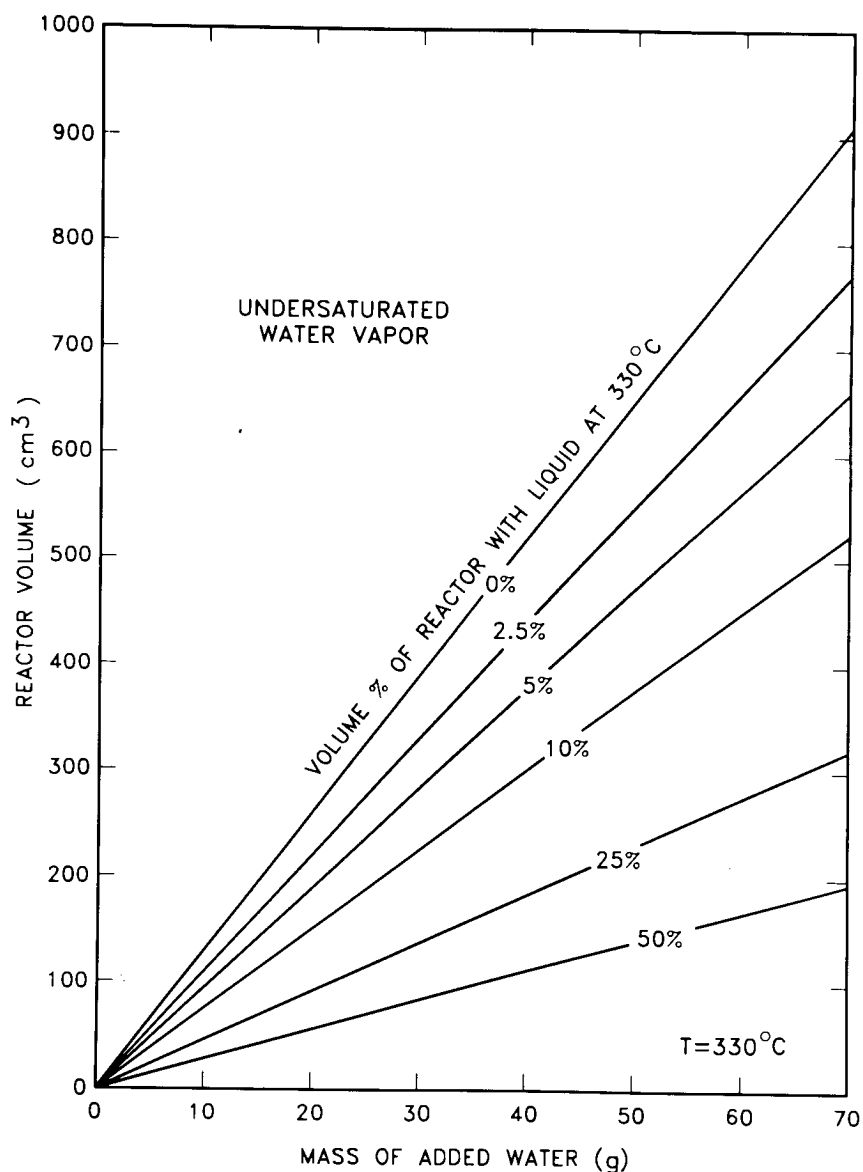


Figure 1. Plot showing volume percent of reactor filled with liquid water at 330°C for varying amounts of added water and reactor volumes.

on their reported experimental data indicate supercritical water fluid and not liquid water existed in their experiments at temperatures as low as 300°C. Supercritical hydrothermal experiments such as these are not hydrous pyrolysis experiments as originally defined.

A salient point of this discussion is that sample size, reactor volume, and amount of added water are key variables in determining whether or not a hydrous pyrolysis experiment has been conducted. Neglecting to report any one of these variables makes it impossible to determine the water phase or phases in contact with a sample during an experiment. If appropriate comparisons of experimental data from differ-

ent laboratories are to be made, it is vital that experimental conditions be thoroughly described when reporting results in the literature.

3. Significance of Expelled Oil

Petroleum formation may be defined as hydrocarbon generation within and expulsion from a source rock. The major problem with anhydrous pyrolysis experiments (i.e., no added water) is their inability to generate and expel an oil-like pyrolysate in a manner analogous to that in the natural system. Closed anhydrous experiments involve pyrolyzing a sample in

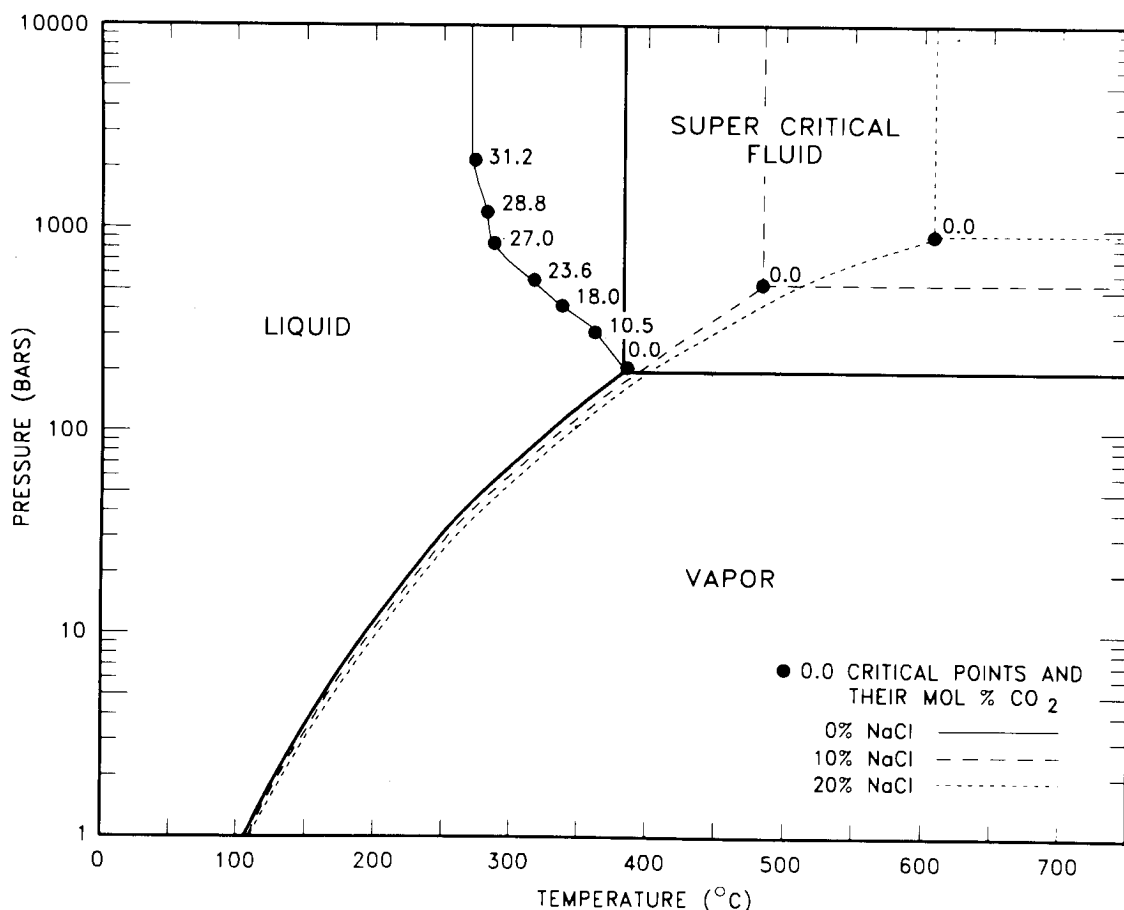


Figure 2. Pressure-temperature diagram showing phase relations and critical points for pure H_2O (—), CO_2 in solution with H_2O (●—●; solid circles refer to critical points at denoted CO_2 mole fractions), 10 wt. % NaCl solution with H_2O (---), and 20 wt. % NaCl solution with H_2O (· · ·). Diagram is based on experimental data reported by Haas (1976), Sourirajan and Kennedy (1962), and Takenouchi and Kennedy (1964).

a sealed reactor with an inert gas or initially *in vacuo*. The reactor is cooled to room temperature at the end of the experiments, and the pyrolyzed sample is extracted with an organic solvent to obtain a pyrolysate product. Open anhydrous experiments allow the escape of components volatilized from a sample while it is being pyrolyzed. The volatile products are removed rapidly from the reactor by sweeping the sample with a carrier gas or by maintaining a vacuum on the system through a cold trap. Although these experiments have provided structural information on kerogens and relative assessments of petroleum potential of rocks, they have not provided information on generation and expulsion of oil from source rocks in the natural system. The ability of hydrous pyrolysis experiments to generate an oil compositionally similar to crude oil and to expel it in a manner similar to that in naturally maturing source rocks gives them a dis-

tinct advantage over anhydrous pyrolysis experiments (Lewan *et al.*, 1979). Some studies have concentrated on compositional similarities between pyrolysates from hydrous and anhydrous pyrolysis experiments (Saxby *et al.*, 1986; Comet *et al.*, 1986) but have not considered the advantage of expelling an oil-like pyrolysate from a rock in hydrous pyrolysis experiments.

Monitoring expelled oil, retained bitumen, and kerogen of a potential source rock through a series of hydrous pyrolysis experiments at different temperatures has shown that petroleum formation may be described by four stages: (1) pre-oil generation, (2) incipient-oil generation, (3) primary-oil generation, and (4) post-oil generation (Lewan, 1985). An example of this is shown in Fig. 3 for aliquots of a sample of Woodford Shale (WD-5) heated isothermally at different temperatures under hydrous py-

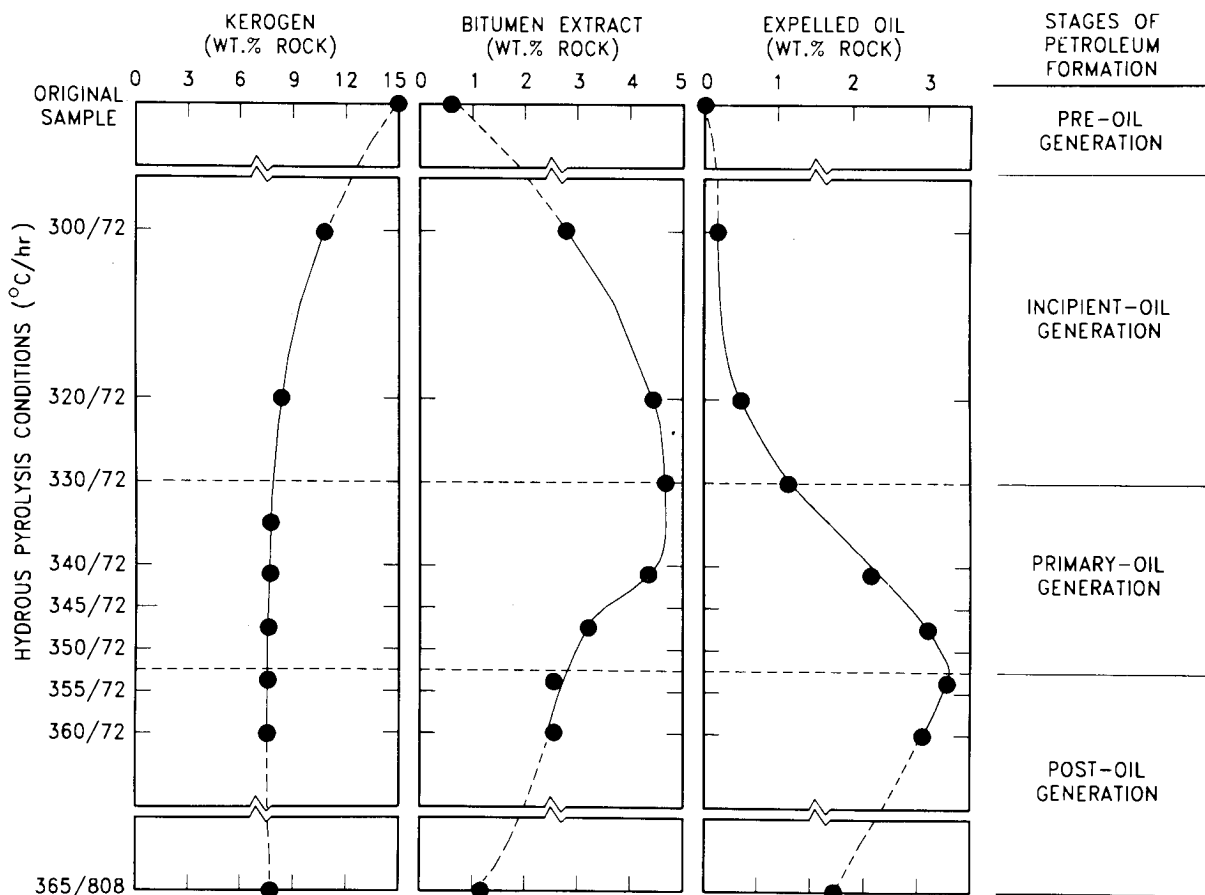


Figure 3. Variations in the amounts of kerogen, bitumen, and expelled oil from aliquots of a sample of Woodford Shale (WD-5) subjected to different temperatures for 72 to 808 h under hydrous conditions.

rolysis conditions. Pre-oil generation represents a thermally immature stage in which the organic matter occurs predominantly as a solid insoluble kerogen. Incipient-oil generation begins when thermal stress is sufficient to initiate decomposition of the kerogen into a tarry-soluble bitumen, which is enriched in high-molecular-weight hydrocarbons and heteroatom compounds. The amount of kerogen remains constant through the primary-oil generation stage, while thermal decomposition of bitumen results in the generation of an expelled oil, which is enriched in saturated hydrocarbons. Thermal decomposition of the expelled oil denotes the start of post-oil generation, in which the expelled oil and bitumen thermally decompose into gas and pyrobitumen.

