

Oil Shale Pyrolysis by Triple Quadrupole Mass Spectrometry: Comparisons of Gas Evolution at 10°C/min Heating Rate.

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Abstract

Kimmeridge, Phosphoria, LaLuna, Teistberget, New Albany, Janus, Lias ϵ , Maoming, Fushun, Woodford, and three Green River oil shales were subjected to programmed temperature pyrolysis at a heating rate of 10°C/min using Triple Quadrupole Mass Spectrometry (TQMS) as the detection method. Volatile compound evolution, including hydrocarbons, non-condensable gases, and heteroatomic compounds were monitored by on-line, real-time detection. As expected, the temperatures of maximum evolution depended on the oil shale and the species evolving. Generally, the T_{\max} values for total light volatile organic compound generation were between 430 to 500°C, with the New Albany giving the lowest values and Brotherson A from Green River giving the highest values. The heteroatomic species had T_{\max} values which were slightly lower than those for hydrocarbon evolution. Non-condensable gas formation was highly dependent upon the mineral matrix of the shale.

Introduction

Locating oil in a formation, and predicting where generation will occur are relevant contemporary problems for geochemistry. We are studying the kinetics of oil generation through laboratory simulated pyrolysis of source rocks to better address these problems.¹ To extend our data base, we have selected several oil shales from various geographical locations, from both marine and lacustrine source types and subjected them to programmed temperature pyrolysis at various heating rates, from room temperature to 900°C using Triple Quadrupole Mass Spectrometry (TQMS) as the detection method. This technique has been utilized previously for several studies on pyrolysis of oil shale,²⁻⁵ tar sands,⁶⁻⁸ and coal.⁹

TQMS is particularly suited for this type of study because it provides on-line, real-time analysis. By these experiments, we follow the evolution as a function of temperature of various light hydrocarbons, N-, S-, and O-containing compounds, and non-condensable gases. The pyrolysis profiles obtained allow determination of evolution range and T_{\max} . Multiple heating rates allow determination of kinetic parameters for which the ultimate aim is extrapolation to geological conditions. This report is a preliminary account of the evolution behavior of several oil shales at the heating rate of 10°C/min. A full report will be issued later. In addition, the kinetics derived from multiple heating rates will be reported separately.

Experimental

Instrumentation. The TQMS utilizes both MS and MS/MS detection coupled with computer controlled acquisition which allows for the detection of over 40 components in mat-

ters of seconds. Full details of this technique have been published elsewhere.^{10,11} Compounds analyzed for are C₁- through C₇-hydrocarbons, C₂- through C₅- volatile sulfur compounds, the non-condensable gases, H₂, CO, CO₂, H₂S, SO₂, and COS, as well as H₂O, CS₂, and several nitrogen- and oxygen-containing compounds. In these experiments, the pyrolysis reactor was a 1/4 inch quartz tube holding approximately 0.5 grams of oil, and was heated at a rate of 10°C/min with a constant Ar sweep of 30 cc/min. The evolving components flowed into a trap kept at 140°C. This allowed for light volatile hydrocarbon and heteroatom (N,S,O) compounds up to C₈ to pass through to the mass spectrometer, while the heavy components were retained. In addition to qualitative detection, several of the volatile components were also quantitated. Total evolution data will be reported later. The width of the T_{max} values indicate in all cases multiple activation energies. This will also be discussed in detail in the kinetics report.

Most of the samples were also characterized pyrolysis in a Pyromat (Lab Instruments) micropyrolysis instrument. 15 mg of sample is held in a quartz tube with a type K thermocouple inside. The sample is heated at a programmed heating rate, chosen to be 9.2°C/min in this case for comparison to the TQMS results. The total pyrolysate is monitored with an adjacent FID detector operated at 500°C.

Samples. Table 1 describes the shales examined in this study. Both marine and lacustrine samples from several locations throughout the world were examined. Pyrolysis experimental conditions and errors were determined by multiple runs on Woodford and NA-13 shales. Less abundant samples were examined generally 1 to 2 times.

