

SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE
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INDIGENOUS MINERAL MATTER EFFECTS IN PYROLYSIS
OF GREEN RIVER OIL SHALE

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INTRODUCTION

Conventional oil shale processing technology is based upon thermal decomposition of kerogen into various grades of oil products. Historically, a variety of pyrolysis conditions, involving both above ground and *in situ* retorting operations, have been used to obtain shale oil. Numerous kinetic studies (1-6) have investigated temperature and pressure effects. Both isothermal and nonisothermal kinetic methods have been used. These studies (1-6) have established that the decomposition involves a series of consecutive reactions in which the kerogen is first converted to bitumen which, in turn, generates a form of volatile matter which eventually is reduced to coke, oil, and gas. The physicochemical properties of oil shale undoubtedly influence the decomposition process.

A number of studies (7-10) have been published concerning the effects of the mineral constituents of oil shale on the pyrolysis process. The inorganic mineral matrix is known to be intimately associated with the organic fraction, both kerogen and bitumen, and therefore, is believed to affect the release of oil products. Previous thermogravimetric studies of oil shale have attempted to demonstrate the influence of minerals by monitoring the characteristic organic carbon decomposition step of specially prepared mixtures and the composition of the pyrolysate (8-10). The results of both Espitalie, et al. (8), and Horsfield and Douglas (9) indicate that the lower oil yield for oil shale rock as compared to isolated kerogen is due to the release of smaller quantities of higher molecular weight hydrocarbons. These results are interpreted either as the result of a trapping mechanism or condensation/gasification processes, respectively. However, extrapolation of these results to *in situ* oil shale processing is questionable since a physical mixture is not likely to reproduce the exact forms of chemical bonding as they exist in the indigenous material.

The effects of indigenous carbonate and silicate minerals on the pyrolysis of Green River and Eastern oil shales have been studied by TG-DTG and TG-MS methods and are presented in the following sections. The samples were obtained by a chemical extraction method which was shown to stepwise preferentially disassociate both of these mineral components from the oil shale. In addition, the effect of oil shale richness on pyrolysis yield was determined. Since the major mineral constituent not separated by the chemical extraction procedure was pyrite, a pyrite concentrate was prepared by standard sink-float techniques from the carbonate/silicate-free kerogen concentrate. A silicate-induced pyrolysis effect in conjunction with pyrite is also discussed based on TG-DTG data of the original and chemically extracted samples.

EXPERIMENTAL

Green River oil shale obtained from the Mahogany Zone (C-a tract) was reduced to 100 x 200 mesh samples by a mechanical pulverizing and sieving procedure. Standard density separation techniques were used to generate shales having the following Fischer assays: 25, 31, and 44 GPT. Several experiments were performed using samples of Eastern oil shale obtained from Lewis County, Kentucky.

The chemical extraction procedure used to preferentially disassociate carbonate and silicate minerals has been previously described in detail (11) and, therefore, will be briefly summarized in this section. The separation scheme is outlined in Figure 1. Initially, bitumen-free oil shale was isolated using the Soxhlet extraction method based on a methanol/benzene mixture. HCl extraction of the bitumen-free oil shale resulted in a bitumen, carbonate-free fraction, a portion of which was subsequently treated with an HF/HCl mixture to remove the majority of the silicate minerals. The effectiveness of this procedure was verified by elemental analysis data discussed in Lit. Cited (11). The bitumen, carbonate, and silicate-free oil shale was further separated into sink-and-float fractions using both 15 wt% ZnCl₂ in distilled water and pure distilled H₂O as the immersion bath media.

TG-DTG measurements were made with a DuPont Model 951 thermogravimetric analyzer equipped with a 1091 disk memory. Weight loss data were obtained both as a function of time and temperature. Samples were heated from room temperature to 900°C at a rate of 10°C/min. The ambient atmosphere was ultra-pure, 99.9%, N₂ which was generally purged at 100 ml/min. Additional thermogravimetric analysis of the oil shale samples was based on TG-MS results obtained using a Cahn RH microbalance coupled with a Finnigan quadrupole mass spectrometer.

