ORGANIC GEOCHEMISTRY OF CONTINENTAL MARGIN AND
DEEP OCEAN SEDIMENTS

by

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ORGANIC GEOCHEMISTRY OF CONTINENTAL MARGIN AND
DEEP OCEAN SEDIMENTS

1. PERSONNEL

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2. RESEARCH PERIOD: 1 March 1989 to 28 February 1991

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3. INTRODUCTION

The objective of this research continues to be the understanding of the complex processes of fossil fuel formation and migration. DoE funded research to date has focused on "case histories" of down-hole well profiles of light hydrocarbons, pyrograms, pyrolysis-GC and -GCMS parameters, and biomarker data from wells in the Louisiana and Texas Gulf Coasts (Huc and Hunt, 1980; Whelan, et al, 1984 & 1988b) and the Alaskan North Slope (Whelan, et al, 1986; Farrington et al, 1988). In the case of the Alaskan North Slope, geological data and one-dimensional maturation modeling have been integrated in order to better constrain possible source rocks, timing, and migration routes for oil and gas generation and expulsion processes (Whelan, et al, 1988; in preparation). Collaboration with Drs Les Magoon and Ken Bird at the US Geological Survey in Menlo Park provided access to an extensive geochemical and geological data base in the NPRA area which also allowed us to interpret our data in the context of geological processes in the area (Whelan, et al, 1986; 1987; 1988; & in preparation; Farrington, et al, 1988). During the current grant period, biomarker analyses and organic petrographic analyses were completed for the Ikpikpuk well.

In the case of the Gulf Coast, we have obtained a one-dimensional maturation model of the Cost B-1 well in E. Cameron field of the Louisiana Gulf Coast (see section

Ai and Figs A1- A12). Model results depicting oil and gas generation are consistent with previous ideas that gas generation and expulsion are currently occurring in these relatively organic lean gas prone sediments (Whelan, et al, 1984).

The completed E. Cameron data set adds to the enigma of the Gulf Coast oils found on the continental shelf of Louisiana. If significant quantities of the oil are coming from relatively organic lean Tertiary rocks, then "non-conventional" expulsion and migration mechanisms, such as gas dissolved in oil (Solokolov, 1963; Solokolov and Mironov, 1962 and others as reviewed in Hunt, 1979, pp213-215) must be invoked to explain the Gulf Coast oils reservoirs on the Louisiana continental shelf. All of these "non-conventional" migration mechanisms require some quantity of gas, which has led to our designing and starting to assemble a hydrous pyrolysis apparatus to follow, the laboratory, rates of generation and expulsion of sediment gases (see Section C).

Initiation of some new research to examine $\delta^{13}\text{C}$ of individual compounds from pyrolysis is described in Section D.

We are beginning to examine both the laboratory and field data from the Gulf Coast in the context of a Global Basin Research Network (GBRN), an interdisciplinary and interinstitutional effort. The purpose of the network is to better understand subsurface fluid flow processes over geologic time in sedimentary basins and their relation to resource accumulation (ie, petroleum and metal ores). Progress to date is described in Section E.

4. RESULTS AND DISCUSSION

A. Summary - Louisiana Gulf Coast - E. Cameron well

i) One-dimensional maturation modeling results

One-dimensional well modeling has been completed on the E. Cameron well in collaborative work with A Yukler (Yukler and Kokesh, 1984). Results provide an over-all interpretational framework which can be tested against the downhole geochemical data (Johnson and Whelan, submitted; Whelan et al, submitted; Whelan, et al, 1984).

Model results show that the sedimentation at the E. Cameron Well No. 1 took place in a shallow water environment, generally less than 150ft, with the deepest water of 400 ft occurring during the Early Miocene (Fig A1). Temperatures at the sediment/water interface ranged from 60 to 71 °F, as a function of paleoclimate and water depth. The optimized heat

flow values were 0.9 HFU from the Oligocene to Pliocene and increased slightly during the last 4 ma reaching 0.95 at the present (Fig A1).

Computed subsidence history at the well shows the basin has continuously subsided and has not experienced uplift or erosion (Fig A2).

Computed excess pressure versus depth at present shows that the well is normally pressured to 6800 ft with a rapid increase below this depth and with the highest excess pore pressures from 11,000 ft to the bottom of the well (Fig A3 and A4).

Computed temperatures at the well show that the geothermal gradient is high down to a depth of 2500 ft with generally lower from 2500 ft down to TD (Fig A5). The good match between the computed and measured temperatures shows that the optimized sediment types (and mineralogic compositions) and resulting calculated heat flow values during the Pleistocene are probably correct. Computed temperature histories at the base of the well in Zones K and A are shown in Fig A6. The optimized temperature histories as a function of the geologic evolution of the basin at the well site and the heat flow distribution resulted in a very good match between computed and measured vitrinite reflectance values (Fig A5). Computed sterane isomerization values predict that equilibrium should have been reached at about 15,000 ft (Fig A7). However, many steranes including the C20 R and S isomers of 5a(H), 14a(H)17a(H)-C29 steranes are either missing or present in such low concentrations that the %20S/(20R-&20S-) sterane ratios could not be calculated to test the model predictions.

The computed hydrocarbon generation, assuming Type II kerogen, versus depth trend shows that the active oil generation zone is from 13,000 to 15,000 ft with the peak oil generation zone at about 15,000ft(Fig A8). The model shows the gas/condensate generation zone to be from 15,000ft to the bottom of the well. Due to high heating rates at the well, the peak petroleum generation zone occurs at fairly low maturity - about 0.65 %Ro for oil and from 0.7 to about 0.9%Ro for condensate. The model results show a good match to the experimental data in figure A12a (from Whelan, 1984) with peak levels of C2-C16 hydrocarbons occurring from about 3800 to 5000m (12,500 to 16,400 ft). However, the peak generation zones are roughly the same for lighter (C2-C5) and heavier alkanes (C8-C16, Fig A12) with no distinction observed for peak generation zones of lighter versus heavier hydrocarbons, as predicted by the model.