Thermal decomposition of kerogen to bitumen and subsequent thermal decomposition of bitumen to oil have long been recognized in studies on oil shale

retorting (Engler, 1913; McKee and Lyder, 1921; Franks and Goodier, 1922). A bitumen intermediate has also been suggested by Louis and Tissot (1967) for petroleum formation in the natural system. Hydrous pyrolysis experiments define this series of overall reactions and demonstrate that maximum bitumen generation does not correspond to maximum oil generation (Fig. 3). These two organic phases are distinguished in this approach by whether they are expelled from or retained in a source rock, which is the same operational distinction usually made in the natural system. Crude oils are expelled products typically reservoirized in non-source rocks, and bitumen extracts are the soluble products retained within a source rock. This experimental and natural distinction is supported by differences in their physical and chemical character. Physical differences are most apparent, with bitumens being viscous tars and oils being free-flowing

liquids. This physical difference is also reflected in their chemical composition. Figure 4 shows the differences in saturated, aromatic, and polar constituents of bitumen extracts and expelled oils from hydrous pyrolysis experiments on the Woodford Shale (Lewan, 1983, 1985). Expelled oils plot within the compositional range of normal crude oils and have less compositional variability than the bitumen extracts. Despite the compositional variations through the different stages of petroleum formation, the expelled oils show no compositional similarities or parallel trends to the bitumen extracts.

Collection of an oil from the water surface with a pipet or syringe at the end of a hydrous pyrolysis experiment provides a full-range C_{5+} product for study. Conversely, solvent extraction of a sample subjected to closed anhydrous pyrolysis provides only a C_{15+} product due to solvent evaporation during the concentration procedure. Low-molecular-weight compounds make up a significant portion of natural

crude oils, and, in addition to C_5 – C_{15} n-alkanes, this boiling range includes thiophenes, benzothiophenes, benzenes, naphthalenes, tetralins, indanes, biphenyls, phenols, and adamantanes. Inclusion of these low-molecular-weight compounds in expelled oils from hydrous pyrolysis experiments is a useful attribute in studying natural petroleum generation. This has been demonstrated in evaluating the types of oil generated from resinites (Lewan and Williams, 1987) and the effects of radiation damage on organic matter in uranium-rich black shales (Lewan and Bucharadt, 1989).

Hydrous pyrolysis as originally described (Lewan *et al.*, 1979) emphasized the use of rock samples in simulating petroleum formation in the natural system. Subsequent hydrous pyrolysis experimentation has been extended to the study of isolated kerogens (Comet *et al.*, 1986). Although studies of this type provide information on compositional aspects and hydrocarbon potential of isolated kerogens, they have not taken advantage of the ability of hydrous py-

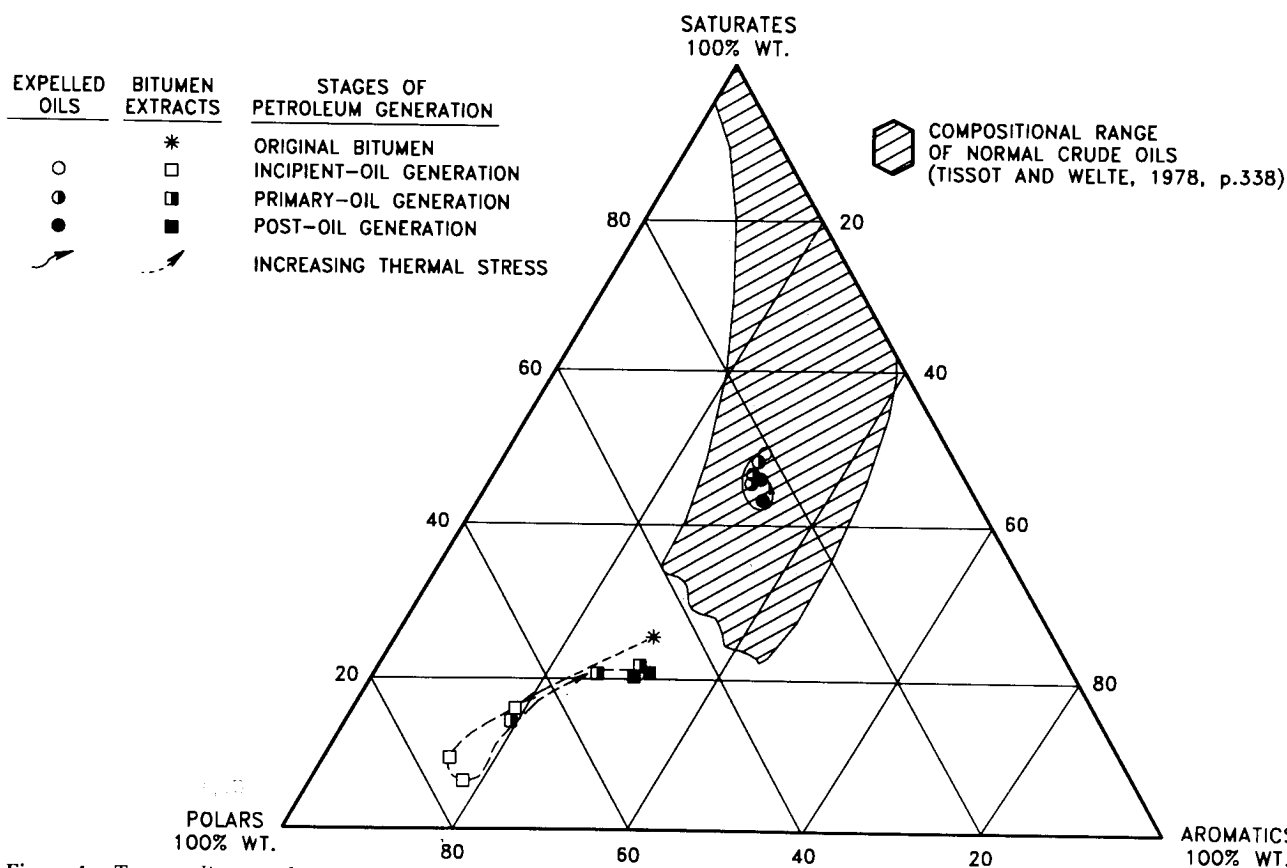


Figure 4. Ternary diagram showing the proportionality of saturate, aromatic, and polar fractions of expelled oils and bitumen extracts from Woodford Shale (WD-5) subjected to hydrous pyrolysis at the temperatures shown in Fig. 3 for 72-h durations. Fractions are defined by solid-liquid chromatography using a 40-cm alumina (MCB Alcoa F-20) column with saturates eluting with n-heptane, aromatics with benzene, and polars with a 40:60 (w/w) methanol:benzene mixture.

rolysis to differentiate between expelled oil and retained bitumen. Isolated kerogen that is oil-prone does generate an oil that accumulates on the water surface under hydrous conditions. Distinguishing oil from bitumen in these hydrous pyrolysis experiments is based solely on density differences relative to water. Therefore, the term floating oil rather than expelled oil is more appropriate in these types of experiments (e.g., Lewan and Williams, 1987).

4. Comparison of Pyrolysate Yields

In addition to generating an expelled oil, the total pyrolysate yields (bitumen + oil + gas) from hydrous pyrolysis are significantly greater than those from closed anhydrous pyrolysis. Comet *et al.* (1986) reported hydrous pyrolysis yields 1.2 to 1.7 times greater than closed anhydrous pyrolysis yields from isolated kerogens at 330°C after 72 h. Similarly, data reported by Tannebaum *et al.* (1986) on kerogen-mineral mixtures indicate hydrous pyrolysis yields 1.1 to 1.8 times greater than closed anhydrous pyrolysis yields at 300°C after 10 and 100 h, respectively. Neither of these comparative studies made a distinction between expelled oil and retained bitumen in their hydrous pyrolysis experiments. In order to make a more complete comparison between hydrous and anhydrous conditions, a series of 72-h pyrolysis experiments at 300, 330, and 350°C were conducted on aliquots of an immature sample of Woodford Shale (WD-26). These experimental conditions were used because they include stages of petroleum formation for the Woodford Shale from incipient-oil generation through primary-oil generation (Fig. 3). All of the experiments were conducted in 1-liter stainless steel-316 reactors with 400 g of crushed rock ranging in size from 0.5 to 2.0 cm. Hydrous pyrolysis experiments were conducted with 320 g of deionized (ASTM type I) water and an initial helium gas-space pressure of 241 kPa. Expelled oil and bitumen were collected by the procedures described by Lewan (1983). Anhydrous pyrolysis experiments at the three different temperatures were conducted in the same manner with the exclusion of added water and an initially evacuated gas space. The total amount of gas generated in each of the experiments was calculated on the basis of the ideal gas law at room temperature using gas-space volumes and mass-spectrometric analyses of the gases. Dissolved gases in the water at the conclusion of the hydrous pyrolysis experiments were not included in the total amount of generated gases at room temperature.

Pyrolysate yields from these comparative experiments are given in Table I in terms of generated gas, expelled oil, bitumen extract, and total pyrolysate (i.e., gas + oil + bitumen). Greater amounts of generated gas, and lack of an expelled oil in anhydrous pyrolysis compared to hydrous pyrolysis are the most obvious differences. The total pyrolysate for hydrous pyrolysis and anhydrous pyrolysis is essentially the same at 300°C after 72 h. This condition represents the incipient-oil generation stage, in which a portion of the kerogen decomposes into bitumen and only a small amount of expelled oil is generated from the bitumen. As the amount of expelled oil generated under hydrous conditions increases at the higher temperatures (i.e., 330 and 350°C), the difference in total pyrolysate between hydrous and anhydrous conditions becomes greater. Total pyrolysate under hydrous conditions is 1.4 and 2.0 times greater than under anhydrous conditions after 72 h at 330 and 350°C, respectively. This suggests that under closed anhydrous conditions the inability to generate an expelled oil results in a reduction in the total pyrolysate yield.

Table I shows the final pressures at experimental temperatures to be significantly higher in hydrous pyrolysis than in anhydrous pyrolysis. The higher pressures in hydrous pyrolysis are a result of water vapor, generated gas, and helium, and the lower pressures in anhydrous pyrolysis are only a result of generated gas. The significance of these pressure differences was evaluated in another series of experiments at 350°C for 72 h using aliquots of the same sample of Woodford Shale (WD-26). The first experiment in this series was under anhydrous conditions with an initial helium pressure of 7.72 MPa at room temperature. After 72 h at 350°C, the final pressure was 23.48 MPa of helium and generated gas. Table I shows that this higher pressure has no significant effect on the amount of total pyrolysate compared to that of the low-pressure anhydrous experiment. Once again, the inability of closed anhydrous pyrolysis to generate an expelled oil reduces its total pyrolysate relative to that generated in hydrous pyrolysis by a factor greater than 2 (Table I).

The second experiment in this series considers the conclusion by Monthioux and co-workers that confinement of generated gas in closed anhydrous pyrolysis produces results similar to those of hydrous pyrolysis (Monthioux *et al.*, 1985; Monthioux, 1988). This experiment involved mechanically pressing 500 g of crushed rock (0.5–1.0 cm) into a 500-ml stainless steel reactor, which was then evacuated. After 72 h at 350°C, a final pressure of 21.76 MPa was reached by

TABLE I. Comparison of Experimental Conditions and Pyrolysate Yields from Hydrous, Anhydrous (No Added Water), and Steam Pyrolysis of Crushed Aliquots (0.5–2.0 cm) of an Immature Sample of Woodford Shale (WD-26)^a

Experimental conditions	Final pressure at experimental temperature (MPa)	Generated gas (wt. % of rock)	Expelled oil (wt. % of rock)	Bitumen extract (wt. % of rock)	Total pyrolysate ^b (wt. % of rock)
300°C/72 h					
Hydrous ^c	9.76	0.43	0.65	8.35	9.43
Anhydrous ^d	2.17	0.78	0.00	8.66	9.44
Δ% ^e	+77.8	-81.4	+100.0	-3.7	-0.1
330°C/72 h					
Hydrous ^c	15.89	1.05	2.79	8.19	12.03
Anhydrous ^d	4.24	1.74	0.00	6.62	8.36
Δ%	+73.3	-65.7	+100.0	+19.2	+30.5
350°C/72 h					
Hydrous ^c	21.13	1.68	4.15	5.71	11.54
Anhydrous ^d	5.69	2.40	0.00	3.30	5.70
Δ%	+73.1	-42.9	+100.0	+42.2	+50.6
Helium-anhydrous ^f	23.48	2.27	0.00	2.99	5.26
Δ%	-11.1	-35.1	+100.0	+47.6	+54.4
Confined gas-anhydrous ^g	21.76	2.60	0.00	2.27	4.87
Δ%	-3.0	-54.8	+100.0	+60.2	+57.8
Steam pyrolysis ^h	18.31	2.08	0.00	6.01	8.09
Δ%	+13.3	-23.8	+100.0	-5.3	+29.9

^aAll of the experiments were conducted with 400 g of rock in 1-liter stainless steel-316 reactors, except for the confined-gas anhydrous experiment, in which 500 g of rock were pyrolyzed in a 500-ml stainless steel-316 reactor.

^bTotal pyrolysate = generated gas + expelled oil + bitumen extract.

^cCrushed rock with 320 g of deionized (ASTM type I) water under an initial He pressure of 241 kPa.

^dCrushed rock initially in an evacuated reactor.

^eΔ% = (Hydrous - Anhydrous)100/Hydrous.

^fCrushed rock under an initial He pressure of 7.72 MPa at room temperature.

^g500g of crushed rock mechanically pressed at 5000 psi into a 500-ml reactor, which was initially evacuated

^hCrushed rock with 75 g of dionized (ASTM type I) water under an initial He pressure of 241 kPa.

the generated gas as a result of the reduced gas space. As shown in Table I, this confined gas pressure is similar to the pressure obtained in hydrous pyrolysis at 350°C after 72 h. However, similar to the He-pressured anhydrous pyrolysis, the total pyrolysate is less than that from hydrous pyrolysis by a factor greater than 2 (Table I). Therefore, these experiments do not support the conclusion that confined gas under anhydrous conditions gives the same results as hydrous pyrolysis.