RESULTS AND DISCUSSION

Oil Shale Sample Composition

Green River oil shale is a sedimentary rock consisting of finely laminated layers of marlstone interspersed with varying amounts of organic matter. These oil shales consist of approximately 30-60% carbonate minerals and 30-40% silicate minerals. The bulk mineralogical compositions of the three shale samples obtained by heavy media separation were found to be fairly similar. The major minerals identified included analcime, clay, quartz, aibite, ankerite/dolomite, and calcite. Elemental analysis of the 25, 31, and 44 GPT samples indicated that the organic matter distribution was essentially identical for all three oil shales. The density separation procedure isolated increasingly richer shales, but the fundamental organic composition did not vary.

Eastern oil shales are basically a silicate-rich rock with only about 1% carbonate minerals. The bulk mineralogy of the Kentucky samples primarily consists of quartz, illite, and kaolinite with some chlorite and pyrite. This is consistent with elemental analysis data which indicated that the major constituents are elemental Si, Al, Fe, and K. The elemental Ca concentration was found to be less than 100 ppm for these Eastern oil shale samples.

Thermogravimetric Analysis

Figure 2 shows typical thermogravimetric data for the 25, 31, and 44 GPT samples. All of the weight loss data discussed in this paper were obtained at a heating rate of 10°C/min. Differential analysis of the TG curves indicates two major regions of volatile product release, peaking near 465 and 740°C, respectively. The majority of the observed weight loss below 200°C is believed due to water vaporization.

Based upon TG-MS results, the DTG peak near 465°C is assigned to organic carbon pyrolysis. The TG-MS results, Figure 3, indicate that the hydrocarbon release profile in the range 350 to 500°C, peaking near 430°C, is a broad mixture of C₁₀-C₁₅ alcohols, alkenes, and other compounds which cannot be easily resolved into specific product identifications. Potential contribution of silicate minerals to the weight loss in this region was checked by thermogravimetric analysis of the major individual silicate minerals identified in the shale samples. The silicate minerals showed insignificant thermal decomposition, ≈1 wt%, over the temperature range 360 to 500°C, further supporting the assignment of this DTG peak to organic carbon pyrolysis.

The thermal decomposition of carbonate groups is reflected by the DTG maximum in Figure 2 at 730-760°C. As will be discussed in the next section, this feature of the DTG curves disappears in samples of carbonate-free oil shale. Thermogravimetric analysis of pure calcite and dolomite show carbonate decomposition at 800°C and 730-780°C, respectively, further supporting this assignment. Interference from silicate minerals in this temperature range is precluded on the basis of DTG measurements of standard silicate minerals. The principal volatile product identified by TG-MS (Figure 3) at temperatures higher than those required for organic carbon pyrolysis was CO₂. This result is expected since the decomposition reactions of calcite and dolomite in oil shale release substantial quantities of CO₂ in the temperature range 600-750°C.

The TG-DTG data correspond quite well with other available analytical data for the shale samples. For example, the ratio of the weight loss in the organic evolution peak at 465°C to that of the CO₂ peak at 740°C increased from about 0.4 for the 25 GPT shale to about 1.5 for the 44 GPT sample. This trend is consistent with the relative organic carbon content of the two samples as well as the bulk mineralogy results which indicate that the 25 GPT sample has approximately 14 wt% calcite and 30 wt% dolomite versus less than 2 wt% calcite and about 20 wt% dolomite for the 44 GPT sample. Carbonate carbon concentrations, as determined by acid leaching and evolved CO₂ titration, were found to be 4.8, 3.9, and 3.2 wt% for the 25, 31, and 44 GPT samples, respectively. These values correspond to an expected weight loss in the TG carbonate decomposition region, 740°C, of approximately 18, 14, and 12 wt%, respectively, for the three shales. The expected weight losses compare favorably to measured weight losses of 21, 14, and 12 wt% for the 25, 31, and 44 GPT shales, respectively.