Computed hydrocarbon generation at the base of the well shows that active oil generation started at 7.5 mabp reaching the peak oil generation at about 3mabp (Fig A9). At the base of Zone K, active condensate generation is predicted to have occurred during the last 3ma; main oil generation started at about 2mabp with peak oil generation now

having been reached (Fig A10). The model shows that early oil generation has now been reached at the base of Zone A (Fig. A11).

A rapid oil generation rate (as a result of high heating rate) could have led to high expulsion efficiencies if an adequate amount of good organic matter existed within the sediments. However, because of the moderately low to marginal source rock quality (Whelan, et al, 1988b; Whelan, et al, submitted), current theories of oil migration predict low expulsion efficiencies. Based on experience with other wells, most of the generated oil would be expected to remain in the source rock. Based on current theories of oil migration (eg, Durand, 1988; Hunt, 1979), primary expulsion would not be expected until the generation of sufficient quantities of gas or condensates had occurred to aid in migration. The apparent co-generation of condensates and oil (Fig A12A) might explain the preferential expulsion of lighter hydrocarbons throughout the oil window (Whelan, et al, 1984). The model results and well data both show apparent preferential retention of heavier hydrocarbons in shale intervals. Therefore, the down-hole profiles of ratios of heavier extractable hydrocarbons from this well may be useful in showing the maturation response of some typical bitumen ratios in the absence of migration effects.

The heat flow pattern found at the E. Cameron well No. 1 is similar to that obtained previously for the San Marcos Arch area in Texas (Fig A12b; Yukler and Dow, unpublished results).

ii) Bitumen extraction data (EI-GCMS results).

Biomarker and extractable aromatic compound analyses were completed for the E. Cameron Well No. 1 and were found to be consistent the one-dimensional well modeling described above. The ratio of tri- to (tri- plus mono-) aromatic steranes versus depth is shown in Fig A13. The concentrations of these compounds were too low to measure by conventional GC-MS mass scan procedures. Therefore, these measurements were carried out by chemical ionization gas chromatography mass spectrometry using isobutane as reactant gas (CI-IB-GCMS), as described in Johnson and Whelan (submitted) and in our last DoE report (Whelan, et al, 1988b). The concentrations of these compounds were so low that we are not sure of the reliability of the measurements. However, a fairly smooth trend is observed for the well which gives us some confidence that the general pattern (if not the precise numbers) are correct. An interesting reversal can be seen below 12,000ft, in the Ro range of <0.5%. Such a reversal would be consistent with conversion of mono- to tri- aromatic steranes at very low maturations, followed by preferential destruction of the triaromatic sterane in higher maturity section. Based on the low amounts

of hydrocarbons present, there is no evidence for selective migration of these somewhat polar and higher molecular weight compounds out of the formation. A similar reversal has been observed by Whelan, et al, (1988 and in preparation) and Johnson & Whelan, submitted, in the Alaskan North Slope, as shown in Fig B2.

Other ratios of alkyl aromatic compounds which have been previously used as maturation ratios (Radke, 1988) are shown for the same well in Figs A14 (alkyl naphthalenes) and Fig A15 (methyl phenanthrenes). None of these shows a simple pattern, consistent with the vitrinite reflectance data. The alkylnaphthalene ratios all show a general decrease with depth to about 15,000ft, followed by an abrupt increase in the two deepest sections. Graphs of the methylphenanthrene ratio, dimethylphenanthrene index, methyl phenanthrene index1, and methylphenanthrene index 2 (calculated from GCMS mass scans according to the definitions in Radke, 1988) show that there is an increase with depth in the top two samples. However, none of the alkyl phenanthrene ratios shows any consistent trend with depth below 12,000ft.

It is possible that catalytic effects are responsible for these results in these highly terrigenous relatively organic lean sediments (TOC typically 0.5 to 1%) containing a mixed Type II/III kerogen (Whelan et al, 1988 and submitted). Thus, if one or more isomers were being generated or decomposed selectively within a particular thermal range, then an erratic pattern of ratios of isomers with depth, such as observed here, might be expected. Consistent with this hypothesis is the observation that the py-GC pattern of the organic matter in the well changes dramatically at a depth of about 14500 to 15000 and again from 15500 ft to the bottom of this well (Whelan, et al, 1984). The results show that changes in minerals and kerogens may influence these ratios, so that caution should be used in their application.

iii) TG-FTIR results

On the basis of previous work (Whelan, et al., 1988), it was suggested that Thermogravimetric Fourier Transform Infrared analysis (TG-FTIR) of petroleum source rocks and kerogen might be valuable in: 1) looking at the degree of maturation throughout both the oil and gas generation zones; 2) examining the degree of maturation of inorganic as well as organic facies; and 3) providing information on depositional environment. A manuscript (Whelan, et al, in press) describes further experiments regarding points 1 and 2 on isolated kerogens covering a wide maturity range ($R_o = 0.46$ to 5.32%). Some of the principal results from that paper are reported here.

It was found in previous work (Whelan, et al, 1988) that the T_{max} values for evolution of both methane and ammonia in whole rocks could be followed up to maturities of about $R_o=2\%$. Therefore, two sets of samples were selected for the current study which appeared to cover two fairly homogeneous rock sequences containing kerogens extending into high maturation ranges (maximum R_o of 3.8% and 5.32% for the two sample sets). Isolated kerogens were analyzed, rather than whole rocks as done previously (Whelan, et al., 1988), in order to minimize interferences of the mineral matrix with the pyrolysis measurements.

Samples and Methods

Samples consisted of: a) kerogens isolated from the predominantly terrigenous Wilcox shales, Texas Gulf Coast and b) kerogens isolated from the Belden Shale from N.W. Colorado, a Pennsylvanian predominantly marine shale. Based on microscopic analysis, the Belden is predominantly a spent oil source rock with 80 to 90% high rank amorphous kerogen. The Belden samples were obtained primarily from outcrops which appeared visually to be unaltered, but which may have undergone some minor surface weathering. The Wilcox samples contain about 50:50 terrigenous:marine kerogen and were obtained from cores. Results are compared with those from whole rocks from the Alaskan North Slope Seabee well, described in detail in Whelan, et al., 1986 and 1988 and refs. cited. Tables A2 and A3 from Whelan, et al, in press, show the data resulting from the study.