Sources of several of the shales have been described previously.¹ In addition, NA-13 is from the New Albany formation; AP-24, Government 33-4, and Brotherson A are from the Green River formation; Wenzel comes from the Lias ϵ formation. AP-24 comes from the Mahogany zone in Colorado. Government 33-4 and Brotherson A come from well cores in Utah. Government 33-4 contains 10% vitrinite and 5% exinite. (Numbers provided by DGS company of The Woodlands, TX.) Brotherson A is just above the oil window. The Wenzel sample is from J. Rullkotter (KFA); LaLuna from S. Talukdar (INTEVEP); Janus and Teistberget from B. Dahl (Norsk Hydro).

Two samples each of Maoming and Fushun shales were also examined. These samples were from the same formation but obtained from different sources. The samples appended with I were obtained from R. C. Rex, Jr. (Hycrude Corporation) and those appended with II were obtained from Zhang Shi Ko of Sinopec International. Janus is a terrestrial shale with some marine mixed in. Full descriptions of the samples will be presented elsewhere.

Results and Discussion

Hydrocarbon Evolution. Figure 1 shows the pyrolysis profiles for the evolution of C₃H₈ for several of the shales listed in Table 1 (some were not presented for figure clarity). These profiles are typical of evolution seen for all the hydrocarbons, having an approximate Gaussian shaped prominent maximum with a temperature of maximum evolution (T_{max}) around 450 to 500°C, depending upon the hydrocarbon species evolving and the particular shale. This maximum has been assigned as due to kerogen breakdown and bitumen cracking.^{2,12-14} Little or no intensity is seen at temperatures below and above this

maximum, except in methane evolution and isolated cases for higher hydrocarbons (see below).

Table 2 shows the T_{\max} for the total light organics evolved, and compares this value to the T_{\max} for the $C_4H_9^+$ ion and the T_{\max} measured by Pyromat. The total light organics evolution value comes from taking the total ion current of all the species evolving (which pass through the 140°C trap) at a specific temperature and subtracting the ion current contributions from non-hydrocarbon gases (SO_2 , CO_2 , H_2S , HS , O_2 , S , H_2O , NH_3 , H_2) and the carrier and analysis gases (Ar, Kr). The $C_4H_9^+$ ion is from monitoring m/z 57 and is a result of contributions from most hydrocarbons of C_4H_{10} and higher. It is meant to be an indicator of these larger alkyl hydrocarbons as opposed to only butane. The Pyromat analysis was included to give a comparison measurement of total hydrocarbons which is not based on MS methods. Generally, for a given sample, the absolute values of the Pyromat technique are slightly lower than the total light organics from the TQMS, but the trends are the same.

Comparing T_{\max} for total volatile organics, two groupings are observed. The marine shales have temperature maxima between 447 and 471°C and the lacustrine shales between 471 and 484°C. This is normal behavior for these types of shales. The Maoming shales, however, are the exceptions. The T_{\max} , as well as other properties (see below), are much more like marine shale than lacustrine shale. The same grouping is observed for the $C_4H_9^+$ ions, but with slightly different temperatures ranges.

Comparing corresponding T_{\max} values for total light organics and $C_4H_9^+$ ions, in general, the values are similar. NA-13 has the lowest T_{\max} for both sets, while Brotherson A has the highest for both sets. The biggest differences between the two sets are for Wenzhen, where the T_{\max} for total light organics evolution is 8 °C higher than for the $C_4H_9^+$ fragment. In some cases (Phosphoria, Wenzhen, Woodford, Government 33-4, Maoming II) the T_{\max} for total light organics generation is higher than the T_{\max} for $C_4H_9^+$ ion, but in many cases it is the same or lower (NA-13, Janus, Maoming I, Kimmeridge, AP-24, Teistberget, Fushun I, Fushun II, Brotherson A, LaLuna).

The Pyromat derived T_{\max} values are generally lower than the corresponding T_{\max} values and exhibit a much smaller spread in values than for both total light organics and $C_4H_9^+$ generation. However, the trends are roughly same. In this case, Phosphoria has the lowest T_{\max} , instead of NA-13. Brotherson A has the highest T_{\max} . Also, the lacustrine shales have a T_{\max} which is around 460°C, while the marine shales have a T_{\max} around 445°C. As in the case for total light organics generation, Maoming shale behaves more like a marine than lacustrine shale.