Although Monthioux *et al.* (1985) used supercritical-water conditions rather than hydrous conditions, this is not likely to be the major cause of the discrepancy in conclusions. More likely, this discrepancy may be explained by the inability of the coals used in their study to generate an expelled oil under hydrous conditions. Pyrolysate yields in Table I show that the inability of anhydrous conditions to generate an expelled oil reduces the total pyrolysate compared to that obtained under hydrous conditions. Under experimental conditions where little or no expelled

oil is generated (e.g., 300°C for 72 h), the difference between hydrous and anhydrous pyrolysis is negligible. Similarly, if the type, amount, or distribution of organic matter in a rock is not conducive for generation of an expelled oil by hydrous pyrolysis, no significant differences in total pyrolysate yields are expected between hydrous and anhydrous pyrolysis. Most of the comparable Rock-Eval data presented by Monthioux *et al.* (1985) are on a sample (no. 32362) that has an initial hydrogen index of only 135 mg HC/g organic C. Coals with hydrogen indices this low do not generate an expelled oil under hydrous conditions, and, therefore, their total pyrolysate yield is expected to be essentially the same as that obtained under anhydrous conditions.

The significance of water is also demonstrated in the third experiment of this series. An aliquot of the same sample of Woodford Shale (WD-26) with sufficient water to provide only water vapor in the reactor was heated at 350°C for 72 h. Results of this steam pyrolysis are given in Table I. Although no expelled

oil was generated in this experiment, the total pyrolysate yield is intermediate between the total pyrolysate yields for hydrous pyrolysis and anhydrous pyrolysis under the same time and temperature conditions. It becomes apparent from this series of experiments that the presence of liquid water is important in generating an expelled oil and that it does not merely act as a confining medium.

Comparisons with hydrous pyrolysis in this discussion have thus far concentrated on closed anhydrous pyrolysis. Another consideration is open anhydrous pyrolysis, which has been used successfully to characterize kerogen (Larter and Douglas, 1980; Larter and Senftle, 1985) and to provide rapid source rock evaluations (Espitalié *et al.*, 1977; Claypool and Reed, 1976). This type of pyrolysis typically uses a carrier gas to sweep volatiles generated from a rock or kerogen as it is heated from room temperature to temperatures in excess of 500°C. Open anhydrous pyrolysis makes no pretense to simulate natural petroleum formation, which is evident by the high concentrations of alkenes in its pyrolysates. Table II compares open anhydrous yields (i.e., Rock-Eval pyrolysis) from thermally immature samples of Woodford Shale and Phosphoria Retort Shale with their hydrous pyrolysis yields at the end of primary-oil generation. The total pyrolysates for both methods are similar, but the measurement of volatile hydrocarbons by a flame ionization detector used in Rock-Eval pyrolysis makes no distinction between gas, oil, or bitumen. Although this composite pyrolysate from Rock-Eval pyrolysis

provides a relative assessment of hydrocarbon potential of a rock, it does not provide an assessment of the amounts of generated oil expelled from a rock. As shown in Table II, the hydrocarbons generated by Rock-Eval pyrolysis (i.e., S_2) are greater than the expelled oils from hydrous pyrolysis by a factor of 2.

Neglecting to distinguish oil from bitumen in open anhydrous pyrolysis limits its use in determining kinetic parameters for modeling natural petroleum formation. Determining kinetic parameters on a composite product of bitumen, oil, and gas results in the need to use activation energy distributions that predict petroleum formation at lower temperatures and over broader temperature ranges than if only generated oil expelled from a rock is considered. Lewan (1985) has shown that the overall reaction of oil generation in hydrous pyrolysis experiments is adequately described by a single set of kinetic parameters, which are also applicable to predicting oil generation in the natural system. A comparative study by Burnham *et al.* (1987a, b) on kinetic parameters determined by Rock-Eval pyrolysis and hydrous pyrolysis shows the consequences of not making a distinction between oil and bitumen. Figure 5 compares the oil generation curves for Phosphoria Retort Shale determined by Rock-Eval-derived kinetics using activation energy distributions and by hydrous pyrolysis-derived kinetics using one activation energy. It is apparent for laboratory (Fig. 5a) and geological (Fig. 5b) heating rates that the inclusion of bitumen formation in Rock-Eval kinetics results in oil generation at significantly lower temperatures and over a broader temperature range than for kinetics determined by hydrous pyrolysis. Although Rock-Eval kinetics may adequately describe hydrocarbon generation (i.e., bitumen + oil + gas), hydrous pyrolysis kinetics more specifically describe oil generation.

A bitumen and oil may be distinguished in isothermal experiments using open anhydrous pyrolysis on the basis of pyrolysate volatility (e.g., Hubbard and Robinson, 1950). These experiments define oil as the condensable organic pyrolysate that is subsequently condensed to a liquid, and bitumen as the solvent-extractable organic pyrolysate that does not vaporize at experimental conditions and remains within the rock. Braun and Rothman (1975) have shown that by making this distinction the generation of vaporized pyrolysate oil may be described with a single set of kinetic parameters without the use of an activation energy distribution. The major concern with this type of pyrolysis is that the oil is obtained by vaporization and condensation, which is not operative in the natu-

TABLE II. Comparison of Rock-Eval and Hydrous Pyrolysis Yields from Woodford Shale and Phosphoria Retort Shale^a

Type of pyrolysis	Yield (wt. % of rock)	
	Woodford Shale WD-5	Phosphoria Retort Shale P-64
Rock-Eval pyrolysis ^b of original sample		
Volatile HC (S_1)	0.25	0.50
Generated HC (S_2)	7.11	13.45
Total pyrolysate	7.36	13.95
Hydrous pyrolysis ^c at the end of primary-oil generation		
Bitumen extract	2.56	6.52
Expelled oil	3.14	6.52
Generated HC gases	0.63	0.94
Total pyrolysate	6.33	13.98

^aLewan, 1985.

^bRock-Eval II, cycle 1.

^cExperimental conditions: 72 h at 355°C for WD-5 and at 350°C for P-64.

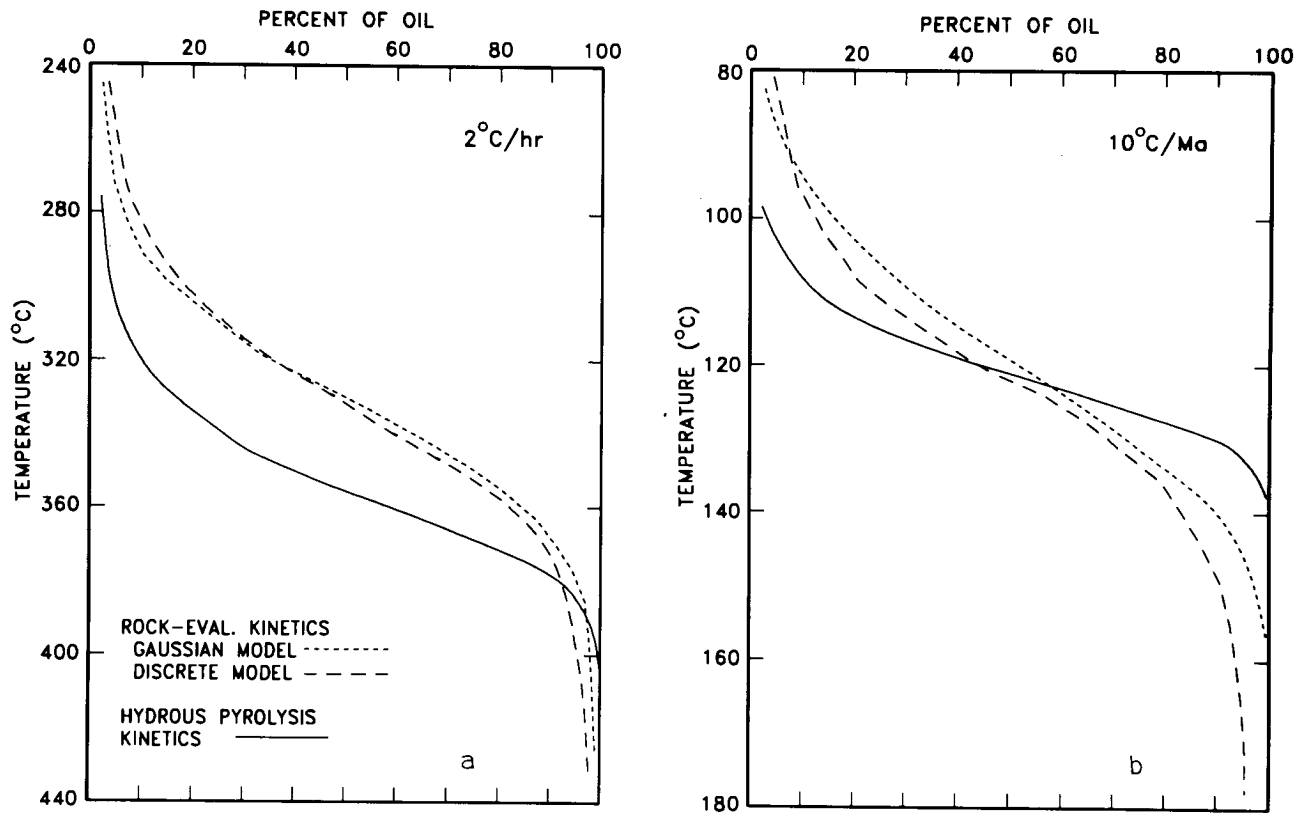


Figure 5. Oil generation curves determined from Rock-Eval kinetics and hydrous pyrolysis kinetics for Phosphoria Retort Shale at two different heating rates: (a) 2°C h^{-1} (Burnham *et al.*, 1987b); (b) $10^{\circ}\text{C Ma}^{-1}$ (Burnham *et al.*, 1987a).

ral system. As a result of vaporization playing a key role in obtaining an oil by open anhydrous pyrolysis, experimental factors including heating rate, rock sample size, and gas pressure have a significant effect on the results.

5. Utility of Rock Samples

Hydrous pyrolysis as described by Lewan *et al.* (1979) used rock samples rather than isolated kerogens to simulate natural petroleum formation. Unlike kerogens isolated by harsh acid treatments involving HCl and HF, organic matter in unpulverized rock samples occurs in its natural embedded state. Tannenbaum *et al.* (1986) have tried an alternative by subjecting artificial mixtures of isolated kerogens and minerals to closed anhydrous and hydrous pyrolysis. They observed that under hydrous conditions, water prevented kerogen-mineral interactions and concluded that these experiments are not representative of the natural system. The problem with simulating natural petroleum formation in these experiments is not the use of hydrous conditions but rather the use of

unconsolidated powdered mixtures instead of inductive rock samples.

Rock samples in the form of cores or crushed chips allow the embedded organic matter to mature in contact with natural mineral fabrics and interstitial waters. The hydrous conditions allow the interstitial waters to be maintained and behave as liquids within the rock during heating as they would in the natural system. As demonstrated in Table I, the added water surrounding the rock chips or cores allows oil expulsion to occur. This added water is considered analogous to water in joints (i.e., regional fractures), which are ubiquitous in the natural system (Pollard and Aydin, 1988). Cores that fill most of the subaqueous portion of a reactor are ideal, but preparing for a series of experiments requiring cores of one rock sample is difficult and tedious. A more practical approach is to use crushed rock in the form of chips ranging in size from 0.5 to 2.0 cm. Provided the rock sample has not been pulverized to a fine powder ($>62\ \mu\text{m}$) that destroys the organic and inorganic matrix-relationship, the size of the rock chips does not have a significant effect on the amounts of expelled oil and generated gas. Table III gives the yields from three

different size ranges of a rock sample from the Monterey Shale after 72 h at 330°C. As shown, there are no significant differences in amounts of expelled oil or generated gas. The recommended 0.5 to 2.0-cm size range can be easily obtained by sieving crushed rock through standard sieves. This size range packs reasonably well into a reactor and is large enough for petrographic thin sections and rock property determinations following the experiments.

Rocks that have generated an expelled oil have a swollen appearance as a result of an echelon parting separations that develop parallel to the bedding fabric. These parting separations pinch out laterally with maximum separations less than 150 μm thick (Lewan, 1987). Although these parting separations render the rocks more fissile, their discontinuous and en echelon character allows the rocks to remain coherent if handled carefully. This ability of rocks to remain coherent after hydrous pyrolysis has been observed for a variety of source-rock lithologies. Based on the laboratory classification by Lewan (1978), these lithologies include quartzose claystones, argillaceous claystones and mudstones, argillaceous and calcareous marlstones, and calcitic micstones and mudstones (i.e., limestones). A notable exception is argillaceous or siallitic claystones with high concentrations (>25 wt. %) of smectite. Hydration of this expandable clay mineral during hydrous pyrolysis results in a mud slurry at the end of an experiment, which makes recovery of products more difficult. The occurrence of shales rich in smectite is not common during natural petroleum generation because the apparent conversion of smectite to illite in the subsurface usually occurs at vitrinite reflectance values less than 0.7% R_0 (Kisch, 1987). Soldan and Cerqueira (1986) have simulated this clay–mineral conversion in hydrous pyrolysis experiments using potassium-rich formation waters and demonstrated that such a con-

version improved the total pyrolysate yield of the rock.

The use of a rock in hydrous pyrolysis experiments is also a more relevant approach to studying primary oil migration and expulsion than the use of isolated kerogens. Studies on primary oil migration have benefited from petrographic thin-section examination of rocks that have been thermally matured in nature and in hydrous pyrolysis experiments (Bertrand *et al.*, 1987; Lewan, 1987; Talukdar *et al.*, 1987). Results from these studies suggest expulsion of oils from rocks in hydrous pyrolysis experiments is mechanically similar to that in the natural system. This is exemplified by the petrographic study by Lewan (1987) on Devonian–Mississippian black shales of the midcontinent region in the United States. These shales in the pre-oil generation stage contain amorphous masses of kerogen dispersed within a translucent orange-brown groundmass (Fig. 6A). As thermal stress increases, the viscous bitumen generated from the decomposition of the kerogen impregnates the planar bedding fabric and micropores of the rock. The continuous bitumen network that develops during this incipient-oil generation stage results in a dark brown groundmass (Fig. 6B). Increasing thermal stress results in partial decomposition of the bitumen network into a liquid oil enriched in saturated hydrocarbons. The net volume increase generated by this overall reaction within the confined inorganic rock matrix results in expulsion of the oil. Following primary-oil generation, the bitumen network is carbonized to pyrobitumen with increasing thermal stress, leaving a black opaque groundmass (Fig. 6C). The net volume increase responsible for bitumen migration within and oil expulsion from the rocks is the result of an overall decrease in density of reaction products and thermal expansion of the generated organic liquids (Lewan, 1987).