The principal findings regarding TG-FTIR analyses of the kerogens from the Wilcox and Belden shales are:

- 1) T_{max} of ethylene shows a good correlation with $\%R_o$ for the more terrigenous Wilcox kerogens (Fig A16).
- 2) Surprisingly, the more terrigenous Wilcox shale shows a higher percentage of combustible sulfur than the more marine Colorado kerogen (Fig A17).
- 3) Carbon dioxide produced by pyrolysis evolved in several peaks, referred to as P1 through P6 in order of increasing T_{max} (Table A2). T_{max} values for three of the CO_2 peaks, P4 through P6, are plotted versus R_o in Figure A18. In most cases, T_{max} was independent of maturity, as exemplified by P6 W (Wilcox), in Fig A18. However, T_{max} for P5 for the marine Belden Shale (P5 C in Fig A18) showed a smooth increase with maturity up to R_o =about 2.5%. The high temperature peaks ($T_{max} > 550^\circ C$) constitute a significant proportion of the CO_2 evolved during the analysis of a number of these kerogens (Table A2). Because the samples have been demineralized by treatment with acid during kerogen preparation, it is presumed that the bulk of the "high temperature" CO_2 must be coming from the organic

(rather than the residual mineral) matrix. Demineralized Argonne Premium Coal Samples also show similar high temperature CO₂ peaks which do not appear to be coming from any common mineral carbonate (e.g., calcite or siderite, Solomon, et al., 1990). Possible sources of high temperature CO₂ and CO from the organic matrix include thermal decomposition of phenolic, quinones or heterocyclic groups, with associated oxygen transfer in the case of CO₂ generation (see Solomon et al., 1990, and refs. cited).

- 4) The Wilcox kerogens produce almost no pyrolyzable carbon dioxide below 480°C, except for the lowest maturity sample (Ro=0.46%) while, the Colorado kerogens give up a significant proportion of pyrolyzable carbon dioxide at temperatures below 450°C (Table A2). Source rocks, particularly those containing Type III kerogen, generally produce significant quantities of CO₂ just above the oil window during maturation (e.g. Jenden, 1983). The TG-FTIR peak 2 CO₂ evolves at Tmax's less than those of tar peak 3 (roughly comparable to Rock Eval S2) and, therefore, may be providing a relative measure of this "pre-oil window" CO₂ generation potential.
- 5) Tmax of ammonia for these isolated kerogens (Table A2) stayed fairly constant and showed no correlation with vitrinite reflectance, as found previously for whole rock samples (Whelan, et al, 1988a). The amounts of pyrolyzable ammonia were about the same as previously found for the whole rocks, but Tmax values were about 100 to 200 °C lower for these isolated kerogens. These findings are consistent with an inorganic, clay source of pyrolyzable ammonia in whole rocks measured previously (Whelan, et al., 1988). The whole-rock mineral-derived ammonia (in contrast to the kerogen-derived ammonia measured in this work) was found to show an increasing Tmax with increasing sample maturity, potentially useful as a mineral (rather than a kerogen) maturity indicator.
- 6) A graph of mg pyrolyzable CO₂/g TOC versus mg pyrolyzable CO/g TOC showed a general correlation between the two parameters (Fig A19, using data from Table A2), in spite of probable different chemical sources for the two gases. Values of both parameters tended to be somewhat higher for the Colorado than for the Wilcox kerogens, possibly due to some effects of weathering in the former case. Neither parameter showed any clear trend with increasing maturation for either set of kerogens.
- 7) Kerogen typing was carried out using HI vs OI plots similar to those used for Rock Eval analysis (Fig A20; Table A2). Tar and methane HI values are plotted separately to reflect both oil and gas generation potential. Because of the large

range of values, it was found more convenient to plot the data on a log-log scale (Fig A21). All of the data needed for the calculation was obtainable using only the TG-FTIR data. For example, the TOC was calculated by summing the weight percentages of all pyrolyzable and combustible carbon evolved during TG-FTIR analysis.

- 8) Tmax of methane, as measured by TG-FTIR, correlates with vitrinite reflectance for two sets of isolated kerogens. Results are comparable to those previously obtained for whole rocks from the Alaskan North Slope Seabee well (Fig A22). Other miscellaneous data, shown by the stars in Fig A22, represents one low maturity E. Cameron kerogen and two additional isolated kerogens from the Inigok well in the Alaskan North Slope. For the isolated kerogens, it was possible to measure Tmax of methane up to a maximum vitrinite reflectance value of 3.96%. A much broader and weaker methane pyrolysis peak was observed for one kerogen sample of Ro=5.32%.
- 9) Tmax of methane could be directly measured on samples contaminated with migrated bitumen, causing an anomalously low Tmax for the tar so that the Tmax of the tar could not be used as a maturation indicator (Table A2).
- 10) A dip in the Tmax methane versus %Ro curves occurs at about Ro=2% and is clearly observable for both the Alaskan whole rock samples and the Colorado isolated kerogens. Therefore, we are assuming that the effect is real and may be due to a phase change similar to that observed for coals. An abrupt molecular aggregation of small aromatic stacks into clusters occurs for coals in the maturity range of Rm = 1.8 to 2.0% (Stach, et al., 1982). The "dip" could also be caused by an anisotropy effect observed in kerogens having vitrinite reflectance values over 2%, proposed to be caused by the effects of pressure, in addition to time and temperature (Durand, et al., 1986).
- 11) The ratio of pyrolyzable to combustible sulfur (Fig A23; Table A2) gave a clear distinction between the more terrigenous Wilcox kerogens (values of 0.07 to 0.33) and the more marine Colorado kerogens (values of 0.49 to 1.12). This parameter was independent of maturity for these two sets of kerogens.