A second feature to be noted concerning the thermal analysis data shown in Figure 2 is a secondary peak at about 520°C following the organic carbon transition. The peak is most pronounced for the 44 GPT sample. TG-MS data, Figure 3, indicate a bimodal H₂S profile with one peak located slightly prior to the organic carbon pyrolysis peak and the second transition occurring at a temperature in between that of carbon decomposition and carbonate decomposition. These combined

results suggest the influence of pyrite on the pyrolysis of the shale samples.

Although DTG analysis of a pyrite standard sample indicated thermal decomposition over the temperature range 480 to 700°C, the major weight loss was observed at 660°C. It is likely that the relatively low concentration of pyrite in the shale samples, about 2 wt%, resulted in the masking of the 660°C peak. On the basis of the TG-MS results, it would appear that the observed 520°C peak is due to pyrite-organic matter reactions involving, for example, FeS₂ and elemental S with aromatic and olefinic compounds. Similar mechanisms have been proposed for the effect of pyrites and iron oxides on the pyrolysis and gasification of coal (12). Rostam-Abadi and Mickelson (10) have shown that for mixtures of Colorado oil shale and pyrite, the pyrolysis rate is reduced.

Weight loss data determined from the TG curves are expressed in terms of the concentration ratio of pyrolyzed organics from TG experiments, to the original organics in the shale $[O_t]^{TG}/[O_t]$. This ratio is an expression of the pyrolysis yield of the sample. Table I summarizes the pyrolysis yields determined for the three oil shales of differing richness and the DTG temperature maxima. The pyrolysis yield is observed to increase with shale organic content from 58.6 to 72.2 wt% of the shale organics. The organic carbon decomposition temperature is reasonably constant as a function of oil shale richness. The temperature at which pyrolysis of carbonates occurs appears to decrease with increasing GPT. The temperature change for the carbonate probably reflects the changing calcite concentrations in the shales. Calcite decomposes at higher temperatures than does dolomite.

For comparison purposes, a sample of Eastern oil shale was thermally analyzed for pyrolysis effects. The mineralogical composition of this oil shale is confirmed by the TG and DTG measurements shown in Figure 2d by the marked absence of the carbonate decomposition characteristic of the 700-800°C temperature range. The pyrolysis yield, 47.4 wt%, determined for this oil shale is substantially lower than that found for the samples of Green River oil shale and is consistent with a lower H/C ratio in the organic fraction. The lower pyrolysis temperature, 453°C, is possibly due to the absence of carbonate mineral bonding and therefore, a lower total enthalpy of reaction. The secondary peak at 520°C was also observed in the TGA data of the Eastern oil shale. This result eliminates a carbonate origin for this transition and is in support of a possible pyrite or pyrite-induced weight loss since this sample contains ~5 wt% pyrite.

TABLE I
SHALE RICHNESS VS. PYROLYSATE CONCENTRATION^{a, b, c}

Oil Shale Richness (GPT)	Elemental Analysis			Thermogravimetric Analysis				Pyrolysis Yield	
	[C _c]	[C _o]	[O _t]	[O _t]	T _i	[C _c]	T _i	Org.	Carb.
	(Wt%)	(Wt%)	(Wt%)	(Wt%)	(°C)	(Wt%)	(°C)	(%)	(%)
25	4.79	11.4	14.2	8.32	463	5.76	758	58.6	120
31	3.91	11.9	14.8	9.75	465	3.88	733	65.9	99
44	3.22	19.4	24.1	17.4	467	3.17	729	72.2	98
Eastern ^d	0.03	12.4	----	5.88	453	----	---	47.4	---

- [C_c], [C_o], and [O_t] represent carbonate carbon, organic carbon, and total organic concentration $[O_t] = [C_o]/0.805$; T_i: inflection point temperature.
- T range for organic matter pyrolysis (ΔT_o) is determined to be 350 to 500°C. T range for carbonate carbon decomposition (ΔT_c) is determined to be 600 to 800°C.
- Pyrolysis yield % : $100[O_t]^{TG}/[O_t]$ for organics and $100[C_c]^{TG}/[C_c]$ for carbonates.
- Pyrolysis yield % is based on concentration of organic carbon, [C_o].