The significance of these observations is that petroleum formation takes place within the rock chips or cores and not within the added water which surrounds the rock. Once petroleum formation commences, the rock matrix becomes oil wet as observed in the natural system (Meissner, 1978; Lewan, 1987). This bituminous system replaces the preexisting aqueous system, and, as a result, mineral transformations and dissolutions are not controlled by aqueous solubilities. The inability of closed anhydrous pyrolysis to generate an expelled oil and the excess water present in hydrous pyrolysis of isolated kerogens emphasizes the importance of using rock samples in hydrous pyrolysis to simulate natural petroleum formation. Water surrounding the rock maintains the liquid water phases within the rock prior to petro-

TABLE III. Weight Percent of Expelled Oil and Generated Gas from Hydrous Pyrolysis of Different Size Fractions of a Rock Sample (MR-83) from the Monterey Formation^a

Size range (cm)	Expelled oil (wt. % of rock)	Generated gas (wt. % of rock)
0.5–2.0	2.61	2.53
1.0–1.5	2.47	2.56
0.1–0.5	2.50	2.56
Mean \pm std. dev.	2.52 \pm 0.06	2.55 \pm 0.01

^aExperiments involved heating 300 g of rock with 365 g of deionized water in a 1-liter stainless steel-316 reactor at 330°C for 72 h.

leum formation and provides an accommodating medium in which generated oil may be expelled during petroleum formation.

6. Effects of Reactor Wall Composition

Alteration of experimental results by the interaction of reactants or products with reactor walls is a common concern. Hydrous pyrolysis experiments using isolated kerogens (e.g., Comet *et al.*, 1986; Eglinton and Douglas, 1988) or model compounds (e.g., Palmer and Drummond, 1986) allow both the reactants and products to be in direct contact with the reactor walls. Conversely, the use of rock chips or cores in hydrous pyrolysis minimizes the contact of reactor walls with reactants (i.e., kerogen, bitumen, and rock matrix), but not with expelled products (i.e., oil and gas). In order to evaluate this latter interaction, a series of hydrous pyrolysis experiments using a crushed rock sample was conducted with reactor walls composed of stainless steel-316, Hastelloy C-276, plated gold, and borosilicate glass.

Reactors composed of stainless steel-316 have proven to be reliable for hydrous pyrolysis experiments using deionized or distilled water (e.g., Lewan, 1983; Lundegard and Senftle, 1987; Eglinton *et al.*, 1988). This austenitic iron-base Cr–Ni–Mo alloy is one of the more corrosion-resistant commercial stainless steels and also has high creep and rupture strengths (King, 1983, p. 614). Another austenitic alloy that has a better corrosion resistance to chloride-bearing solutions such as seawater and brines is Hastelloy C-276, which is a nickel-base Mo–Cr–Fe–W alloy (Haynes International, Inc., Kokomo, Indiana). Expelled products from hydrous pyrolysis experiments conducted in reactors made of these two alloys were compared with those from a gold-plated stainless steel reactor. All of the reactors had fresh metal walls that had not been subjected to prior hydrous pyrolysis experiments or other heat treatments. The experiments consisted of heating 300 g of crushed (0.5–2.0 cm) Monterey Shale (MR-216) with 365 g of deionized (ASTM type I) water for 72 h at 330°C in 1-liter reactors with the different wall compositions.

In Table IV, expelled products generated in these

TABLE IV. Amount and Composition of Expelled Oils from 300-g Aliquots of a Sample of Monterey Shale (MR-216) Heated with 365 g of Deionized Water for 72 h at 330°C in 1-Liter Reactors with Different Wall Compositions

	Reactor					
	Fresh metal walls			Carburized metal walls		
	Gold-plated SS-316	Stainless steel-316	Hastelloy C-276	Stainless steel-316	Hastelloy C-276	Borosilicate glass liner in SS-316
Amount of expelled oil (g/300 g rock)	4.38	4.10	4.52	4.53	4.71	4.19
GC/MS ratios ^a						
$\frac{n-C_{10}}{n-C_{10} + n-C_{20}}$	0.33	0.32	0.33	0.34	0.35	0.34
$\frac{n-C_{30}}{n-C_{30} + n-C_{20}}$	0.21	0.20	0.22	0.27	0.24	0.23
$\frac{\text{Pristane}}{\text{Pristane} + n-C_{20}}$	0.56	0.58	0.55	0.55	0.55	0.56
$\frac{\text{Thiophenes}^b}{\text{Thiophenes} + n-C_{10}}$	0.74	0.72	0.73	0.74	0.74	0.74
$\frac{\text{Hopanes}^c}{\text{Hopanes} + n-C_{30}}$	0.09	0.11	0.09	0.09	0.10	0.08
$\frac{\text{Steranes}^d}{\text{Steranes} + n-C_{30}}$	0.10	0.13	0.11	0.10	0.12	0.08
$\frac{\text{TA steroids}^e}{\text{TA steroids} + n-C_{30}}$	0.33	0.39	0.33	0.33	0.34	0.30

^aThese ratios are based on intensities of specific peaks from the *m/z* 57 ion chromatograms, except where otherwise noted.

^bThiophenes include peak intensities of C₁- and C₂-substituted thiophenes from the *m/z* 45 ion chromatograms.

^cHopanes include peak intensities of C₂₉, C₃₀, and C₃₁ hopanes from the *m/z* 191 ion chromatograms.

^dSteranes include peak intensities of C₂₆, C₂₇, and C₂₉ ααS steranes from the *m/z* 217 ion chromatograms.

^eTriaromatic steroid hydrocarbons (TA) include peak intensities of C₂₇, C₂₈, and C₃₀ steroids from the *m/z* 231 ion chromatograms.

experiments from the original 300-g aliquots of rock sample are tabulated. The amount of expelled oil for the three fresh-metal walls is highest for Hastelloy C-276, lowest for stainless steel-316, and intermediate for gold plating. Comparison of the resulting expelled oils on the basis of gas chromatography (Fig. 7) and gas-chromatographic/mass-spectrometric analyses (Table IV and Figs. 8–10) show no significant differences in the relative concentrations or distributions of *n*-alkanes, acyclic isoprenoids, thiophenes, terpanes, steranes, and triaromatic steroids. Therefore, it is apparent that these compound classes are not involved in the reactions responsible for the differences in amounts of expelled oil from the fresh-metal reactors.

Amounts of generated gases from these experiments are less variable, with stainless steel-316 having the higher yield and the other two reactor types having similar lower yields (Table V). Compositions of these generated gases presented in Table V show that H_2S and CO_2 have the most variability and an inverse relationship with one another. The variation in the amount of H_2S is related to the amount of iron sulfide formed on the reactor walls. In the gas space of the fresh stainless steel-316 reactor, the walls are coated with a thin ($<3 \mu m$) plating of iron sulfide at the end of the experiment. This is a result of H_2S gas reacting with iron from the reactor walls. X-ray diffraction patterns and scanning electron microscopic (SEM) examinations clearly identify this iron sulfide coating as hexagonal pyrrhotite ($Fe_{1-x}S$ with $x < 0.1$). In contrast, the low-iron-bearing, fresh Hastelloy C-276 walls had only a light dusting of pyrrhotite in the gas space of the reactor. The composition of generated gas from this experiment (Table V) has considerably more H_2S than that from the experiment with fresh stainless steel-316 walls. The gold-plated walls had a coating of pyrrhotite powder in the gas space of the reactor where the gold plating had deteriorated and exposed the underlying stainless steel-316 surface. This intermediate amount of pyrrhotite corresponds to an intermediate amount of H_2S relative to that for the other two fresh metal walls (Table V). Qualitatively, these results indicate that the amount of H_2S gas recovered in a hydrous pyrolysis experiment is inversely proportional to the amount of available iron in the reactor walls.

Although pyrrhotite in coals has been reported to catalyze coal-liquefaction reaction through the enhancement of free-radical generation (Srinivasan and Seehra, 1982, 1983), the amount of pyrrhotite on the gas-space reactor walls is inversely proportional to the amounts of expelled oil. This lack of a catalytic

effect in hydrous pyrolysis may be explained by the limited exposure expelled oils have with pyrrhotite in the gas space of the reactors. Despite variations in the amount of pyrrhotite in the gas space of the reactors, there is an equal amount of pyrrhotite occurring as a light dusting in the liquid space of all three fresh-metal reactors. In addition, significant increases in free-radical generation with pyrrhotite in coals only occurs at temperatures in excess of $400^\circ C$ (Srinivasan and Seehra, 1983; Murakami *et al.*, 1986). It is also worth noting that while pyrrhotite is forming on the reactor walls, the pyrite (FeS_2) within the rock sample remains unchanged. This apparent disequilibrium is explained by the bitumen-impregnated matrix of the rock (Fig. 6B and C) preventing interaction with the surrounding water.

In addition to pyrrhotite formation, the bright silvery finish of the fresh-metal reactors dull and darken with successive experiments in spite of wire-brush cleanings after each experiment. X-ray photoelectron spectroscopic analyses of these darkened but smooth surfaces indicate that graphitic carbon is being introduced into the reactor walls. Auger electron spectroscopic analysis on a piece of reactor wall (stainless steel-316) subjected to more than 50 hydrous pyrolysis experiments showed that this introduced carbon extended only $3.9 \mu m$ into the reactor wall (C. Willey and T. Fleisch, 1985, personal communication). This process by which carbon is introduced into steel or other alloys is referred to as carburization. The source of carbon that diffuses into alloys during this process may be hydrocarbons or carbon dioxide (Stanley, 1970). Consecutive hydrous pyrolysis experiments show that the gas space of the reactors carburizes more readily than the liquid portion, but eventually the entire wall surface is carburized. It has also been observed in hydrous pyrolysis experiments that stainless steel-316 carburizes more readily than Hastelloy C-276.

The degree of carburization is variable in the gas space of the three fresh metal reactors. A dark carburized surface was apparent under the pyrrhotite plating on the stainless steel-316 reactor, but only a dull silvery surface was observed under the light pyrrhotite dusting on the Hastelloy C-276 reactor. Under the pyrrhotite powder coating on the gold-plated reactor, the exposed stainless steel surface was dull and slightly darkened. These different degrees of carburization correspond inversely with the amounts of expelled oil. This suggests that expelled oil is the source of carbon for carburization of the fresh metal walls. Additional support of this comes from two hydrous pyrolysis experiments conducted with the

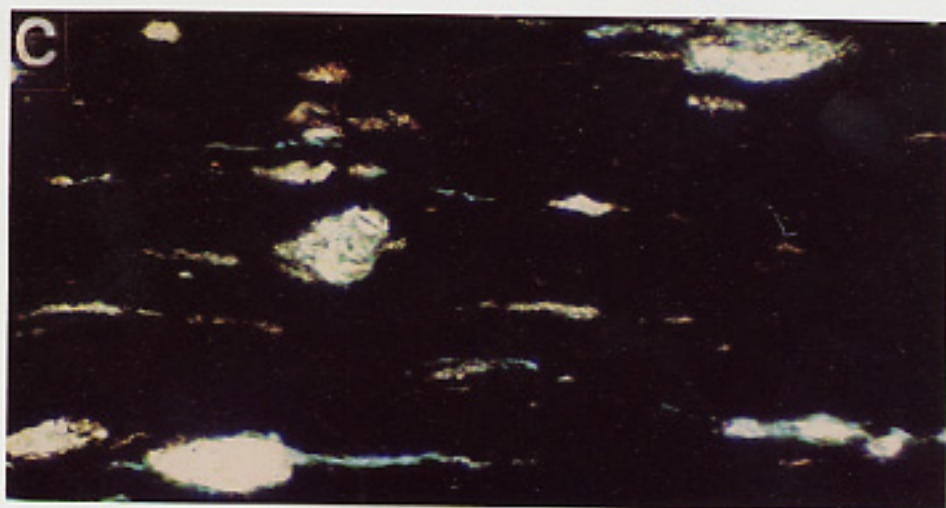
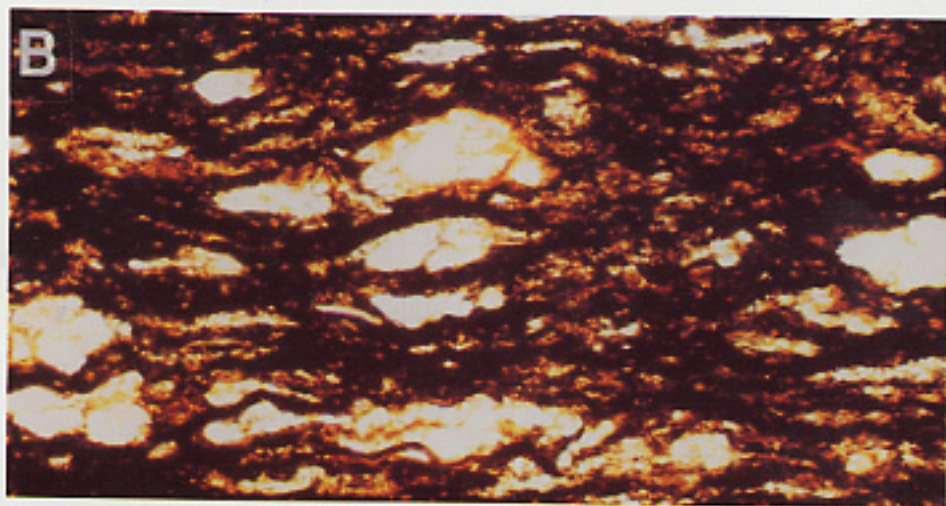
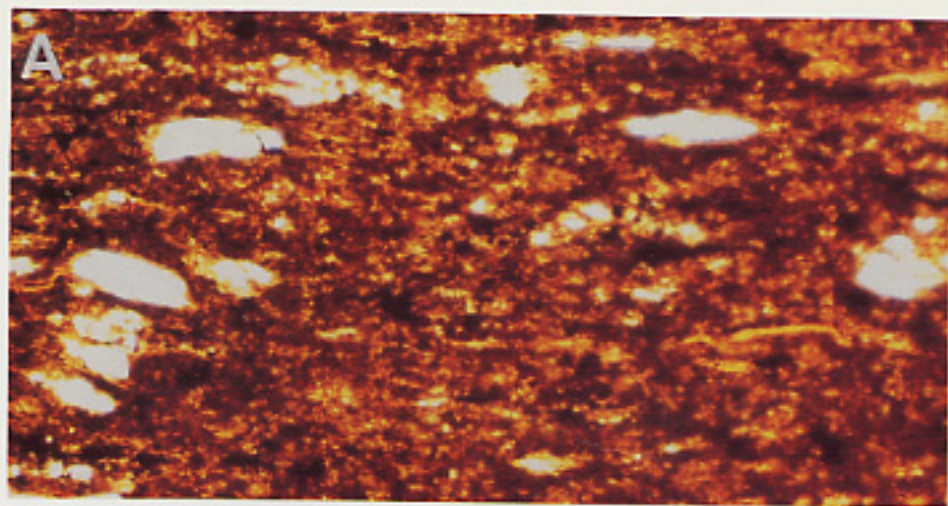


Figure 6. Photomicrographs of thin sections of cores taken from the same sample of Woodford Shale (WD-7) before hydrous pyrolysis (A), after hydrous pyrolysis for 72 h at 300°C (b), and after hydrous pyrolysis for 72 h at 352°C (C). Basal lengths of photomicrographs are 0.52 mm.