Table 3 shows the T_{\max} values for C_2H_4 , C_2H_6 , C_3H_8 , and C_4H_{10} evolution. The value in parentheses in the T_{\max} column indicates another maximum is observed having a T_{\max} at the listed temperature in addition to the maximum assigned to hydrocarbon evolution. This low temperature maximum can be assigned to entrapped material in the mineral matrix which becomes labile when the bitumen in the shale begins to soften. This behavior is very prominent in tar sands where the bitumen content is much higher than in oil shale and has been assigned as such.⁶⁻⁸

For all cases, the C_2H_4 evolution T_{max} values are higher than the T_{max} for total light organics evolution for the corresponding shale. For the lacustrine shales, Fushun I, Fushun II, Government 33-4, and Brotherson A show very little difference between the C_2H_4 T_{max} and the total light organics evolution T_{max} (2 to 6 °C) as shown in Table 2. For the marine shales, the difference between the T_{max} for C_2H_4 evolution and the T_{max} for total light organics evolution is very large (15 to 35 °C). The two Maoming samples, however, behave like marine samples also which has been seen above for the total light organics, $C_4H_9^+$ evolution, and Pyromat T_{max} .

Interestingly, the lacustrine samples tend to have T_{max} values for total light organics evolution which are *higher* than that for the marine shales, but in the case of C_2H_4 evolution, the T_{max} values are *lower*. Fushun I and Fushun II have the lowest C_2H_4 evolution T_{max} values for all the shales listed. Brotherson A which has the highest T_{max} for total light organics and $C_4H_9^+$ ion evolution, and Pyromat T_{max} , is not even close for that value in Table 3.

Contrary to total light organics and C_2H_4 evolution, the T_{max} values for C_2H_6 evolution show no apparent grouping according to type. However, the differences in the T_{max} values for C_2H_6 evolution compared to the T_{max} values for total light organics evolution are generally much larger for the marine shales than the lacustrine shales. Even the Maoming samples are consistent with this.

The difference in the T_{max} values for C_2H_4 evolution and C_2H_6 evolution are much larger for the marine shales than the lacustrine shales. (The ethane to ethene ratio are much closer to 1 for the marine shales). Once again, the Maoming samples are the exception as noted above. Brotherson A is also an exception. This shale is different than the other samples in that it is just above the oil generation window. As seen in Table 2, it has the highest T_{max} for total light organics and $C_4H_9^+$ ion evolution. This is consistent with the lighter material being converted in the formation.

Our results are similar to earlier results for eastern Devonian shale,^{2,13} Chinese shale,² and Green River shale.^{2,12} Our T_{max} values are generally higher because our faster heating rate, but these appear to be minor differences from the earlier work¹²⁻¹⁴ due to improvements in techniques.

The T_{max} values for C_3H_8 evolution listed in Table 3 are lower than the T_{max} values for C_2H_4 and C_2H_6 evolution, and are similar to the T_{max} for total light organics evolution, for a given shale. This has been seen before NA-13 oil shale at 4°C/min¹³ and for several tar sands.⁶⁻⁸ Only Fushun II and Brotherson A counter this trend.

Of all the hydrocarbons listed in Table 3, C_4H_{10} had the lowest T_{max} for a given shale. These values are significantly lower than the T_{max} for total light organics evolution. The differences in T_{max} values of C_2H_4 and C_4H_{10} for a given shale ranged from 54 °C to 10 °C. The lacustrine shales generally had smaller differential than the marine shales, which is expected. However, as seen before, the Maoming shales had behavior which was similar to marine shales. Brotherson A was another exception, which exhibited very little difference in the T_{max} values for all the hydrocarbons listed in Table 3. As stated above, Brotherson A is located above the oil generation window, which is probably responsible for its aberrant behavior. The T_{max} for C_4H_{10} generation for NA-13 is slightly lower (3°C)

than the value found at 4°C/min, but probably within experimental error.¹³ The AP-24 value is higher as expected for the higher heating rate.¹²