TG Results of Extracted Fractions

The influence of the mineral matrix on the pyrolysis of Green River oil shale was investigated for the 44 GPT sample. In contrast to earlier studies (8-10) based on the physical combination of mineral additives with oil shale and/or a kerogen concentrate, the approach used in this work involved a chemical extraction technique (11), Figure 1, which preferentially disassociated the carbonate and silicate minerals. In addition to the original H₂O-washed sample, the following five fractions were analyzed by TG: bitumen-free, bitumen/carbonate-free, bitumen/carbonate/silicate-free or kerogen concentrate, float fraction of kerogen concentrate, and sink fraction of kerogen concentrate. The thermogravimetric data, including pyrolysis yields are summarized in Table II.

The net pyrolysis yield is observed to increase by 2.4% after the removal of the bitumen component contrary to initial expectations. Although the bitumen component is pyrolyzed quantitatively, the kerogen component appears to be converted to products more readily in the absence of bitumen. It is also noted that the secondary peak at 520°C is still present. Thus, the peak is

not associated with bitumen pyrolysis and therefore, by inference, is due to the mainly bitumen-free kerogen component.

TABLE II
THE INFLUENCE OF THE MINERAL MATRIX ON
THE PYROLYSIS OF OIL SHALE^a

Sample	Elemental Analysis			Thermogravimetric Analysis				Pyrolysis Yield	
	[C _c]	[C _o] (Wt%)	[O _i]	W _o (Wt%)	T ₁ ^b (°C)	W _c (Wt%)	T ₁ ^b (°C)	Org. (%)	Carb.
H ₂ O Washed O. S.	2.93	20.49	25.45	15.33	464	11.68	724	60.2	109
Bitumen- Free O. S.	3.05	19.34	24.02	14.81	459	13.04	704	61.7	107
Carbonate- Free O. S.	0.15	25.69	31.91	20.80	472	---	---	68.8	---
Kerogen Conc. ^c	0.18	66.55	82.67	47.59	456	---	---	57.6	---
Float Fraction	0.18	66.64	82.78	56.66	468	---	---	68.4	---
Sink Fraction	0.18	65.28	81.09	45.70	463	---	---	56.4	---

a. Colorado, C-a tract, Mahoghany zone oil shale, 44 GPT, 100x200 mesh

b. ΔT_0 : 350 to 500°C, ΔT_c : 600 to 800°C

c. Kerogen Conc.: Bitumen, Carbonate and Silicate-free Oil Shale

A significant increase in the net pyrolysis yield to 14% was obtained as the result of removal of the carbonate minerals by HCl treatment. The second DTG maximum near 730°C, due to carbonate decomposition, was noticeably absent. An explanation of the increased pyrolysis yield for the carbonate-free shale, as expected, is certainly a combination of several factors. It appears that carbonate minerals, thermochemically and/or kinetically, act to hamper the pyrolysis process or possibly modify the mechanistic reaction scheme to yield a higher percentage of coke. The observed increase in the pyrolysis yield is not due to the release of bitumen trapped by the carbonate minerals since such trapped soluble organic matter was removed by a Soxhlet extraction prior to TG analysis.