TG-FTIR analyses have also been obtained for a downhole series of kerogens from the E. Cameron well, as shown in Figs A24 - A31. Figure A24 shows the typical output for pyrograms of individual gases. Both the tar and methane peaks are relatively strong in this sample from 12230 to 12320ft, which is above the oil window. Figure A25 shows downhole profiles of tar yield (ie, all compounds showing strong C-H IR bands, other than methane.) The presence of an S1 peak, representative of generated oil, is apparent in the

14300-14390 and 14600 ft samples, within the oil window. By 15290 ft going into the zone below the oil window, the S2 peak is much weaker and no S1 peak is observable. At 17000 ft, a series of weak tar peaks can be observed, possibly from residual pyrobitumen remaining in the sample below the oil window. Fig A26 shows the downhole profile for pyrolyzable methane, which can be observed at all depths. The increase of Tmax in going downhole to higher maturities is also apparent.

Profiles for CO₂ and CO, shown in Figs A27 & A28, show no particular trends with increasing maturity, except for a possible shift of the broad complex peaks to higher temperatures with increasing maturities. Curves for H₂O, COS (Fig A29), ethylene, CS₂ (Fig A30), and ammonia (Fig A31) remain fairly constant with increasing depth. The constant Tmax observed for ammonia is consistent with observations for the Wilcox and Colorado kerogens (see above) that Tmax of ammonia does not increase with maturation in isolated kerogens. The increase is observed only for some whole rocks subjected to increasing maturation, such as those from the Alaskan North Slope (Whelan, et al, 1988).

Some interesting changes seem to be occurring in SO₂ with depth (Fig A31), with the signal becoming less complex and the lower temperature peak becoming smaller with increasing maturity. It also appears that there may be a slight shift in the Tmax of the largest SO₂ peak with increasing sample maturity.

Figure A32 shows a plot of $\ln(k)$ versus $1/T_m$ for an immature kerogen from the E. Cameron well heated at several different rates via TG-FTIR. The resulting calculated activation energy for kerogen to tar (oil) evolution (56.13 kcal/mole or 235 kJ/mole) is also shown. This value is high, but is in roughly the range estimated by others for type II or III kerogens (218.3 kJ/mole) for the Type II Woodford Shale (Lewan, 1985; values for other shales summarized recently by Hunt et al, in press).

B. Summary - Alaskan North Slope

i) Ikpikpuk - Torok formation biomarkers

Samples of the Torok formation of the Ikpikpuk well (of poorer source rock quality and more terrigenous than deeper sections) were extracted and the resulting data is plotted together with that for the deeper intervals reported previously (Farrington, et al, 1988) in Figs B1-B4. The nC17/nC18 ratios are very similar for the Torok and the underlying Kingak and Shublik formations, except for one anomalously high value at 4000ft. The Pristane/nC17 ratio is much higher in the Torok than in any of the deeper formations, including those for the Sag/Shublik (Fig B1) which showed values about two times

Figure A1: E. Cameron well No. 1 - Paleowater depths, temperatures at sediment/water interface and optimized heat flow values for input into model

Figure A2: E. Cameroon well No.1 - Computed subsidence history; tops of various time horizons located from well-logs and paleontology are shown.

Figure A4: E. Cameron well No. 1 - Computed excess pressure history at the base of the Zone K (see Fig A2)

Figure A3: E. Cameron well No. 1 - Computed excess pressure and porosity versus depth trends.

Figure A6: E. Cameron well No. 1 - Computed temperature histories at the base of the well. Zone K and Zone A (see Fig A2)

Figure A7: E. Cameron well No. 1 - Computed vitrinite reflectance and sterane isomerization ratios versus depth trends

Figure A8: E. Cameron well No. 1 - Computed hydrocarbon generation versus depth trend

Figure A9: E. Cameron well No. 1 - Computed hydrocarbon generation history at the base of the well

Figure A10: E. Cameron well No. 1 - Computed hydrocarbon generation history at the base of Zone K (Fig A2).

Figure A11: E. Cameroon well No. 1 - Computed hydrocarbon generation history at the base of Zone A (Fig A2).

Figure A13: East Cameron well, ratio of tri- to (tri- plus mono-) aromatic steranes versus depth, as determined by chemical ionization gas chromatography mass spectroscopy using isobutane as reactant gas (CI-IB-GCMS).

Figure A14: East Cameron well, plots of methyl naphthalene ratio (MNR), ethyl naphthalene ratio (ENR), and dimethyl naphthalene (DNR) ratios versus depth.

Figure A15: East Cameron well, plots of methyl phenanthrene ratio (MPR), dimethyl phenanthrene index (DPI), methyl phenanthrene index 1 (MPI 1) and methyl phenanthrene index 2 (MPI 2) versus depth.

Figure A16: TG-FTIR data, isolated kerogens, Tmax ethylene versus % vitrinite reflectance (Ro) for, terrigenous Wilcox formation, Texas Gulf Coast, and marine N.W. Colorado, Belden Shale.

Fig. 9a

Fig. 9b

Figure A17: TG-FTIR data, isolated kerogens, wt % SO₂ evolution in low temperature (P1) through high temperature (P6) peaks and combustion peak (SO₂ comb). Same samples as in A 16; C=Colorado and W = Wilcox.

Figure A18: TG-FTIR data, isolated kerogens, Tmax CO₂ peaks. Same samples and symbols as in Figs A16 & A17.

Figure A19: TG-FTIR data, isolated kerogens, mg CO/g TOC versus mg CO₂/g TOC. Same samples and symbols as in Figs A16 & A17.

Figure A20: TG-FTIR data, isolated kerogens, hydrogen index vs oxygen index, same samples and symbols as in Figs A16 & A17.

Figure A21: TG-FTIR data, isolated kerogens, hydrogen index vs oxygen index, log-log plot. Same samples and symbols as in Figs A16 & A17.

Figure A22: TG-FTIR data, T_{max} methane, whole rocks and kerogens, combined data examined to date.