Methane. Figure 2 shows the pyrolysis profiles for the evolution of methane as a function of pyrolysis temperature for selected shales. In contrast to the other hydrocarbon evolution profiles, the typical methane profile exhibits not only the prominent maximum at hydrocarbon evolution temperatures, but also a shoulder on the high temperature side of this maximum. The prominent maximum has a T_{max} higher than for the corresponding other hydrocarbons, ranging from 2 to 146 °C above the T_{max} for total light organics generation, depending upon the shale. This has also been assigned to kerogen breakdown and bitumen cracking reactions.¹²⁻¹⁴

The evident shoulder on many of the profiles in Figure 2 has been assigned to evolution of methane by secondary charring reactions. As the kerogen is further pyrolyzing, and the non-volatile bitumen is laying down as pre-coke and coke on the mineral matrix, more methane is evolved. This behavior has been seen previously for oil shale¹² and tar sands.⁶⁻⁸ However, for several shales (LaLuna, Phosphoria, Government 33-4) have shoulders in the methane profiles on the low temperature side of the prominent maximum. This behavior has been seen before for NA-13 shale.² This suggests the major peak is due to charring reactions instead of organic evolution. Because at the higher heating rates, the shoulders are poorly resolved, this aspect will be examined in more detail at the 1°C/min heating rate.

Table 4 lists the T_{max} for methane evolution for all the shales studied. Kimmeridge exhibits the highest T_{max} while AP-24 exhibits the lowest. The AP-24 value is 15°C higher than the T_{max} reported earlier at a 4°C/min heating rate, which is consistent with the higher heating rate.¹² The T_{max} for NA-13 also agrees with values for eastern shales heated at 4°C/min reported by Coburn¹³ and Oh et al.² We also observe a shoulder on the low temperature side of the prominent maximum at about 470°C. This is in agreement with Oh et al. who see the shoulder at 450°C and assign it as probably due to CH₄ generation from kerogen pyrolysis. Oh et al. also reports the Maoming I and Fushun I shales having T_{max} at 500°C. These values are reasonably close to those in Table 4 which would not be expected at the different heating rates. Because of the broad nature of the CH₄ peak, T_{max} values are difficult to assign when the signal-to-noise is not optimal. In addition, they observed shoulders at temperature around 600°C, which is also consistent with Table 4.

Regardless of the T_{max} for a particular shale, the shoulder appears at approximately 100°C higher. Although there is no shoulder temperature listed for Janus, examination of the profile in Figure 2 shows a very broad peak which defies resolution in the temperature range expected for the shoulder. This could be due to the noise in the profile, or the two methane forming reaction pathways being about equal in intensity. Experiments at different heating rates will help clarify this, and are in progress.

Evident in Figure 2 for Government, LaLuna, Teistberget, and AP-24 oil shales are small maxima in the 700 to 900°C evolution range. Because the data is from the unique MS/MS combination of 16/14, these are not artifacts of other species which produce m/z 16 ions.¹¹ Examination of the CO₂ profiles show that these maxima coincide with intense CO₂ evolu-

tion for the same shale. This suggests CO₂ gasification of organic char (from decomposing kerogen and bitumen) in the mineral matrix. Equation (1) describes this reaction:



Carbon Oxide Evolution. The CO₂ evolution profiles for the shales can be grouped into three types: 1) high carbonate shales (LaLuna, Wenzen, Brotherson A, Government 33-4, Teistberget, and AP-24), 2) low CO₂ mineral shales (Phosphoria, Woodford, Kimmeridge, and Janus), and 3) high siderite shales (Maoming I, Maoming II, Fushun I, and Fushun II). The high carbonate type shales show a very small maximum around 400 to 450°C, and prominent evolution in the 650 to 900°C range. The former has been previously tentatively assigned in oil shales and tar sands to be due to the decomposition of oxygen-containing organic compounds, such as carboxylic acids and salts, and ketones.^{6-8,12,13,15,16} The high temperature evolution is has been assigned to carbonate mineral decomposition dominating the CO₂ evolution. Table 1 lists Brotherson A, Wenzen, LaLuna, and AP-24 having calcite and/or dolomite as the major mineral. Government and Teistberget are the only other shales that have any appreciable carbonate minerals. Independent acid carbonate determinations show this is the case for AP-24, Wenzen, and LaLuna (Government and Teistberget are being determined). These results are in agreement with previously published results on AP-24 and NA-13 shales.^{2,12,13}