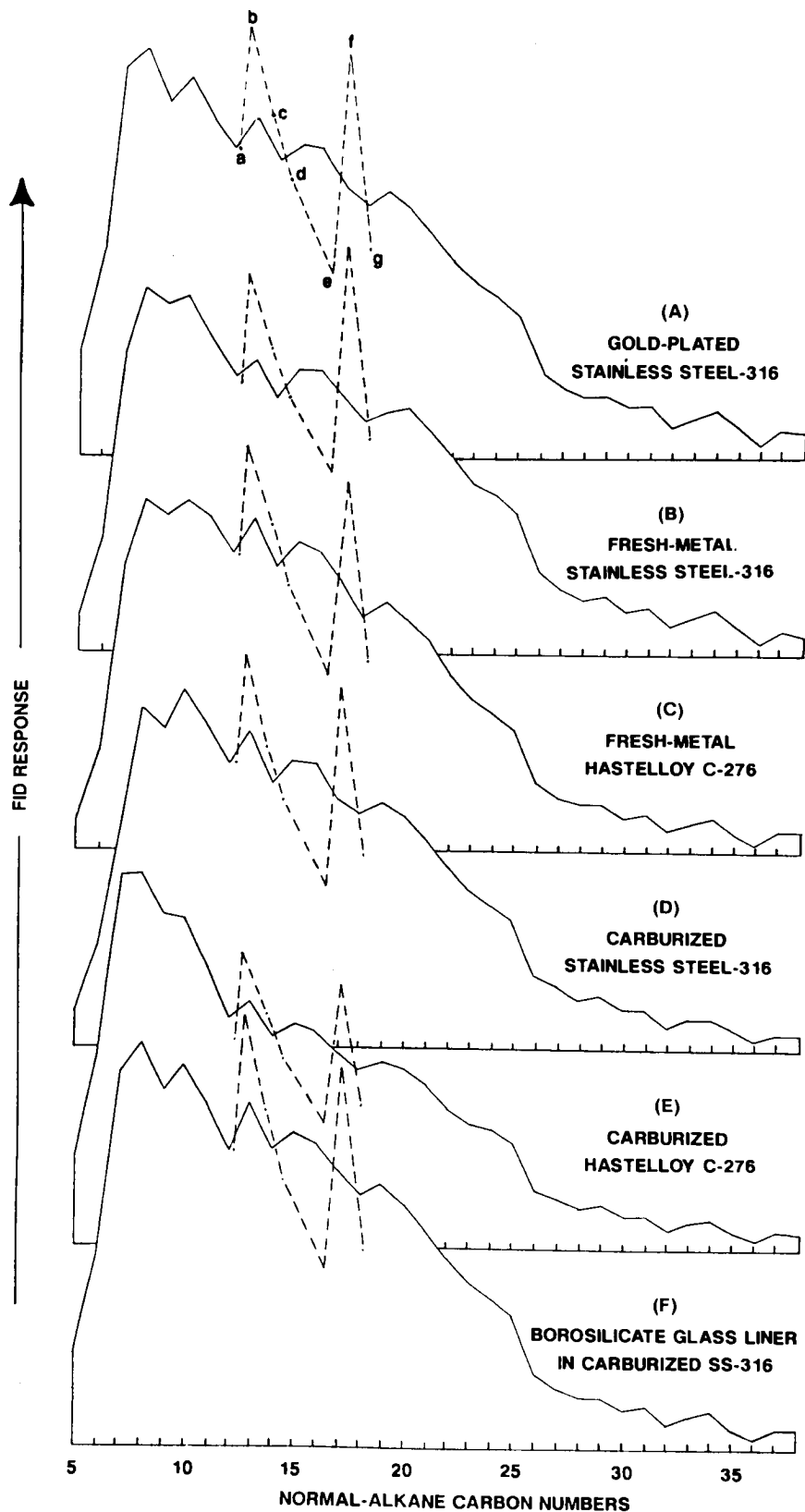


Figure 7. Comparison of n-alkane (—) and acyclic isoprenoid (---) distributions from gas chromatograms of expelled oils generated from aliquots of a sample of Monterey Shale (MR-216) subjected to hydrous pyrolysis at 330°C for 72 h in 1-liter reactors with different wall compositions. The solid lines represent n-alkane distributions and dashed lines represent acyclic isoprenoid distributions with a, C₁₃; b, C₁₄; c, C₁₅; d, C₁₆; e, C₁₈ (norpristane); f, C₁₉ (pristane); g, C₂₀ (phytane).

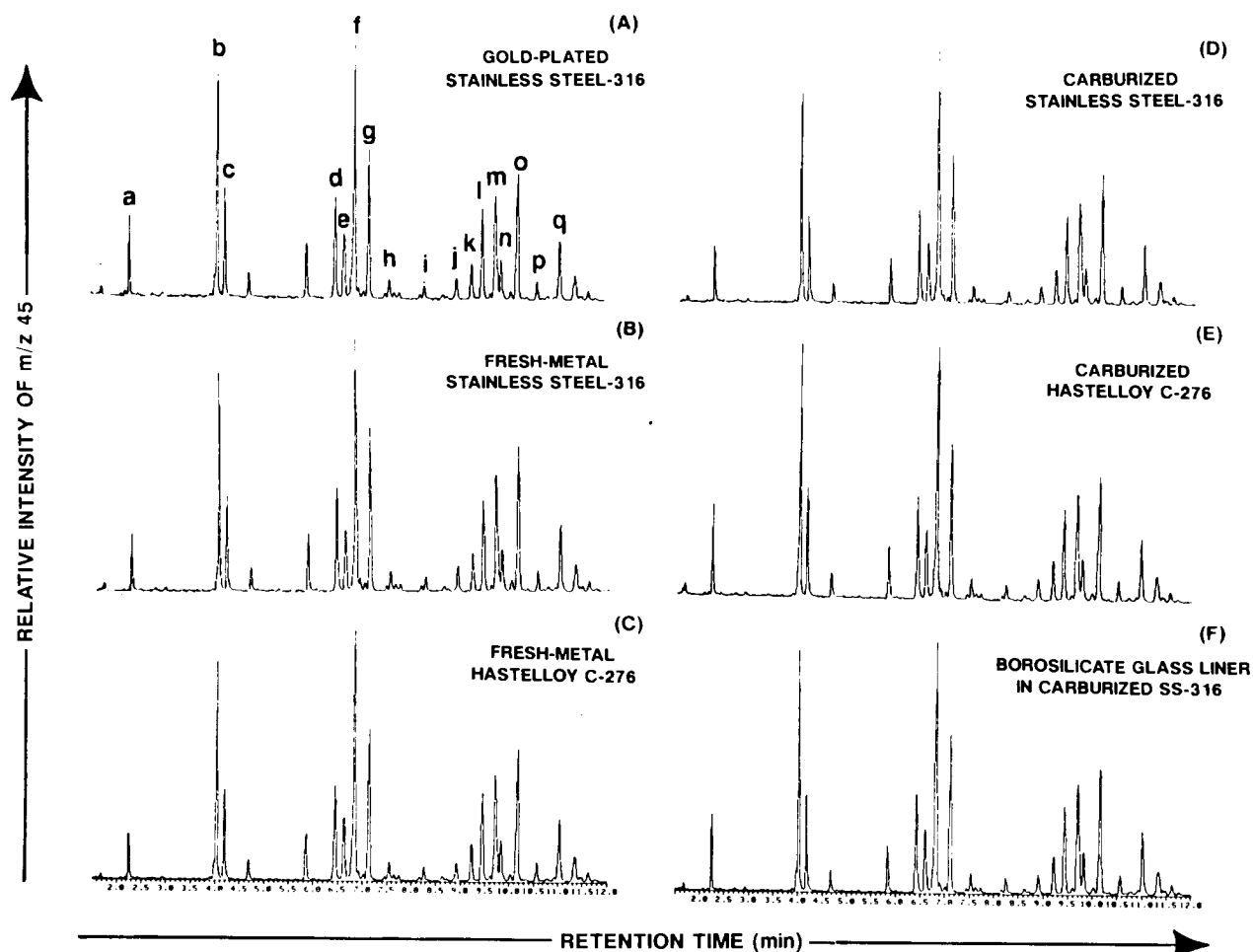


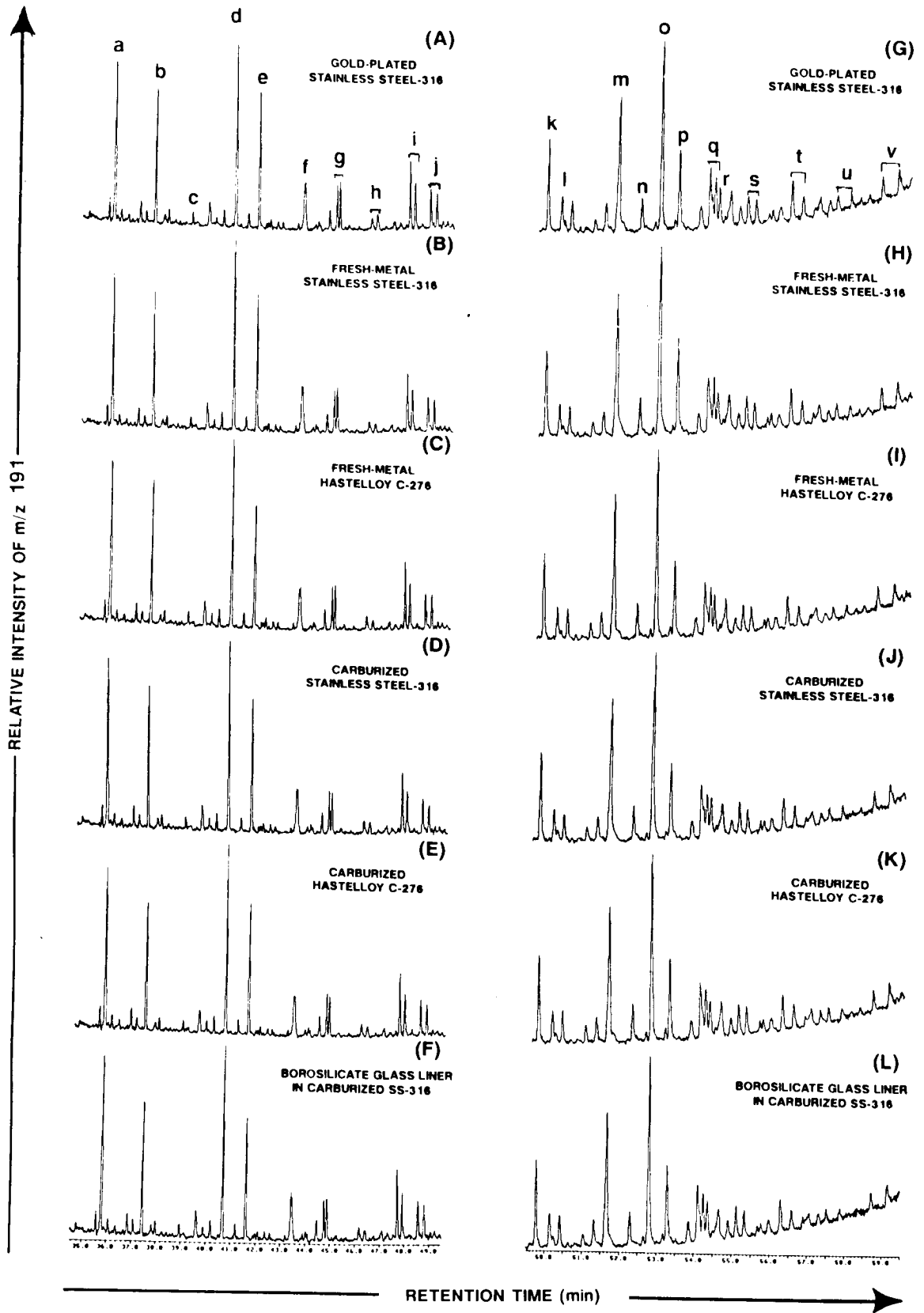
Figure 8. Comparison of m/z 45 ion chromatograms of expelled oils generated from aliquots of a sample of Monterey Shale (MR-216) subjected to hydrous pyrolysis in reactors with different wall compositions at 330°C for 72 h. The thiophenes identified in these chromatograms are as follows: a, thiophene; b, 2-methylthiophene; c, 3-methylthiophene; d, 2-ethylthiophene; e, 2,5-dimethylthiophene; f, 2,4-dimethylthiophene + 3-ethylthiophene; g, 2,3-dimethylthiophene; h, 3,4-dimethylthiophene; i, 2-isopropylthiophene; j, thiolane; k, 2-n-propylthiophene; l, 2-methyl-5-ethylthiophene; m, 3-methyl-2-ethylthiophene; n, 2-methyl-4-ethylthiophene; o, 2,3,5-trimethylthiophene; p, 3-methyl-4-ethylthiophene; q, 2,3,4-trimethylthiophene.

same sample (MR-216) under the same conditions (330°C/72 h) in stainless steel-316 and Hastelloy C-276 reactors that were completely carburized prior experiments. Table IV shows that the amounts of expelled oils in these experiments are higher than in those with their fresh-metal equivalents.