Figure A23: TG-FTIR data, isolate kerogens, pyrolysis sulfur/combustible sulfur vs Ro. Colorado (marine) kerogens vs Wilcox (terrigenous) kerogens.

TG-FTIR ANALYSIS OF EAST CAMERON (12230-12320 ft.) KEROGEN DURING THE PYROLYSIS CYCLE

Figure A24: TG-FTIR data, isolated kerogen, summary of all data for

Figure A25: TG-FTIR data, Isolated kerogens, E. Cameron well, downhole profile, tar pyrograms.

Figure A26: TG-FTIR data, Isolated kerogens, E. Cameron well, downhole profile, methane.

Figure A27: TG-FTIR data, Isolated kerogens, E. Cameron well, downhole profile, carbon dioxide.

Figure A28: TG-FTIR data, isolated kerogens, E. Cameron well, downhole profile, carbon monoxide.

Figure A29: TG-FTIR data, isolated kerogens, E. Cameron well, downhole profile, COS and H₂O.

Figure A30: TG-FTIR data, isolated kerogens, E. Cameron well, downhole profile, Ethylene and CS_2 evolution.

Figure A31: TG-FTIR data, isolated kerogens, E. Cameron well, downhole profile, NH_3 and SO_2 evolution.

Figure A32: TG-FTIR data, isolated kerogens, E. Cameron well, downhole profile, kinetic calculations for tar evolution.

East Cameron Well, Louisiana Gulf Coast

Depth (Feet)	MNR	ENR	DNR	DPI	MPI1	MPI2
6830	1.97			.22	.56	.75
9890	1.38	3.64	6.13	.62	.85	.89
12230	1.36	3.88	5.11	.45	.74	.81
14300	1.28	2.88	4.77	.41	.65	.71
14600	1.10	2.55	4.78	.36	.60	.63
15290	1.35	2.23	5.71	.46	.71	.69
15740	1.86	4.58	9.06	.51	.96	1.06
17000	1.57	4.29	8.48	.31	.66	.70

Ikpikpuk Well, Alaskan North Slope

Depth (Feet)	MNR	ENR	DNR	DPI	MPI 1	MPI 2
3890	1.22	2.85	2.66	0.25	0.68	0.73
5270	1.36	2.98	2.82	0.26	0.53	0.54
5630	1.36	2.99	2.84	0.23	0.46	0.48
6170	1.02	0.98	1.33	0.23	0.48	0.49
6470	0.85	1.44	1.70	0.18	0.53	0.55
7460	0.96	1.73	3.37	0.70	0.65	0.72
7700	1.31	2.72	3.60	0.74	0.68	0.76
8000	1.00	1.90	3.29	0.77	0.68	0.74
8300	1.13	2.61	4.19	0.70	0.70	0.78
8600	1.14	2.40	4.03	0.78	0.72	0.79
8900	1.10	3.28	3.83	0.77	0.77	0.84
9200	1.65	3.15	5.01	0.77	0.81	0.91
9500	0.94	3.30	5.17	0.95	0.91	1.05
9800	1.52		5.54	1.05	1.06	1.28
9950	1.27	2.05	4.80	0.93	0.77	0.85
10010	1.29	2.11	4.82	0.92	0.81	0.97
10280	1.08	2.18	4.69	1.01	0.98	1.09
10320	1.27	2.59	4.39	1.03	1.03	1.28
10820	1.58	2.57	5.49	1.39	1.16	1.42
11210	0.99	3.04	4.03	1.18	1.20	1.42
11420	1.16		3.07	1.05	1.17	1.50

Table A1: Maturation indices for E. Cameron Well (Louisiana Gulf Coast) and Torok formation of Ikpiuk well (Alaskan North Slope)

Table A2: TG-FTIR data, methane, tars and ethylene (pyrolysis)

Sample %Ro	Methane				Tars				Ethylene		
	Peak 1		Peak 2		Peak 1		Peak 2		Peak 3		P.L. (IG+)
	Tmax	Wt%	Tmax	Wt%	Tmax	Wt%	Tmax	Wt%	Tmax	Wt%	
Willcox											
0.46	570	0.18					230	1.34	530	5.07	0.21
0.59	570	0.14					280	0.52	545	1.42	0.27
0.69	640	0.46					320	1.28	560	4.72	0.21
1.48	675	0.27					360	1.13	540	0.03	0.97
2.21	690	0.05					225 to 430			0.70	
3.96	430 to 910	0.04			175	0.53	375	4.70			
5.32	530 to 910	0.08			300 to 500		340	2.62			
Colorado											
0.90	530	1.25	610	0.52	175	1.50	no peak		460	56.50	0.03
1.40	650	0.51			175	2.50	240	7.80	475	6.50	0.61
1.80	622	0.01			310	1.10			485	2.05	0.35
1.80	610 9.00E-03				270	0.36	360	0.49	480	0.35	0.71
2.00	630 9.00E-03		910	1.10E-02	no peak				no peak		
2.00	630	0.01			no peak				no peak		
2.40	no data				no data				no peak		
2.40	700	0.03				0.00			no peak		
2.80	630 to 730 2.40E-02				270	0.32			no peak		
3.80	480 to 600	0.01	855	0.01		0.00			no peak		

Table A2 (cont): TG-FTIR data, ammonia

Sample %Ro	NH3 (pyrolysis)													
	Peak 1		Peak 2		Peak 3		Peak 4		Peak 5		Peak 6		Peak 7	
	Tmax	wt%	Tmax	wt%	Tmax	wt%	Tmax	wt%	Tmax	wt%	Tmax	wt%	Tmax	wt%
Wilcox														
0.46					400	0.83	570	0.02			770	0.01		
0.59					420	0.91	no peak				700	0.08		
0.69					465	1.14	no peak		no peak					
1.48					450	1.32	no peak							
2.21					460	1.07	no peak						910	0.08
3.96					470	2.77							900	0.25
5.32					450	3.65					770	0.08	850	0.09
Colorado														
0.90	170	0.11			390	0.77	560	0.19	615 to 670	0.07	740	0.03		
1.40					435	0.15								
1.80			405	0.50	430	0.04	595	0.03						
1.80			390	0.55										
2.00			190	1.50E-02	405	0.17	510-600	0.14						
2.00	175	0.01	270	7.00E-03	420	0.17	560	4.20E-02						
2.40	175	0.02	260	0.02	390	0.33	430	0.07	490	0.03				
2.40					380	0.41	580	0.02						
2.80	235	0.02			430	0.39	520	0.05	610	0.04				
3.80	100	0.03			415	1.02	500	0.08						