The low mineral shales show CO₂ evolution behavior which is very complex. In most cases, CO₂ evolution correlates well with water and H₂S evolution in the temperature range around 475 to 600°C. Some of this evolution can be described by: 1) the α to β transition for quartz around 560°C (evolves not only water, but some CO₂),¹⁷ and 2) the reaction of H₂S is also known to react with iron and mixed metal carbonates¹⁸ at fairly moderate temperatures.

The high siderite shales (Chinese shales), minerals release CO₂ at relatively low temperatures (Shale, T_{max}: Maoming I, 465°C; Maoming II, 462°C; Fushun I, 497°C; Fushun II, 487°C) most likely due to the decomposition of siderite. For the Maoming shales, CO₂ release is coincidental with H₂S and hydrocarbon evolution, indicating reaction of H₂S (probably generated from organo-sulfur compound decomposition) with minerals may be catalyzing the release in this temperature range.

No evolution of CO is seen below 300°C, after which evolution begins. In most of the profiles, a small maximum is evident around 440°C and falls in the range of hydrocarbon evolution due to kerogen breakdown and bitumen cracking reactions. The chemical species responsible for this evolution is not certain, but may be the decarbonylation of carboxylic acids and salts.¹⁹

The majority of the CO evolved occurs above 600°C, and is not directly related to hydrocarbon generation. This high temperature CO could have a variety of origins²⁰: 1) the water-gas shift reaction, 2) the Boudouard reaction (similar to equation 1), and 3) char gasification by water from mineral breakdown.

Hydrogen. Figure 3 shows the H₂ evolution profiles as a function of temperature for several of the oil shales studied. Except for Wenzen, the profiles show no hydrogen evolution before approximately 350°C. Several maxima are seen above this temperature, depending

upon the oil shale. For AP-24, Teistberget, Maoming I, Maoming II (not shown), Fushun I (not shown), Fushun II (not shown), the best defined maximum is around 475°C. This is also evident to a lesser extent for all the other shales. Table 5 lists the T_{max} for this maximum, along with the % of total evolution (by integration) accounted for by this maximum, and the total evolution of hydrogen (cc/gr of TOC) for the entire profile. No correlation between shale type and T_{max} was observed. This maximum occurs at the same temperature range as the maximum for total light organic evolution and is attributed to kerogen breakdown, aromatization, cracking, and dehydrogenation reactions of non-volatile bitumen. The differences between this T_{max} , and the T_{max} for total light organic evolution (see Table 2) depended upon the shale, varying from 0 (Wenzen) to 48°C (NA-13). This type maximum has been observed before in oil shale,^{2,12-14} and tar sands⁶⁻⁸ pyrolysis.

Figure 3 also shows the majority of the hydrogen is evolving above this maximum assigned to sources other than hydrocarbon generation, and can be attributed to several reactions, depending upon the temperature and the shale. The H_2 evolving in the 500 to 650°C ranging has been assigned previously¹² to char pyrolysis reactions where the residual kerogen, and non-volatile bitumen are further decomposing yielding surface coke, H_2 , and CH_4 (see above discussion). H_2 evolving above this can have additional contributions from a variety of secondary reactions including the water-gas shift equilibrium, char gasification, and the Boudouard reaction.