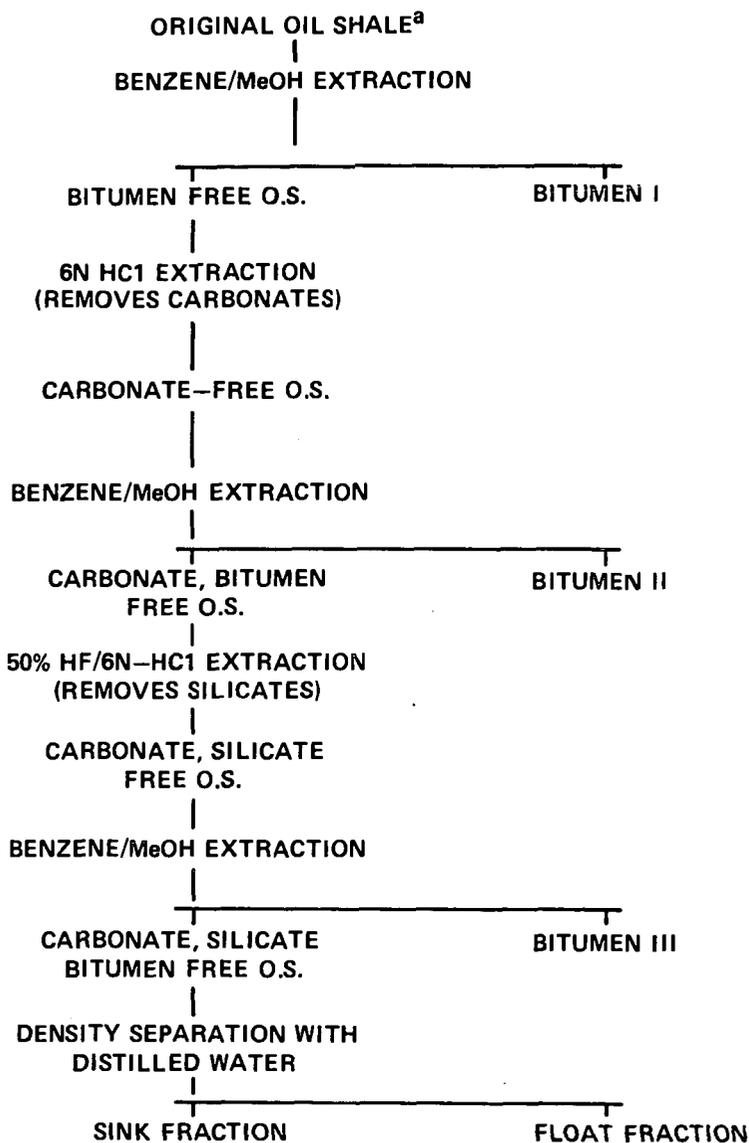
The decomposition of pure phase carbonate minerals has been extensively studied and reviewed (13). The influence of these materials on oil shale pyrolysis kinetics has not been as thoroughly investigated, but the studies of Jukkola, et al. (14), and Campbell (7) are notable. The results of both of these studies indicate that the major calcite decomposition step is not to produce CaO, but rather reaction with silicate minerals in the oil shale to form calcium and calcium-magnesium silicates. The observed enhancement of pyrolysis yield after carbonate removal may be indicative of the catalytic role of silicate minerals in paraffinic and aromatic compound decompositions. In effect, the apparent preference for calcite-silicate interactions precludes silicate-catalyzed organic reactions which would presumably result in enhanced oil recovery.

This proposed silicate mineral catalytic effect is further demonstrated by TG measurements of the kerogen concentrate which indicated a decrease in the pyrolysis yield from 68.8 wt% for the carbonate-free fraction to 57.6 wt% for the carbonate- and silicate-free fraction. These results suggest that the optimum pyrolysis oil yield is achieved for oil shales which are carbonate-free but still retain their original silicate mineral concentration or possibly, an increased silicate concentration.

The positive effect of silicate minerals on oil shale pyrolysis was not a priori predictable and its origin is difficult to precisely quantify. However, one possible explanation seems to involve the combined chemistry of silicate minerals, kerogen, and pyrite. It is known that pyrite usually occurs in the form of microcrystals coated with organic matter which aggregate together to form spherical framboids (15). It is proposed that the dissolution of the pyrite-organic matter interface may be catalyzed by silicate minerals which act as an effective third body for the formation of thiophenic compounds. Liberation of this organic matter coating via pyrite decomposition and subsequent transformation would result in the observed oil yield trend. It has been shown that the reactions of S or H₂S with various organic molecules results in the formation of thiophenic structures as does the reaction of FeS₂ with organics (16).

The catalytic effect of silica and aluminosilicates has been previously suggested in other chemical systems, but to the authors' knowledge, has not been experimentally verified. A possible experimental observation of this catalytic effect may be the 520°C DTG peak. Removal of the

**FIGURE 1 PREFERENTIAL MINERAL MATTER DISSOLUTION
BY CHEMICAL METHODS**



a) COLORADO, C-a TRACT, MAHOGANY ZONE, 100X200 MESH, 44 GPT; IN ORDER TO REMOVE FINES AND CONTAMINATED IRON, THE ORIGINAL OIL SHALE WAS WATER WASHED, FILTERED AND DRIED AT 85°C UNDER VACUUM (400 TORR WITH N₂) FOR 24 HR.