Tannenbaum and Kaplan (1985a) stated that borosilicate-glass reactors minimize catalytic effects in hydrous pyrolysis experiments compared with metal reactors, but no supportive data or references were presented. An actual comparison of hydrous pyrolysis in glass and metal reactors was conducted with isolated kerogens by Comet *et al.* (1986). Their results showed that steranes and hopanes in solvent extracts of isolated kerogens after hydrous pyrolysis

were present in stainless steel reactors but absent in silica-glass reactors. In order to provide an assessment of the effects of glass reactors on hydrous pyrolysis of rock samples, an additional experiment was conducted on an aliquot of sample MR-216 in a borosilicate-glass liner within a carburized 1-liter stainless steel-316 reactor. The closed base and full-reactor length of the glass liner prevented rocks chips, expelled oil, and liquid water from making contact with the metal walls, but the open top of the glass liner did not prevent generated gas and water vapor from making contact with the metal walls.

Similar to results reported by Tannenbaum and Kaplan (1985b) and Comet *et al.* (1986), corrosion of the originally transparent glass liner resulted in a



white frosted surface. The expelled oil layer at the experimental temperature (i.e., 330°C) was marked by a 2.8-cm interval of black to medium gray frosted glass at the expanded water level within the liner. Analysis of silica scraped from this interval indicated the darkening resulted from introduction of carbon into the glass. Carbon deposits on glasses during pyrolysis experiments are enhanced by the presence of boron (Dawidowicz *et al.*, 1984, 1986). The lower yield of expelled oil in the glass liner experiment compared to that in the carburized metal reactors (Table IV) is attributed to carbon deposits resulting from diffusion of oil into the glass. Similar to carburization of metal reactor walls, this process does not appear to be selective of particular compound classes as shown by the analyses on the gases (Table V) and expelled oils (Table IV and Figs. 7–10). This is contrary to observations made by Comet *et al.* (1986), but their comparative experiments involved isolated kerogens in direct contact with silica glass.

Overall, these results indicate that the effects of reactor wall composition on expelled oils generated by hydrous pyrolysis of rock samples do not significantly alter molecular compositions but do significantly alter recoverable yields. Alterations in the amount of expelled oil are minimized by using well-carburized metal reactors. This pretreatment is especially important for stainless steel-316 reactors and less critical for Hastelloy C-276 reactors. Carburization also reduces the interaction of generated H₂S gas with iron in the reactor walls (Table V). New and remachined metal reactors should be subjected to several preliminary hydrous pyrolysis experiments with oil-prone rock samples to carburize the walls before conducting quantitative experiments. This is a common practice that is an important prerequisite for experimental studies involving organic compounds. Palmer and Drummond (1986) reported in their study on thermal decarboxylation of acetate that several preliminary experiments were necessary to render the titanium alloy walls of their reactors inert to the reaction.

7. Consideration of Experimental Artifacts

One of the most noticeable artifacts of open anhydrous pyrolysis is the generation of alkenes, which rarely occur in natural crude oils (Hoering, 1977). Lewan *et al.* (1979) reported no detectable alkenes in oil-like pyrolysates generated from rock samples by closed pyrolysis under hydrous and helium-pressured anhydrous conditions. Similar results were also reported in subsequent studies using isolated kerogens (Hoering, 1985; Saxby *et al.*, 1986; Comet *et al.*, 1986). Contrary to these observations, Huizinga *et al.* (1987) reported three normal alkenes (C₂₁, C₂₂, and C₂₄), prist-1-ene, and phytene in closed hydrous and anhydrous pyrolysis of isolated kerogens. Generation of pristenes and phytene by hydrous and anhydrous pyrolysis has also been reported by Eglinton *et al.* (1988) for isolated kerogen from the Kimmeridge Blackstone Band and by Jones *et al.* (1987) for isolated asphaltene from Douk Daka and Boscan crude oils. Alkene concentrations in all of these studies are most apparent at temperatures less than 300°C for 72-h durations and are negligible at higher thermal stress levels (i.e., ≥300°C for ≥72 hr). At the lower thermal stress levels, bitumen generation dominates (Lewan, 1985), and this does not represent generation of expelled oils, which do not contain these alkenes when derived from rock samples (Lewan *et al.*, 1979) rather than isolated kerogens.

A study by Tannenbaum and Kaplan (1985b) of gases from the same experiments reported by Huizinga *et al.* (1987) also showed the presence of significant quantities of low-molecular-weight alkenes under hydrous and anhydrous conditions. Analyses of their gases generated at 300°C under hydrous conditions by kerogens isolated from the Monterey Shale and Green River Shale are compared in Table VI with analyses of gases generated under hydrous conditions by rock samples from the same rock units. The only gaseous alkenes generated from the rock samples are a trace of ethene from the Monterey Shale and

Figure 9. Comparison of *m/z* 191 ion chromatograms of expelled oils generated from aliquots of a sample of Monterey Shale (MR-216) subjected to hydrous pyrolysis in reactors with different wall compositions at 330°C for 72 h. Tricyclic terpanes are shown in chromatograms A through F with the following peak identifications: a, C₂₀; b, C₂₁; c, C₂₂; d, C₂₃; e, C₂₄; f, extended C₂₅ (C-22S and R); g, extended C₂₆ (C-22S and R); h, extended C₂₇ (C-22S and R); i, extended C₂₈ (C-22S and R); j, extended C₂₉ (C-22S and R). Pentacyclic terpanes are shown in chromatograms G through L with the following peak identifications: k, 18α(H)-22,29,30-trisnorhopane (T_s), l, 17α(H)-22,29,30-trisnorhopane (T_m); m, 17α(H),21β(H)-30-norhopane; n, 17β(H),21α(H)-30-normoretane; o, 17α(H),21β(H)-hopane; p, 17β(H),21α(H)-moretane; q, 17α(H),21β(H)-30-homohopane (C-22S and R); r, gammacerane; s, 17α(H),21β(H)-30,31-bishomohopane (C-22S and R); t, 17α(H),21β(H)-30,31,32-trishomohopane (C-22S and R); u, 17α(H),21β(H)-30,31,32,33-tetrakishomohopane (C-22S and R); v, 17α(H),21β(H)-pentakishomohopane (C-22S and R).

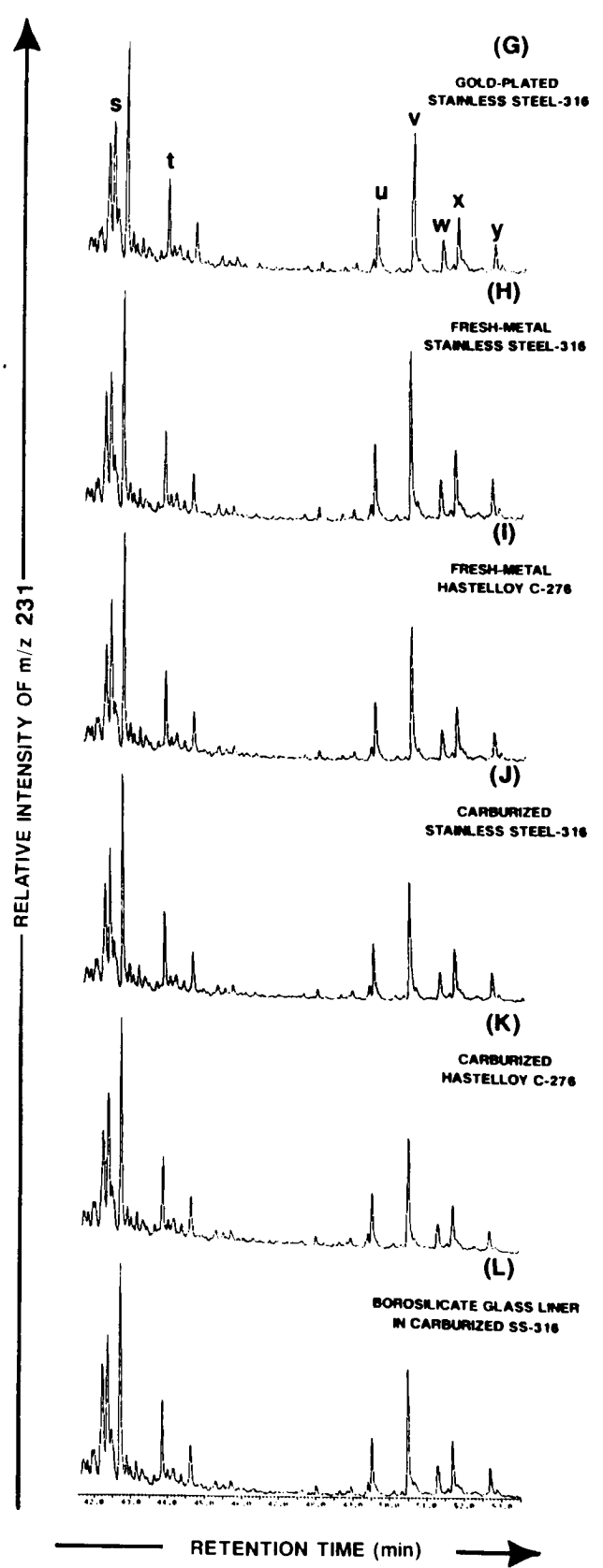
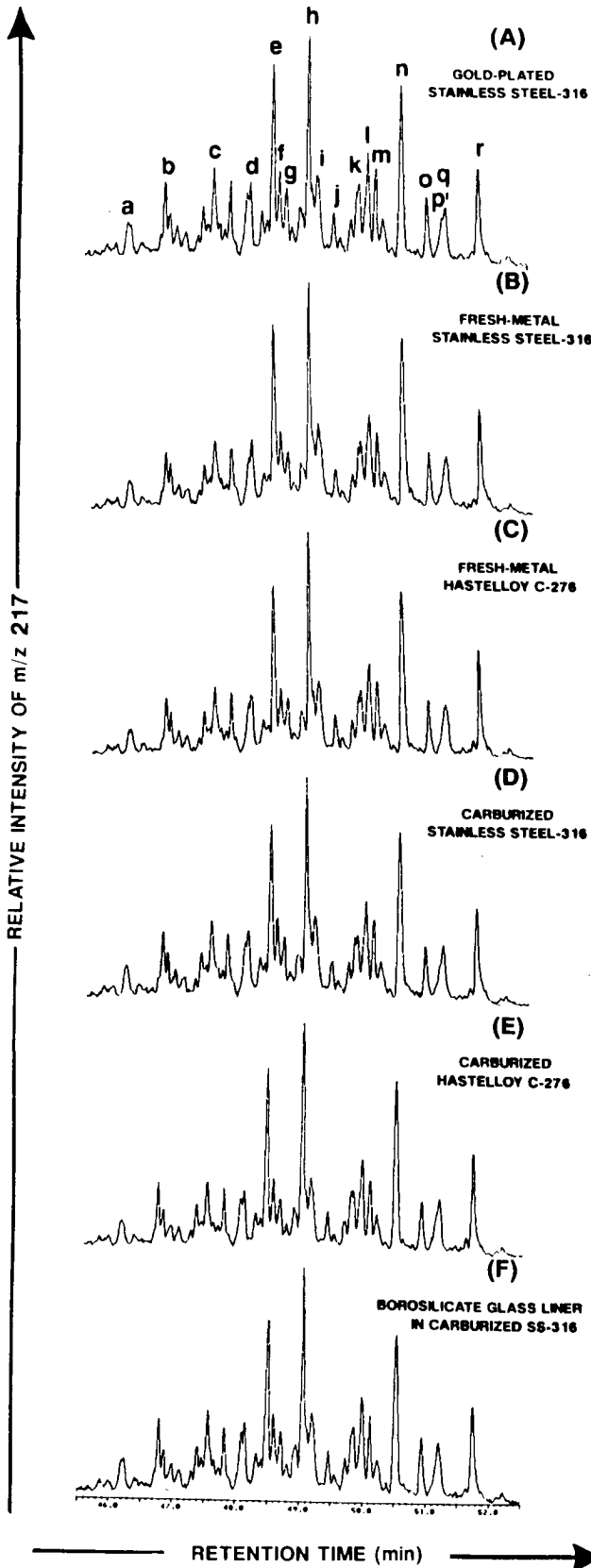


TABLE V. Amount and Composition of Gases Generated from 300-g Aliquots of a Sample of Monterey Shale (MR-216) Subjected to Hydrous Pyrolysis for 72 h at 330°C in 1-Liter Reactors with Different Wall Compositions

Generated gases	Amount of gas (mg/300 g rock) collected from reactor ^a					
	Fresh metal walls			Carburized metal walls		
	Gold-plated SS-316	Stainless steel-316	Hastelloy C-276	Stainless steel-316	Hastelloy C-276	Borosilicate glass liner in SS-316
Methane	172	179	180	194	189	174
Ethane	137	143	135	146	140	146
Propane	101	101	75	103	83	101
Isobutane	51	46	23	45	23	46
n-Butane	48	45	88	52	84	50
Pentanes	4	20	24	25	33	30
Hexanes	0	0	0	0	0	0
C ₇ + ^b	0	16	0	0	0	0
Ethene	1	2	2	2	3	1
Propene	3	4	1	1	0	1
Butenes	0	0	0	0	0	0
Butadienes	0	1	1	0	2	0
C ₅ H ₁₀ ^c	28	24	33	37	32	41
C ₆ H ₁₂ ^c	34	15	34	31	0	39
CO ₂	4284	4489	4198	4668	4306	4573
CO	0	0	0	0	0	5
H ₂	14	13	10	9	11	10
H ₂ S	577	504	649	706	604	644
Total	5454	5602	5453	6019	5510	5856

^aGenerated gases were collected from reactors at room temperature and analyzed on a mass spectrometer.

^bHydrocarbon gases with 7 or more carbon atoms.

^cAnalysis does not differentiate between cyclic alkanes and acyclic alkenes.

a trace of propene from the Green River Shale. As shown in Table VI, these trace amounts of alkenes are significantly less than those from isolated kerogens reported by Tannenbaum and Kaplan (1985b). In addition, the gas analyses for isolated kerogens show an increase in the ratio of alkenes to alkanes plus alkenes with increasing carbon number, which is not observed in the gases generated from rock samples. Although an explanation for this discrepancy requires additional experimentation, it is apparent that conclusions made by Tannenbaum and Kaplan (1985a) may not be extended to hydrous pyrolysis of rock samples.