Heteroatomic Compounds. Several sulfur-, nitrogen-, and oxygen-containing compounds also evolved during the pyrolysis of the oil shales. Of all these compounds, methylthiophene generally produced the most intense signal due to concentration and response of the species. Figure 4 shows the methylthiophene evolution profiles as a function of pyrolysis temperature for most of the shales studied. The profile behavior is very similar to that of the hydrocarbons, where maximum evolution occurs at temperatures of oil generation. Also listed in Figure 4 are the T_{max} for the methylthiophene. The values, in °C, for the shales not shown are: Maoming II, 454; Woodford, 437; Fushun II, 446; Brotherson A, 487; NA-13, 436; Janus did not evolve methylthiophene. In general, these values are lower than the corresponding T_{max} for total light organics generation listed in Table 2 from 4 to 32°C. However, there appears no grouping according to shale type. Excluding Brotherson A, LaLuna exhibited the smallest difference (4°C), while Wenzen exhibited the largest (32°C). Brotherson A is the exception, where T_{max} is 3°C higher than the T_{max} for total evolution. No other shale has exhibited this behavior. However, this may be due to Brotherson A being above the oil generation window. This evolution behavior for methylthiophene and other heteroatomic species has been seen before for AP-24, NA-13,⁵ Maoming,² Kimmeridge,¹ and Fushun,² oil shales, and tar sands.⁶⁻⁸

Figure 5 shows the acetic acid evolution profiles for several shales studied. The T_{max} values are also listed. The T_{max} values, in °C, for the shales not shown in the figure are: NA-13, 391; Wenzen, 431; Fushun II, 442; Maoming II, 400; Woodford, 389; Janus and Brotherson A did not evolve any acetic acid. In general, the profiles are similar to the methylthiophene and hydrocarbon profiles except the acetic acid profiles tend to be broader, and the T_{max} values are even lower than the corresponding T_{max} values for methylthiophene. The difference between T_{max} for acetic acid evolution and T_{max} for total light organics evolution was as much as 74°C (Woodford).

The T_{\max} for acetic acid suggests these compounds may not be bound in the kerogen the same way the hydrocarbons are. The most obvious choice would be binding through a carbon oxygen bond. This should have less bond strength, and therefore a lower T_{\max} . Another possibility is the acid is entrained in the matrix, but due to donor-acceptor interactions, evolves at much higher temperatures than entrapped hydrocarbons (see bimodal distribution shown in Table 3, for example). These, and other alternatives are under investigation in our laboratories.

Conclusions

1) For all shales studied, the hydrocarbon evolution behaved approximately the same. Evolution did not begin until approximately 300°C, reaching a maximum for total light organics hydrocarbon evolution ranging from 447 to 484°C (depended upon the shale), and rapidly decreasing to completion about 550°C.

2) The T_{\max} values for total light organics evolution for lacustrine shales were generally higher than for marine shale. The Maoming samples were the exceptions, acting more like marine than lacustrine shales.

3) The T_{\max} values for $C_4H_{10}^+$ ion evolution were quite similar to the T_{\max} from total light organics evolution, and exhibited similar trends with shale type.

4) The hydrocarbons, C_2H_4 , C_2H_6 , C_3H_8 , and C_4H_{10} , all exhibited individualized behavior. The T_{\max} for C_2H_4 and C_2H_6 evolution is much higher than the T_{\max} for total light organics evolution. In addition, type behavior is opposite that for total light organics evolution: lacustrine shales have T_{\max} for C_2H_4 which is lower than that for marine shales. The T_{\max} values for C_3H_8 and C_4H_{10} hydrocarbons were progressively lower in temperature for a given shale.

5) CO_2 generation divided the shales into three categories: 1) high carbonate shales, which the evolution was dominated by the high temperature decomposition due to calcite, and dolomite, 2) low carbonate mineral shales, where the CO_2 evolution exhibited no distinctive source, and 3) siderite shale which exhibited prominent CO_2 evolution in the 450 to 475°C evolution range.

6) CO evolution occurs in two regimes: 1) a minor amount in the temperature range around 400 to 450°C which corresponding to kerogen breakdown and bitumen cracking, and 2) the major amount at high temperature due to char gasification reactions and water-gas shift equilibrium.

7) Hydrogen evolution exhibited a sharp maximum concurrent with kerogen breakdown and bitumen cracking. The majority of the hydrogen evolution occurred above 500°C due to char pyrolysis and mineral decomposition induced gasification reactions.

8) Heteroatomic compound behavior was typified by methylthiophene and acetic acid evolution, where the T_{\max} values were generally lower than the corresponding T_{\max} for total light organics evolution by as much as 32°C for methylthiophene, and even lower for acetic acid. In addition, the profiles were much broader than those observed for hydrocarbon and other heteroatom compound evolution.