Table A2 (cont): TG-FTIR data, carbon monoxide

Sample %Ro	CO (pyrolysis)						(combustion)	
	Peak 1 Tmax	wt%	Peak 2 Tmax	wt%	Peak 3 Tmax	wt%	Peak 4 Tmax	wt%
Wilcox								
0.46					(Broad):		900	2.10
0.59					(Broad):		850	1.91
0.69			425	0.1	(Broad):		905	2.96
1.48			500	0.12	(broad):		910	1.16
2.21			505	0.20	(broad):		870	2.80
3.96			530	0.02			900	0.93
5.32			505	0.09	570	0.07	910	2.24
Colorado								
0.90			460	0.80	670	0.60	830	2.90
1.40			500	0.70	730	2.70	910	1.60
1.80	335	0.02	490	0.25	540	0.32	705	1.42
1.80				480 to 770		0.85	910	0.95
2.00			(broad:)		720	1.12		
2.00	365	0.05			715	1.12	910	1.62
2.40			580	1.20	720	1.20	910	2.10
2.40			no peak		690	1.60	910	2.20
2.80			430 to 910		760	0.90		
3.80	385	0.01	500	0.05	875	1.25	weak broad peak	0.31

Table A2 (cont): TG-FTIR data: Carbon dioxide

Sample %Ro	(Combustion)									
	Peak 1 Tmax	Peak 2 Tmax	Peak 3 Tmax	Peak 4 Tmax	Peak 5 Tmax	Peak 6 Tmax	wt%	wt%	wt%	wt%
Wilcox										
0.46		330 0.04	500 0.35	695 0.58		910	0.12			5.72
0.59		Broad (230 to 850)					0.90			5.42
0.69			500 0.26	695 0.53		910	0.20			10.4
1.48			490 0.47	660 0.47		910	0.60			9.3
2.21			495 0.35		870 0.40					8
3.96			480 0.39	660 1.30	0.66					10.2
5.32			480 0.78	730 0.65		910	0.26			21.1
Colorado										
0.90	175	0.12	330 0.50	400 1.00		700 1.12	860	0.75		
1.40		360 1.00	490 1.75	640 1.12	740 1.00	910	0.20			25
1.80	210 7.50E-02	360 0.45	525 2.10							5.8
1.80		340 0.32	480 0.71							6.6
2.00	210 3.50E-02	360 0.31	460 0.37	600 to 800 0.15						4
2.00	260 7.50E-02	370 0.28	460 0.58	500 to 800 1.15	800 0.35	910 7.50E-02				3.15
2.40		430 1.20	545 2.20			900	0.20			9.7
2.40		445 1.20	530 0.70		870 0.01					6.5
2.80			*460-590	0.60						13.8
3.80	broad	0.08	360 0.38	640 1.10						2

Table A2 (cont): TG-FTIR data, sulfur dioxide

Sample %S ₂ O	(pyrolysis)										(combustion)	
	Peak 1		Peak 2		Peak 3		Peak 4		Peak 5		Peak 6	
	Tmax	wt%	Tmax	wt%	Tmax	wt%	Tmax	wt%	Tmax	wt%	Tmax	wt%
Wilcox												
0.46			360	0.10					610	0.14	900	0.27
0.59			360	0.18					490 to 580	0.12	910	0.09
0.69			390	0.16			500	0.14		615	0.14	
1.48	175	0.10	390	0.17			570	0.76		617	0.89	
2.21	175	0.02	360	0.15			530	0.34		577	0.50	
3.96										597	1.80	
5.32			330	0.31						620	5.62	
Colorado												
0.90	175	0.10	400	0.45						590	0.45	900 0.25
1.40					330	0.25	530	1.15				1.02
1.80	175	0.04	280	0.06			480	0.06				0.08
1.80	175	0.04	280	0.06			500	0.04				0.09
2.00	175	4.50E-02	320	0.08			510	0.13				0.26
2.00	175	3.50E-02	290	0.10			480	0.26		670	0.01	0.18
2.40	175	0.06	250	0.04			510	0.22		790	0.02	910 0.06
2.40	175	0.03	240	0.04	350	0.03	510	0.07				0.18
					365	0.07	500	0.07				
2.80	175	0.04	260-	0.06			500	0.09				0.1
3.80	175	0.04	290	0.07			480	0.18				0.13

Table A2 (cont): TG-FTIR data, water

Sample %Bo										
	Peak 1 Tmax wt%	Peak 2 Tmax wt%	Peak 3 Tmax wt%	Peak 4 Tmax wt%	Peak 5 Tmax wt%					
Wilcox										
0.46	150 1.91	247 1.86								
0.59	175 1.87	265 1.77		570 0.45	760 0.13					
0.69	175 5.70	275 6.60		610 1.02						
1.48	175 7.90	280 4.80								
2.21	175 3.00	330 12.70			810 2.90					
3.96	175 5.80	210 8.43		625 0.33						
5.32	175 3.28	260 3.32		620 0.44						
Colorado										
0.90	175 1.80	220 1.10	305 0.67	470 3.60	830 1.10					
1.40	175 2.40	260 3.80		525 2.20	865 1.60					
1.80	175 6.00	260 5.90	390 0.50	>430 0.60						
1.80	175 7.50	260 9.20			900 0.40					
2.00	175 9.75	260 10.90								
2.00	175 6.30	265 11.00								
2.40	175 6.90	230 4.70								
2.40	170 8.50	260 6.60			890 0.65					
2.80	175 4.60	240 6.00								
3.80	175 5.50	285 9.50								