FIGURE 2 NON-ISOTHERMAL TG-DTG CURVES OF WESTERN ((a) 25 GPT (b) 31 GPT (c) 44 GPT) AND EASTERN (d) OIL SHALES (HEATING RATE 10°/MIN)

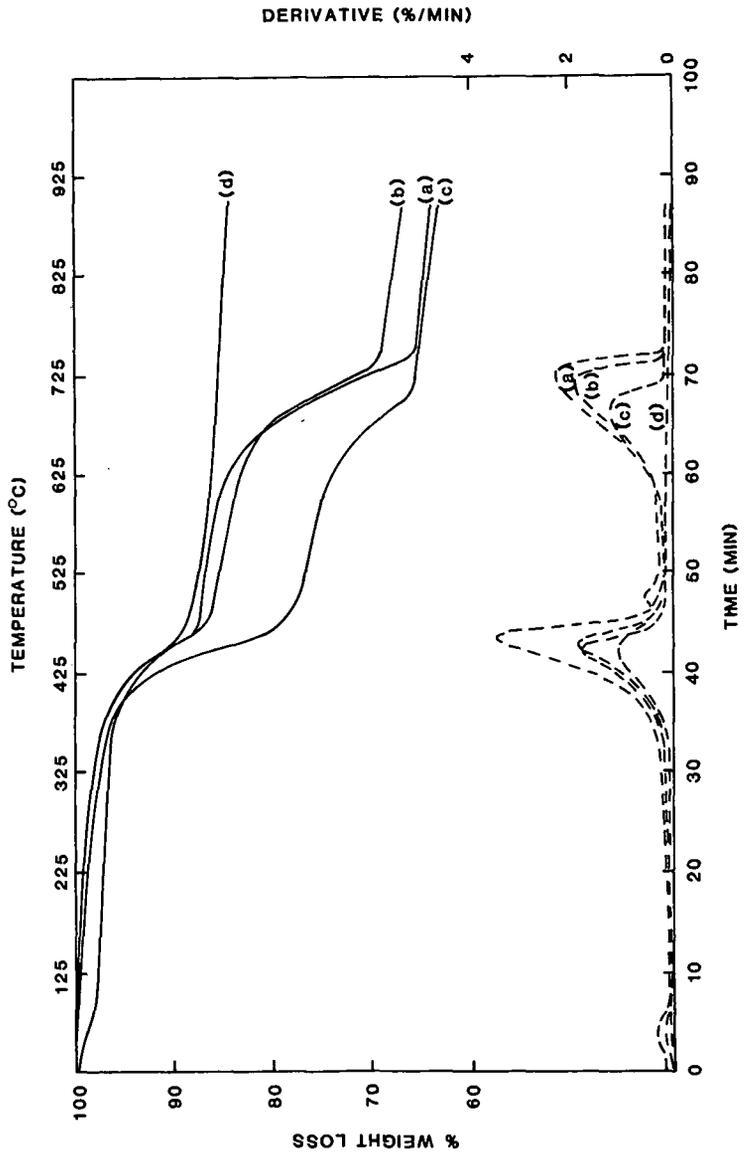
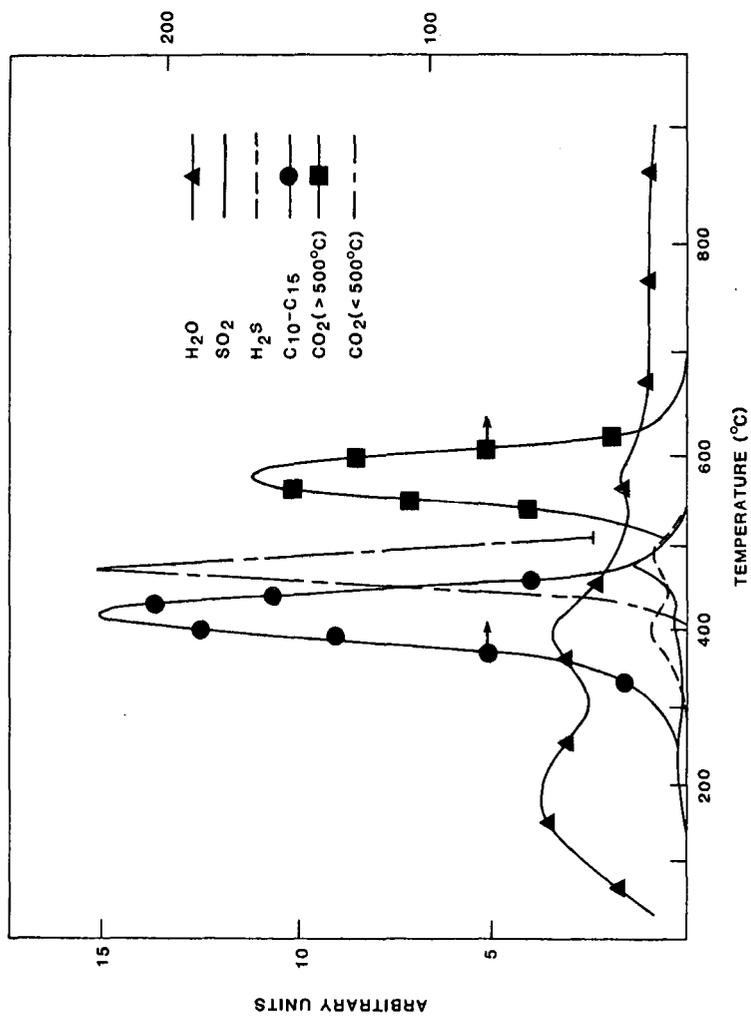