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Table 1. Oil Shale Descriptions

| Shale | Country | Type | Minerals |
|-----------------|--------------|--------------------|-------------------------------------------------------------------------------------|
| Kimmeridge | North Sea | Marine | Quartz, Illite, Pyrite (m), Feldspar (tr), Dolomite (tr), Kaolinite (tr) |
| Phosphoria | Montana | Marine | Quartz, Illite (m), Siderite (tr), Pyrite (tr), Siderite (tr), Kaolinite (tr) |
| Teisberget | Norway | Marine | Quartz, Siderite (m), Calcite (m), Pyrite (m), Illite (m), Kaolinite (m) |
| NA-13 | Kentucky | Marine | Quartz, Illite (m), Kaolinite (tr), Feldspar (tr), Pyrite (tr) |
| Janus | Norway | Terrestrial/Marine | Quartz, Illite (m), Kaolinite (tr), Pyrite (tr) |
| Woodford | Oklahoma | Marine | Quartz, Pyrite (tr), Kaolinite (tr), Illite (tr), Smectite (tr) |
| LaLuna | Venezuela | Marine | Calcite, Quartz, Kaolinite (tr) |
| Wenzen | West Germany | Marine | Calcite, Quartz, Kaolinite (m), Illite (tr), Pyrite (tr) |
| Maoming I | China | Lacustrine | Quartz, Kaolinite, Siderite (tr), Illite (tr) |
| Maoming II | China | Lacustrine | Quartz, Kaolinite, Siderite (m), Illite (tr) |
| Fushun I | China | Lacustrine | Quartz, Kaolinite, Siderite (m), (Halite), Illite (tr), Smectite (tr) |
| Fushun II | China | Lacustrine | Quartz, Kaolinite, Siderite (m), (Halite) |
| AP-24 | Colorado | Lacustrine | Dolomite, Quartz, Calcite (m), Feldspar (m), Analcime (m), Pyrite (tr), Illite (tr) |
| Government 33-4 | Utah | Lacustrine | Quartz, Dolomite (m), Calcite (m), Illite (m), Analcime (tr), Kaolinite (tr) |
| Brotherson A | Utah | Lacustrine | Dolomite, Quartz, Calcite, Feldspar (m), Smectite (m), Analcime (m), Illite (tr) |

Minerals in {} are tentative
(m) = minor components
(tr) = trace components

Table 2

Temperatures of Maximum Evolution for Total Light Organics, C₄H₉⁺ Ions From Hydrocarbons, and Total Pyrolysate From Pyromat Micropyrolyzer

| Shale | Total Light, °C Organics | C ₄ H ₉ ⁺ , °C | Pyromat, °C |
|-----------------|-----------------------------|-------------------------------------------------|-------------|
| Kimmeridge | 454 | 454 | 442 |
| Phosphoria | 465 | 461 | 441 |
| Teistberget | 466 | 469 | 456 |
| NA-13 | 447 | 447 | 443 |
| Janus | 471 | 471 | 463 |
| Woodford | 463 | 460 | 444 |
| LaLuna | 462 | 466 | 444 |
| Wenzen | 467 | 459 | 444 |
| Maoming I | 465 | 465 | 451 |
| Maoming II | 466 | 463 | na |
| Fushun I | 473 | 476 | 462 |
| Fushun II | 471 | 472 | na |
| AP-24 | 452 | 456 | 459 |
| Government 33-4 | 478 | 474 | 452 |
| Brotherson A | 484 | 487 | 467 |