Table A3: TG-FTIR data, kerogens, selected Ratios

Sample %Ro											
	%TOC (TG-FTIR)	Tar index: mg P3 Tar/ gTOC	Tar + Bit index: mg P2+P3 tar/ gTOC	gas index: mg CH4/ g TOC	CO2 index: mg CO2/gTOC (<600°C)	CO2 index: mg CO2/gTOC (total)	CO index: mg CO/gTOC (<600°C)	CO index: mg CO/gTOC (total)	Pyr	S/comb	S (TG+)
Wilcox											
0.46	14.43	351.42	444.30	12.48	27.03	75.55	0.00	145.56			0.13
0.59	9.63	147.46	201.46	14.54	77.89	171.35	0.00	198.35			0.07
0.69	20.01	235.87	299.83	22.99	12.99	49.47	5.00	152.91			0.03
1.48	12.87	2.33	90.16	20.99	36.53	119.70	9.33	99.49			0.33
2.21	11.26	62.17	62.17	4.44	31.08	66.61	17.76	266.42			0.22
3.96	17.34	0.00	271.00	2.02	22.49	135.50	1.15	54.78			0.21
5.32	27.12	0.00	96.60	2.95	28.76	62.31	5.90	88.49			0.31
Colorado											
0.90	62.26	907.42	907.42	28.43	24.09	56.05	12.85	69.06			
1.40	54.74	118.75	261.26	9.32	50.24	92.63	12.79	91.35			0.69
1.80	11.39	180.02	180.02	0.88	223.93	230.52	23.71	176.51			1.00
1.80	9.64	36.30	87.12	0.93	106.83	106.83	0.00	186.70			0.75
2.00	1.13	0.00	0.00	17.72	602.46	766.37	0.00	992.29			0.49
2.00	1.84	0.00	0.00	5.42	466.44	1361.34	27.12	1513.21			1.13
2.40	3.42	0.00	0.00	0.00	994.72	1053.23	351.08	1316.54			0.90
2.40	2.50	0.00	0.00	12.78	758.54	762.53	0.00	1517.08			0.58
2.80	2.29	0.00	0.00	10.48	0.00	262.07	0.00	393.10			0.95
3.80	0.97	0.00	0.00	24.64	1519.67	1601.81	61.61	1345.11			1.12

higher than those for the Kingak and Sadlerochit formations. If only maturation were affecting this ratio, a decrease with depth would be expected, as observed from 5500 and 8000 ft, an interval which includes both the Torok and the top of the underlying Kingak. The phytane/nC18 ratio is low in the Torok (< 0.5) and increases to values of 4 to 12 within the Kingak and Shublik. This is not a trend typical of increasing maturation. It would be consistent with preferential migration of the straight chain nC18 out of the bottom of the Kingak. The pristane/phytane ratios (Fig B1) are very formation dependent. In fact all the ratios in Fig B1 show some difference between the more terrigenous Torok and the more marine Kingak formation.

The complete profile of tri- to (tri- plus mono-) aromatic steranes versus depth for the Ikpikpuk well is shown in Fig B2. These ratios were determined by the CI-IB-GCMS method (Johnson and Whelan, submitted) - the same method used above for obtaining similar ratios for E. Cameron. The ratio increases smoothly with increasing depth and maturation within the Torok formation. In deeper intervals, the ratio becomes noisier and decreases, particularly within the Shublik formation. This decrease was discussed in detail and tentatively attributed to migrational effects in our past DoE report (Whelan, et al, 1988b). This hypothesis is supported by additional petrographic work carried out here (section B11). Alternatively, the reversal could also be due to selective destruction of the triaromatic steranes in the deeper hotter formations.

Various alkyl naphthalene ratios are shown in Fig B3. The methyl naphthalene ratio shows considerable noise. The ethyl naphthalene ratio (ENR) shows a fairly smooth increase in the Kingak, as discussed previously (Farrington, et al, 1988). The trend continues upward into the lower 6000 to 6500 ft interval of the more terrigenous Torok formation. However, much higher values in the 4000 to 6000 ft depth interval, suggesting that this ratio is strongly dependent on the exact nature source organic matter, particularly in more terrigenous intervals. Similar arguments apply to the dimethyl naphthalene ratio, also shown in Fig B3.

The alkyl phenanthrene indeces, MPI 1 and MPI 2, show the smoothest changes with increasing maturation and the least dependence on formation (Fig B4). In both cases, trends previously observed for the Kingak (Farrington, et al, 1988) continue upward into the Torok. The decreases in both ratios at the top of the Shublik are probably due to migrational effects discussed in detail previously (Whelan, et al, 1988b and in preparation). The dimethyl phenanthrene index appears to be more formation dependent, with values consistently being about four times lower (and fairly constant) in the Torok in comparison to the Kingak formation.

11) Ikpikpuk - kerogen - organic petrographic results

Previous reports on the Alaskan North Slope Ikpikpuk well have shown a good maturation sequence covering all of the oil and gas generation zones (maximum $R_o = 2.5\%$) and penetrating many of the important regional formations (Bird, 1985; Magoon and Claypool, 1985; Whelan, et al, 1986). Because of uplift in the Cretaceous and subsequent erosion, many wells in this area south of Prudhoe Bay penetrate only highly overmature sections of potential Prudhoe Bay source rocks. At the Ikpikpuk well, modeling results and downhole organic geochemical profiles showed that two of the most probable source rocks of the Prudhoe Bay oil were the Kingak Shale and the underlying Shublik formation which were within and just below the oil window, respectively, prior to regional uplift and erosion (Whelan, et al, 1988b; and in preparation). Previous measurements of maturation based on vitrinite reflectance show an increase in maturation in going from the bottom of the Kingak into the top of the Shublik Formation (Whelan, et al, 1986). However, a variety of organic geochemical maturation indicators, including methyl phenanthrene indices and mono to (mono + triaromatic) sterane ratios reflect an apparent drop in maturity of bitumens in the interval between the two formations (eg, Fig B4).