The most apparent artifact of hydrous pyrolysis is the large polar fraction that is not recovered from solid-liquid column chromatography of the expelled oils (Lewan *et al.*, 1979). Figure 4 shows that the proportionality of the eluted saturate, aromatic, and polar fractions of expelled oils is similar to that for natural crude oils. However, Table VII shows that the fraction not recovered from activated alumina columns typically comprises 31 to 40 wt. % of these expelled oils. The majority of this unrecovered fraction consists of highly polar organics that remain on the column and, to a lesser extent, low-molecular-weight organics that are lost during solvent evapora-

Figure 10. Comparison of *m/z* 217 and 231 ion chromatograms of expelled oils generated from aliquots of a sample of Monterey Shale (MR-216) subjected to hydrous pyrolysis in reactors with different wall compositions at 330°C for 72 h. Ion chromatograms A through F show the steranes (*m/z* 217) in saturate column cuts of the expelled oils. Identifications of the steranes are as follows: a, 13β(H),17α(H)-diacholestane (20S); b, 13β(H),17α(H)-diacholestane (20R); c, 24-methyl-13β(H),17α(H)-diacholestane (20S); d, 24-methyl-13β(H),17α(H)-diacholestane (20R); e, 14α(H),17α(H)-cholestane (20S) + 17α(H)-diacholestane (20S); f, 14β(H),17β(H)-cholestane (20R) + 24-ethyl-13α(H),17α(H)-diacholestane (20S); g, 14β(H),17β(H)-cholestane (20S) + 24-methyl-13β(H),17β(H)-diacholestane (20R); h, 14α(H),17α(H)-cholestane (20R); i, 24-ethyl-13β(H),17α(H)-diacholestane (20R); j, 24-ethyl-14α(H),17α(H)-diacholestane (20S); k, 24-methyl-14α,17α-cholestane (20S); l, 24-methyl-14β(H),17β(H)-cholestane (20R) + 24-ethyl-13α(H),17β(H)-diacholestane (20R); m, 24-methyl-24β(H),17β(H)-cholestane (20S); n, 24-methyl-14σ(H),17α(H)-cholestane (20R); o, 24-ethyl-14α(H),17α(H)-cholestane (20S); p, 24-ethyl-14β(H),17β(H)-cholestane (20R); q, 24-ethyl-14β(H),17β(H)-cholestane (20S); r, 24-ethyl-14α(H),17α(H)-cholestane (20R). Ion chromatograms G through L show the triaromatic steroid hydrocarbons (*m/z* 231) in aromatic column cuts of the expelled oils. Identification of these steroids is as follows: s, C₂₀; t, C₂₁; u, C₂₆ (20S); v, C₂₆ (20R) + C₂₇ (20S); w, C₂₈ (20S); x, C₂₇ (20R); y, C₂₈ (20R).

TABLE VI. Comparison of Gases Generated by Hydrous Pyrolysis of Isolated Kerogens and Rock Samples from the Monterey Shale and Green River Shale^a

Generated gases	Monterey Shale		Green River Shale	
	Kerogen ^b	Rock ^c	Kerogen	Rock ^d
	300 °C/100-h pyrolysis	300 °C/72-h pyrolysis	300 °C/100-h pyrolysis	300 °C/144-h pyrolysis
Methane	3.7	3.02	2.2	3.15
Ethane	2.2	2.08	0.80	1.08
Ethene	0.39	0.03	0.14	0.00
Propane	1.8	1.50	0.87	1.09
Propene	0.53	0.00	0.27	0.07
n-Butane	0.86	0.69	0.32	0.00
Isobutane	0.47	0.48	0.48	1.37
Butenes	0.93	0.00	0.50	0.00
Butadienes	—	0.00	—	0.00
Pentanes	0.87	0.66	0.59	0.00
C ₅ H ₁₀ ^e	0.49	0.42	0.56	0.94
Hexanes	0.86	0.00	1.02	0.00
C ₆ H ₁₂ ^e	0.80	0.11	0.61	0.00
Total	13.90	8.99	8.36	7.70
Ethene				
Ethane + ethene	0.15	0.01	0.15	0.00
Propene				
Propane + propene	0.23	0.00	0.24	0.06
Butenes				
Butanes + butenes	0.41	0.00	0.39	0.00

^aData for isolated kerogens are from Tannenbaum and Kaplan (1985a, b); data for rock samples are from the author's laboratory. Concentrations are expressed as mg/g of kerogen for rock samples and isolated kerogens.

^bThis analysis is actually from an anhydrous experiment, but is described by Tannenbaum and Kaplan (1985a, b) as being comparable to the hydrous experiment under the same time-temperature conditions.

^cExperiment involved heating 300 g of crushed (0.5–2.0 cm) Monterey Shale (MR-178) with 365 g of deionized water in a 1-liter carburized stainless steel-316 reactor. The reactor gas space was purged three times with 8–14 MPa of helium and then filled with 240 kPa of helium at the start of the experiment.

^dExperiment involved heating 400 g of crushed (0.5–2.0 cm) Green River Shale (GR-49) with 325 g of deionized water in a 1-liter stainless steel-316 reactor. Procedure for purging and filling with helium is the same as described in footnote c.

^eNo distinction is made between cyclic alkanes and acyclic alkenes.

TABLE VII. Compositional Fractions^a of Expelled Oils Generated from Aliquots of a Sample of Woodford Shale (WD-5) Subjected to Hydrous Pyrolysis under Different Temperature–Time Conditions as Described by Lewan (1983)

Stage of petroleum formation and experimental conditions	Saturate fraction (wt. %)	Aromatic fraction (wt. %)	Polar fraction (wt. %)	Unrecovered fraction (wt. %)
Incipient-oil stage				
330°C/72 h	29.8	17.6	12.2	40.4
Primary-oil stage				
340°C/72 h	31.6	19.0	14.0	35.4
345°C/72 h	32.1	20.2	16.2	31.5
350°C/72 h	30.9	20.9	16.1	32.1
Post-oil stage				
355°C/72 h	26.1	19.7	14.4	39.8
360°C/72 h	29.6	19.7	14.7	36.0
365°C/808 h	12.0	20.3	6.6	61.1

^aFractions were separated on a 40-cm alumina (MCB Alcoa F-20) column with eluting solvents being n-heptane for saturates, benzene for aromatics, and a 40:60 (w/w) methanol:benzene mixture for polars. Unrecovered fraction includes highly polar organics that remained on the column, and to a lesser extent, low-molecular weight components lost during evaporation of eluting solvents.

tion in the isolation of the eluted fractions. One explanation for this highly polar fraction is that it remains within the rock as bitumen and is not expelled with the oil at the lower temperatures under which the natural system operates. This is supported in part by the observation that polyaromatic hydrocarbons such as perylene and triaromatic steroids are preferentially concentrated in the bitumens of rocks subjected to hydrous pyrolysis versus the expelled oils (Lewan *et al.*, 1986). Another possible explanation is that the expelled oils from hydrous pyrolysis migrate only short distances in the rock samples without being subjected to secondary migration. The highly polar organics in the natural system may be chromatographically removed from crude oils during secondary migration. As discussed by Hunt (1979, pp. 498–513), it is not uncommon for the highly polar fraction of natural crude oils to decrease with increasing migration distance from their source rocks.

Although these explanations may account for the large polar fractions in expelled oils generated in the incipient- and primary-oil generation stages, it is doubtful that they account for the even larger polar fractions of expelled oils generated in the post-oil generation stage (Table VII). Formation of these polars at the higher experimental temperatures may be attributed to aromatization of saturated cyclic hydrocarbons and their condensation with preexisting aromatic hydrocarbons to form polycyclic aromatic compounds. Compared with the overall thermal decomposition of bitumen to oil, these aromatization and condensation reactions appear to be more temperature dependent. This results in larger aromatic and polar fractions in expelled oils generated by hydrous pyrolysis than in crude oils generated by the natural system. Although this degree of aromatization and condensation is not likely during natural oil generation, it is likely in high-thermal-stress regimes where reservoir crude oils develop into pyrobitumens.

8. Conclusions

Hydrous pyrolysis is a laboratory technique used to simulate petroleum formation. The technique maintains a liquid water phase in contact with potential source rocks while they are heated at subcritical water temperatures. If the proper experimental time and temperature conditions are employed, a free-flowing liquid oil similar in composition to natural crude oil is generated and expelled from the rock. The expelled oil accumulates on the surface of the water, where it

may be quantitatively collected at the end of an experiment. Petrographic studies on naturally and experimentally matured source rocks indicate that a net volume increase of the organic matter within the confining rock matrix is the driving force for primary migration of bitumen and expulsion of oil. The ability of hydrous pyrolysis to generate an oil compositionally similar to natural crude oil and to expel it in a manner similar to that operative in naturally maturing source rocks gives it a distinct advantage over anhydrous pyrolysis experiments. Depending on whether an open or closed system is employed, anhydrous pyrolysis experiments either generate products compositionally different from natural crude oil or obtain a pyrolysis product by processes that are not operative in the natural system (e.g., vacuum cryogenic trapping, carrier gas flushing, and organic solvent refluxing).

Simulating petroleum formation by hydrous pyrolysis has shown that four stages may be defined: (1) pre-oil generation, (2) incipient-oil generation, (3) primary-oil generation, and (4) post-oil generation. Pre-oil generation represents a thermally immature stage in which the organic matter occurs predominantly as a solid insoluble kerogen dispersed within a rock matrix. Incipient-oil generation begins when thermal stress is sufficient to initiate the decomposition of kerogen into a tarry-soluble bitumen, which is enriched in high-molecular-weight hydrocarbons and heteroatom compounds. The net volume increase generated by this overall reaction results in bitumen expansion along the planar bedding fabric of the rock matrix to form a continuous bitumen network. As thermal stress increases, primary-oil generation begins, with the bitumen network partially decomposing into a liquid oil, which is enriched in saturated hydrocarbons. The net volume increase generated by this overall reaction results in expulsion of the generated oil from the bitumen-impregnated rock. This suggests that oil expulsion from a rock is a consequence of its generation within a rock, and, therefore, generation and expulsion of oil may be considered collectively as one overall process. Post-oil generation begins when oil generation ceases. As thermal stress continues to increase, the bitumen generates gas and condenses into an insoluble pyrobitumen.

Hydrous pyrolysis of rock samples in the form of chips (0.5 to 0.2 cm) or cores provides a better simulation of natural petroleum generation than that of isolated kerogens or unconsolidated mixtures of kerogen and mineral powders. Organic matter in a rock sample is embedded naturally within its inorganic

matrix. This condition more accurately simulates the natural system than the use of kerogens, which are isolated from their host rock with HCl, HF, and LiAlH_4 . Although the use of the term "excess" water in describing hydrous pyrolysis of isolated kerogens or their mixture with unconsolidated mineral powder is appropriate, it is not appropriate in describing hydrous pyrolysis of rock samples. The pore system of source rocks during thermal maturation in the natural system and in hydrous pyrolysis experiments changes from an aqueous system to a bituminous system. Once the bituminous system has developed within a rock, only the water surrounding a rock in joints, fractures, or faults is important in facilitating oil expulsion. As shown in anhydrous pyrolysis experiments with and without the confinement of generated gas, the lack of liquid water prevents oil expulsion from a rock and significantly reduces the total pyrolysate yield (i.e., gas + oil + bitumen). Although specifics on the role of water remain to be elucidated, the presence of water appears to be an important factor in simulating petroleum formation in the laboratory.

ACKNOWLEDGMENTS. The author thanks the management of Amoco Production Company for support of this research and permission to publish. John C. Winters (Amoco Production Co.) initiated the experimental concept of hydrous pyrolysis in 1977, which was fostered by his earlier association with research on upgrading heavy oils by Dr. John D. McCollum (Amoco Research). The author is indebted to John C. Winters for introducing him to this type of experimentation in 1977 and for supporting the author's research and development of hydrous pyrolysis in the subsequent years. Drs. Attila Kilinc and John Grover (University of Cincinnati) are gratefully acknowledged for their lectures and discussions, which instilled in the author an interest in hydrothermal experimentation and a realization of the importance of water in natural processes. Drs. Barry Maynard and Wayne A. Pryor (University of Cincinnati) are acknowledged for indoctrinating the author into the tenet that one should look at the rocks one studies.