na = not available

Table 3

Volatile Hydrocarbon Evolution for Selected Shales at 10°C/min Heating Rate

| Shale | C ₂ H ₄ T _{max} , °C | C ₂ H ₆ T _{max} , °C | C ₃ H ₈ T _{max} , °C | C ₄ H ₁₀ T _{max} , °C |
|-----------------|--------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|---------------------------------------------------------|
| Kimmeridge | 480 | 465 (187) | 453 | 433 |
| Phosphoria | 500 | 477 | 463 | 454 |
| Teistberget | 491 | 474 (225) | 465 | 462 |
| NA 13 | 480 (176) | 458 | 446 | 437 |
| Janus | 495 | 482 (192) | 480 | 471 |
| Woodford | 495 | 467 | 458 | 441 |
| LaLuna | 482 | 474 | 464 | 455 |
| Wenzen | 482 | 467 | 459 | 448 |
| Maoming I | 499 | 472 (200) | 468 | 451 |
| Maoming II | 487 | 469 | 459 | 447 |
| Fushun I | 476 | 473 (250) | 471 | 462 |
| Fushun II | 473 | 469 (244) | 471 | 459 |
| AP-24 | 478 | 470 | 469 | 461 |
| Government 33-4 | 484 | 478 | 473 | 474 |
| Brotherson A | 489 | 488 | 493 | 479 |

Table 4
CH₄ Evolution for Selected Shales at 10°C/min Heating Rate

| Shale | T _{max} °C | Shoulder °C | Evolution cc/gr of TOC ^a |
|-----------------|------------------------|----------------|----------------------------------------|
| Kimmeridge | 500 | 600 | 30.12 |
| Phosphoria | 520 | 588 | 62.24 |
| Teist | 513 | 610 | (3.24) ^b |
| NA 13 | 500 | 460 | 60.59 |
| Janus | 509 | 600 | (0.78) ^b |
| Woodford | 504 | 584 | 48.54 |
| LaLuna | 512 | - | 55.73 |
| Wenzen | 482 | 600 | 38.40 |
| Maoming I | 500 | 600 | 30.52 |
| Maoming II | 490 | 582 | 30.46 |
| Fushun I | 487 | 590 | 39.96 |
| Fushun II | 479 | 590 | 41.06 |
| AP-24 | 454 | 540 | 34.44 |
| Government 33-4 | 500 | 620 | 82.46 |
| Brotherson A | 492 | 595 | 27.05 |

a. TOC = total organic carbon

b. cc/gr of shale

Table 5
Hydrogen Evolution Behavior for Selected Oil Shales at 10°C/Min

| Shale | T _{max} , °C ^a | % Total Evolution ^b | Total Evolution cc/gr of TOC ^c |
|-----------------|------------------------------------|--------------------------------|----------------------------------------------|
| Kimmeridge | 472 | 26.4 | 100.8 |
| Phosphoria | 494 | 16.5 | 137.5 |
| Testberget | 469 | 22.2 | (9.5) ^d |
| NA-13 | 495 | 23.4 | 92.0 |
| Janus | 482 | 31.8 | (4.26) ^d |
| Woodford | 471 | 23.5 | 113.5 |
| LaLuna | 466 | 23.8 | 96.0 |
| Wenzen | 467 | 32.4 | 75.2 |
| Maoming I | 472 | 23.1 | 155.2 |
| Maoming II | 473 | 35.2 | 137.2 |
| Fushun I | 508 | 37.6 | 244.9 |
| Fushun II | 500 | 36.2 | 191.5 |
| AP-24 | 470 | 36.5 | 117.0 |
| Government 33-4 | 500 | 37.2 | 170.3 |
| Brotherson A | 515 | 42.1 | 168.0 |

a. T_{max} for maximum at hydrocarbon evolution

b. % of total hydrogen evolution due to primary peak at hydrocarbon evolution

c. TOC = total organic carbon

d. cc/gr of shale

Figures

Figure 1. C_3H_8 Evolution as a Function of Pyrolysis Temperature for Selected Oil Shales at the Heating Rate of $10^\circ C/min$.

Figure 2. Methane Evolution as a Function of Pyrolysis Temperature for Selected Oil Shales at the Heating Rate of $10^\circ C/min$.

Figure 3. Hydrogen Evolution as a Function of Pyrolysis Temperature for Selected Oil Shales at the Heating Rate of $10^\circ C/min$.

Figure 4. Methylthiophene Evolution as a Function of Pyrolysis Temperature for Selected Oil Shales at the Heating Rate of $10^\circ C/min$.

Figure 5. Acetic Acid Evolution as a Function of Pyrolysis Temperature for Selected Oil Shales at the Heating Rate of $10^\circ C/min$.