FIGURE 3 TG-MS ANALYSIS OF 44GPT WESTERN OIL SHALE (C₁₀-C₁₅ AND CO₂ (>500°C) REFER TO RIGHT HAND SIDE SCALE)



silicate minerals by HF/HCl extraction resulted in a significant reduction of the thermal decomposition process at this temperature. Reproduction of this peak could only be obtained with substantial additions of the kerogen concentrate to a low temperature ash sample. In addition, an increase in the relative amount of weight loss at 520°C in comparison to the organic carbon decomposition was obtained only by adding to the original 44 GPT sample a fairly large amount of pyrite. On the basis of X-ray diffraction data of the separated fractions, it is probable that both clay minerals and quartz contribute to the catalytic process.

The last step outlined in Figure 1 is the addition of various media to the kerogen concentrate to obtain sink-float fractions. All three GPT oil shales exhibited organic carbon decomposition at 460-470°C in float fractions with density $<1.145 \text{ g ml}^{-1}$. The sink fractions showed a variety of transitions, the most notable being the presence of organic matter as evidenced by the peak near 465°C. This effect is due to very strong organic matter interactions with quartz and pyrite which resulted in the separation of a significant portion of the bitumen-free organic matter with the mineral constituents. This interpretation is consistent with X-ray diffraction results and elemental analysis data. The other major TG inflection point common to all three GPT samples is at $T=530^\circ\text{C}$. This thermal decomposition is especially pronounced for the 25 GPT sink sample. A sample of Eastern oil shale was also sink-floated at $\rho=1.145 \text{ g ml}^{-1}$ with similar results as the Green River oil shale.

Reducing the density to 1.00 g ml^{-1} caused the separation of additional components which previously floated and were not detected due to the relative weight loss of organic carbon. In addition to the transition observed at 470 and 530°C for the higher density separation, two peaks appeared at 670 and 790°C. A shoulder at 370°C prior to the onset of the organic carbon decomposition was observed. It is suggested that the 370°C transition is due to analcime and the 790°C decomposition to calcite based on standard mineral TG-DTG data. The 670°C peak is the first indication of pyrite based on the close match between the observed DTG temperature maximum and that of the pyrite standard at 660°C. This separated fraction is clearly a relatively concentrated pyrite sample as is confirmed by elemental analysis data.

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