References

- Amestica, L. A., and Wolf, E. E., 1986, Catalytic liquefaction of coal with supercritical water/CO/solvent media, *Fuel* **65**:1226.
- Appell, H. R., Fu, Y. C., Friedman, S., Yavorsky, P. M., and Wender, I., 1971, Converting Organic Wastes to Oil: A Replenishable Energy Source, U.S. Department of the Interior, Bureau of Mines Rept. Invest. 7560.
- Appell, H. R., Fu, Y. C., Illig, E. G., Steffgen, F. W., and Miller, R. D., 1975, Conversion of Cellulosic Wastes to Oil, U.S. Department of the Interior, Bureau of Mines Rept. Invest. 8013.
- ASME, 1979, *ASME Steam Tables—Thermodynamic and Transport Properties of Steam*, American Society of Mechanical Engineers, New York.
- Berl, E., and Schmidt, A., 1932, Über die Entstehung der Kohlen, II. Die Inkohlung von Cellulose and Lignin in neutralem Medium, *Ann. Chemie* **493**:97.
- Bertrand, P., Martinez, L., and Pracher, B., 1987, Petrology Study of Primary Migration by Hydrous Pyrolysis, in: *Migration of Hydrocarbons in Sedimentary Basins* (B. Doligez, ed.), Editions Technip, Paris, pp. 633–647.
- Brooks, J. D., and Smith, J. W., 1969, The diagenesis of plant lipids during the formation of coal, petroleum, and natural gas—II. Coalification and the formation of oil and gas in the Gippsland Basin, *Geochim. Cosmochim. Acta* **33**:1183.
- Braun, R. L., and Rothman, A. J., 1975, Oil-shale pyrolysis: Kinetics and mechanisms of oil production, *Fuel* **54**:129.
- Burnham, A. K., Braum, R. L., Gregg, H. R., and Samoun, A. M., 1987a, Comparison of methods for measuring kerogen pyrolysis rates and fitting kinetic parameters, *Energy Fuels* **1**:452.
- Burnham, A. K., Braum, R. L., and Samoun, A., 1987b, Further Comparison of Methods for Measuring Kerogen Pyrolysis Rates and Fitting Kinetic Parameters, Lawrence Livermore National Laboratory, UCRL-97352.
- Claypool, G. E., and Reed, R. P., 1976, Thermal-analysis technique for source-rock evaluation: Quantitative estimate of organic richness and effects of lithology, *Am. Assoc. Petrol. Geol. Bull.* **60**:608.
- Comet, P. A., McEvoy, J., Giger, W., and Douglas, A. G., 1986, Hydrous and anhydrous pyrolysis of DSDP Leg 75 kerogens—A comparative study using a biological marker approach, *Org. Geochem.* **9**:171.
- Dawidowicz, A. L., Nazimek, D., Pikus, S., and Skubiszewska, J., 1984, The influence of boron atoms on the surface of controlled porous glasses on the properties of the carbon deposit obtained by pyrolysis of alcohol, *J. Anal. Appl. Pyrolysis* **7**:53.
- Dawidowicz, A. L., Pikus, S., and Nazimek, D., 1986, Properties of the material surfaces obtained by pyrolysis of alkanols on boron-enriched controlled porous glasses, *J. Anal. Appl. Pyrolysis* **10**:59.
- Deshpande, G. V., Holder, G. D., Bishop, A. A., Gopal, J., and Wender, I., 1984, Extraction of coal using supercritical water, *Fuel* **63**:956.
- Eglinton, T. I., and Douglas, A. G., 1988, Quantitative study of biomarker hydrocarbons released from kerogens during hydrous pyrolysis, *Energy Fuels* **2**:81.
- Eglinton, T. I., Curtis, C. D., and Rowland, S. J., 1987, Generation of water-soluble organic acids from kerogen during hydrous pyrolysis: Implications for porosity development, *Miner. Mag.* **51**:495.
- Eglinton, T. I., Douglas, A. G., and Rowland, S. J., 1988, Release of aliphatic, aromatic, and sulfur compounds from Kimmeridge kerogen by hydrous pyrolysis: A quantitative study, *Org. Geochem.* **13**:655.
- Engler, K. O. V., 1913, *Die Chemie und Physik des Erdöls*, Vol. 1, S. Hirzel, Leipzig.
- Espitalié, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P., Paulet, J., and Boutefeu, A., 1977, Méthode rapide de caractérisation des roches mères de leur potentiel pétrolier et de leur degré d'évolution, *Rev. Inst. Fr. Pet.* **32**:23.
- Ferry, J. M., 1983, Regional metamorphism of the Vassalboro Forma-

- tion, south-central Maine, U.S.A.: A case study of the role of fluid in metamorphic petrogenesis, *J. Geol. Soc. London* **140**:551.
- Fischer, F., 1925, *The Conversion of Coal into Oils*, Ernest Benn Ltd., London.
- Franks, A. J., and Goodier, B. D., 1922, Preliminary study of the organic matter of Colorado Oil Shales, *Quart. Colo. Sch. Mines* **17**:3.
- Gavin, M. J., 1922, Oil-shale: An historical, technical, and economic study, U.S. Department of the Interior, Bureau of Mines Bulletin 210, Bradford-Robinson, Denver.
- Goranson, R. W., 1931, The solubility of water in granite magmas, *Am. J. Sci.* **22**:481.
- Goranson, R. W., 1932, Some notes on the melting of granite, *Am. J. Sci.* **23**:227.
- Haas, J. L., Jr., 1976, Thermodynamical properties of the NaCl component in boiling NaCl solutions, U.S. Geological Survey Bulletin 1421-B.
- Harwood, R. J., 1977, Oil and gas generation by laboratory pyrolysis of kerogen, *Am. Assoc. Petrol. Geol. Bull.* **61**:2082.
- Hoering, T. C., 1977, Olefinic hydrocarbons in Bradford, Pennsylvania, crude oil, *Chem. Geol.* **20**:1.
- Hoering, T. C., 1985, Thermal reactions of kerogen with added water, heavy water, and pure organic substances, *Org. Geochem.* **5**:267.
- Houser, T. J., Tiffany, D. M., Li, Z., McCarville, M. E., and Houghton, M. E., 1986, Reactivity of some organic compounds with supercritical water, *Fuel* **65**:827.
- Hubbard, A. B., and Robinson, W. E., 1950, A Thermal Decomposition Study of Colorado Oil Shale, U.S. Department of the Interior, Bureau of Mines Rept. Invest. 4744.
- Huizinga, B. J., Tannenbaum, E., and Kaplan, I. R., 1987, The role of minerals in the thermal alteration of organic matter—IV. Generation of n-alkanes, acyclic isoprenoids, and alkenes in laboratory experiments, *Geochim. Cosmochim. Acta* **51**:1083.
- Hunt, J. M., 1979, *Petroleum Geochemistry and Geology*, W. H. Freeman and Co., San Francisco.
- Jones, M., Douglas, A. G., and Connan, J., 1987, Hydrocarbon distributions in crude oil asphaltene pyrolyzates. 1. Aliphatic compounds, *Energy Fuels* **1**:468.
- Jurg, J. W., and Eisma, E., 1964, Petroleum hydrocarbons: Generation from fatty acid, *Science* **144**:1451.
- King, R. J., 1983, Steel, in: *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 21, John Wiley & Sons, New York, pp. 552–625.
- Kisch, H. J., 1987, Correlation between indicators of very low-grade metamorphism, in: *Low Temperature Metamorphism* (M. Frey, ed.), Blackie, Glasgow, pp. 227–300.
- Larter, S. R., and Douglas, A. G., 1980, A pyrolysis-gas chromatographic method for kerogen typing, in: *Advances in Organic Geochemistry 1979* (A. G. Douglas and J. R. Maxwell, eds.), Pergamon Press, Oxford, pp. 579–584.
- Larter, S. R., and Senftle, J. T., 1985, Improved kerogen typing for petroleum source rock analysis, *Nature* **318**:277.
- Larter, S. R., Horsfield, B., and Douglas, A. G., 1977, Pyrolysis as a possible means of determining petroleum generating potential of sedimentary organic matter, in: *Analytical Pyrolysis* (C. E. R. Jones and C. A. Cramers, eds.), Elsevier, Amsterdam, pp. 189–202.
- Lewan, M. D., 1978, Laboratory classification of very fine-grained sedimentary rocks, *Geology* **6**:745.
- Lewan, M. D., 1983, Effects of thermal maturation on stable organic carbon isotopes as determined by hydrous pyrolysis of Woodford Shale, *Geochim. Cosmochim. Acta* **47**:1471.
- Lewan, M. D., 1985, Evaluation of petroleum generation by hydrous pyrolysis experimentation, *Philos. Trans. R. Soc. London Ser. A* **315**:123.
- Lewan, M. D., 1987, Petrographic study of primary petroleum migration in the Woodford Shale and related rock units, in: *Migration of Hydrocarbons in Sedimentary Basins* (B. Doherty, ed.), Editions Technip, Paris, pp. 113–130.
- Lewan, M. D., and Buchardt, B., 1989, Irradiation of organic matter by uranium decay in the Alum Shale, Sweden, *Geochim. Cosmochim. Acta* **53**:1307.
- Lewan, M. D., and Williams, M. D., 1987, Evaluation of petroleum generation from resinites by hydrous pyrolysis, *Am. Assoc. Petrol. Geol. Bull.* **71**:207.
- Lewan, M. D., Winters, J. C., and McDonald, J. H., 1979, Generation of oil-like pyrolyzates from organic-rich shales, *Science* **203**:897.
- Lewan, M. D., Bjørøy, M., and Dolcater, D. L., 1986, Effects of thermal maturation on steroid hydrocarbons as determined by hydrous pyrolysis of Phosphoria Retort Shale, *Geochim. Cosmochim. Acta* **50**:1977.
- Louis, M. C., and Tissot, B. P., 1967, Influence de la température et de la pression sur la formation des hydrocarbures dans les argiles à kérogen, *Proceedings of the 7th World Petroleum Congress*, Vol. 2, Elsevier, Amsterdam, p. 47.
- Lundegard, P. D., and Senftle, J. T., 1987, Hydrous pyrolysis: A tool for the study of organic acid synthesis, *Appl. Geochem.* **2**:605.
- McCollum, J. D., and Quick, L. M., 1976a, Process for upgrading a hydrocarbon fraction, U.S. Patent 3,960,708.
- McCollum, J. D., and Quick, L. M., 1976b, Process for upgrading a hydrocarbon fraction, U.S. Patent 3,989,618.
- McKee, R. H., and Lyder, E. E., 1921, The thermal decomposition of shales. I—Heat effects, *J. Ind. Eng. Chem.* **13**:613.
- Meissner, F. F., 1978, Petroleum geology of the Bakken Formation, Williston Basin, in: *Williston Basin Symposium*, Montana Geological Society 24th Annual Conference, pp. 207–227.
- Monthioux, M., 1988, Expected mechanisms in nature and in confined-system pyrolysis, *Fuel* **67**:843.
- Monthioux, M., Landais, P., and Monin, J.-C., 1985, Comparison between natural and artificial maturation series of humic coals from the Mahakam delta, Indonesia, *Org. Geochem.* **8**:275.
- Murakami, K., Yokono, T., and Sanada, Y., 1986, An investigation of the role of hydrogen sulfide in coal liquefaction catalysis by high-temperature and high-pressure e.s.r., *Fuel* **65**:1079.
- Palmer, D. A., and Drummond, S. E., 1986, Thermal decarboxylation of acetate. Part I. The kinetics and mechanism of reaction in aqueous solution, *Geochim. Cosmochim. Acta* **50**:813.
- Pollard, D. D., and Aydin, A., 1988, Progress in understanding jointing over the past century, *Geol. Soc. Am. Bull.* **100**:1181.
- Rullkötter, J., Aizenshtat, Z., and Spiro, B., 1984, Biological markers in bitumens and pyrolyzates of Upper Cretaceous bituminous chalks from the Ghareb Formation (Israel), *Geochim. Cosmochim. Acta* **48**:151.
- Rumble, D., III, Ferry, J. M., Hoering, T. C., and Boucot, A. J., 1982, Fluid flow during metamorphism at the Beaver Brook fossil locality, New Hampshire, *Am. J. Sci.* **282**:886.
- Saxby, J. D., and Riley, K. W., 1984, Petroleum generation by laboratory scale pyrolysis over six years simulating conditions in a subsiding basin, *Nature* **308**:177.
- Saxby, J. D., Bennett, A. J. R., Corcoran, J. F., Lambert, D. E., and Riley, K. W., 1986, Petroleum generation: Simulation over six years of hydrocarbon formation from torbanite and brown coal in a subsiding basin, *Org. Geochem.* **9**:69.
- Schuhmacher, J. P., Huntjens, F. J., and van Krevelen, D. W., 1960,

- Chemical structure and properties of coal XXVI. Studies on artificial coalification, *Fuel* **39**:223.
- Soldan, A. L., and Cerqueira, J. R., 1986, Effects of thermal maturation on geochemical parameters obtained by simulated generation of hydrocarbons, *Org. Geochem.* **10**:339.
- Sourirajan, S., and Kennedy, G. C., 1962, The system H_2O -NaCl at elevated temperatures and pressures, *Am. J. Sci.* **260**:115.
- Srinivasan, G., and Seehra, M. S., 1982, Changes in free radicals in coal-derived pyrites upon heating in N_2 , H_2 , and vacuum: Role of pyrite-pyrrhotite conversion, *Fuel* **61**:1249.
- Srinivasan, G., and Seehra, M. S., 1983, Effects of pyrite and pyrrhotite on free radical formation in coal, *Fuel* **62**:792.
- Stanley, J. K., 1970, The carburization of four austenitic stainless steels, *J. Matter* **5**:957.
- Takenouchi, S., and Kennedy, G. C., 1964, The binary system H_2O - CO_2 at high temperatures and pressures, *Am. J. Sci.* **262**:1055.
- Talukdar, S., Gallango, O., Vallejas, C., and Ruggiero, A., 1987, Observations on the primary migration of oil in the LaLuna Source rocks of the Maracaibo Basin, Venezuela, in: *Migration of Hydrocarbons in Sedimentary Basins* (B. Doligez, ed.), Editions Technip, Paris, pp. 59-77.
- Tannenbaum, E., and Kaplan, I. R., 1985a, Role of minerals in the thermal alteration of organic matter—I: Generation of gases and condensates under dry conditions, *Geochim. Cosmochim. Acta* **49**:2589.
- Tannenbaum, E., and Kaplan, I. R., 1985b, Low- M_r hydrocarbons generated during hydrous and dry pyrolysis of Kerogen, *Nature* **317**:708.
- Tannenbaum, E., Huizinga, B. J., and Kaplan, I. R., 1986, Role of minerals in thermal alteration of organic matter—II: A material balance, *Am. Assoc. Petrol. Geol. Bull.* **70**:1156.
- Tissot, B. P., and Welte, D. H., 1978, *Petroleum Formation and Occurrence*, Springer-Verlag, Berlin.
- Tissot, B., Durand, B., Espitalié, J., and Combaz, A., 1974, Influence of nature and diagenesis of organic matter in formation of petroleum, *Am. Assoc. Petrol. Geol. Bull.* **58**:499.
- Tuttle, O. F., and Bowen, N. L., 1958, Origin of granite in the light of experimental studies in the system $NaAlSi_3O_8$ - $KAlSi_3O_8$ - SiO_2 - H_2O , *Geol. Soc. Am. Mem.* **74**.
- Winkler, H. G. F., 1974, *Petrogenesis of Metamorphic Rocks*, 3rd ed., Springer-Verlag, New York.
- Winters, J. C., Williams, J. A., and Lewan, M. D., 1983, A laboratory study of petroleum generation by hydrous pyrolysis, in: *Advances in Organic Geochemistry 1981* (M. Bjørøy, ed.), John Wiley & Sons, New York, pp. 524-533.