It was previously postulated (Whelan, et al, 1987) that this discrepancy might be due to migrational effects (Whelan, et al, 1986; Farrington, et al, 1988; Whelan et al, 1987). In order to gain further information regarding this point, detailed organic petrographic analyses were carried out on the Ikpikpuk well, concentrating on deeper sections of the Kingak and underlying formations.

Ten cuttings samples were examined using reflected and fluorescence light microscopy techniques over the depth interval 9,500 - 11,730 ft. in this well. Reflectance measurements were obtained using a Leitz MPV 3 microscope system fitted with a x50 oil immersion objective and a 5 μ measuring diaphragm. Fluorescence observations were made on a Zeiss axiophot microscope fitted with a x40 oil immersion objective, a x1.25 ocular magnification, and an LP520 BP450 -490 filter set.

JURASSIC (? - 9,905 ft.)

Kingak Shale (? - 9,845 ")

The upper two samples (9,500 ft., 9,800 ft. near the bottom of the Kingak shale) are microlaminated, calcareous shales and have a moderate to high organic content. The organic material is dominated by micrinite, a residual product of bitumen after oil generation (50%) and Inertinite (35 %) with significant vitrinite (15%). Bitumen staining throughout both samples is strong and indicates significant hydrocarbon migration through this sediments.

In fluorescence light there is a high liptinite content comprised of spores (60%) and algal remains (40%) at 9,500 ft. The spores fluoresce a light to mid orange colour with a moderate intensity. By 9,800 ft hydrogen rich macerals are less abundant (low) and this material is primarily comprised of scattered algal fragments which fluoresce a light to mid orange colour with a low fluorescence intensity.

TRIASSIC. (9,905 - 10,395 FT.)

Shublik Fmt. (9,905 - 10,395 FT.)

Four samples were analysed from this formation. The sample at 9950 ft. is a carbonate but shaley in places. The sample is organically lean and has a low bitumen stain. Under blue light excitation this samples appears to be low in fluorescence particles, however traces of tentatively indentified algal remains were noted which may be from caved material. The majority of the liptinites, however, have lost their fluorescence. The lithology was clearly different at this depth and has the appearance of ma metamorphic sediment. By 10,010 ft. lithology changes to a mudstone with calcareous shale intercalations and an occasional fossiliferous marl. There is a moderate phytoclast content comprised dominantly of micrinite (60 %) with significant poor quality, high reflecting vitrinite (25%) and inertinite (15%). Fluorescence observations indicate that most of the fluorescence has ceased apart from immature spores present in a coaly, drilling introduced contaminant. At 10,280 ft. sediments are more shaley , commonly feldspathic with traces of carbonate. Organic matter content is moderate to high and the dominant maceral present in this sediment is micrinite (<70 %) and significant high reflecting vitrinite (25 %) and inertinite (>15 %). Organic bitumen staining is dark brown/grey indicative of increased degree of hydrocarbon generation/migration. Fluorescence data from 10,280 ft. shows that the majority of the sample no longer fluoresces and one tentatively identified spore was

noted which fluoresced dark orange with a very weak intensity. Trace caved shales are present in this sample. By 10,310 ft. a feldspathic shale and occasionally calcareous shale (partially metamorphosed lithology ?) is rich in high reflecting vitrinite and inertinite. In fluorescence light this sample is extinct and contains minor caved particles. Organic staining is black/grey indicative of sediments exposed to a higher degree of heating. There is some evidence of vesiculated bitumen fragments also characteristic of localized heating (eg. sill or dyke). However, this may also be attributed to bacterial degradation.

All samples in this zone contain drilling introduced contaminants.

PERMO-TRIAS (10,395 - 11,445 ft.)

Sadlerochit Group (10,395 - 11,445 ft.)

Two samples were analysed from this group. One sample from 10,820 ft. is a silty shale low in organic matter and with a variable trace - moderate intensity of organic bitumen staining. By 11,210 ft. the shale becomes more calcareous and contains a moderate to high abundance of organics. This is dominated by high reflecting vitrinite (65%) and inertinite (35 %) and a moderate bitumen staining. Liptinitic matter in both samples has ceased to fluorescence.

PERMIAN (11,445 - ? ft.)

Lisburne Group (11,445 - ? ft.)

Two samples were examined in this section (11,660 ft., 11,730 ft.) The upper sample is a fossiliferous calcareous shale. Organic content is low to moderate while background organic staining is moderate to strong in intensity and a brown/black colour. Pyrobitumen is significant in the more carbonate rich areas of this sample. At 11,730 ft. at the base of the analysed section a carbonate comprises a moderate vitrinite and inertinite content and strong bitumen staining. This staining is a red-brown colour and indicative of hydrocarbons either from migration or alternatively contamination. This could mark a significant migration conduit through these Permian shales.

Observations in blue light show that all organic fluorescence has extinguished in both samples. Mineral calcite rhombs fluoresce yellow in the sample from 11,660 ft. At 11,730 ft. traces caved lithologies are apparent.

THERMAL MATURITY

Vitrinite reflectance measurements (Table B1) and spore fluorescence colour data were measured for this well. Figure B5 shows thermal maturity (vitrinite reflectance) versus depth; Figs B6 and B7 show vitrinite reflectance histograms.

Vitrinite reflectance fluctuates from 0.78 % R_o at 9,500 ft to 0.75 % R_o at 9,800 ft within the Kingak shale. No samples were analysed from the Sag River Fmt. There is an abrupt increase in vitrinite reflectance within the Shublik Fmt. at 9950 ft. Vitrinite reflectance increases to 1.31 % R_o and reaches a maximum of 1.56 % R_o at 10,310 ft at the base of this formation. Vitrinite reflectance values stay fairly constant throughout the Sadlerochit and Lisburne Group. Thermal gradients are very small in this section (0.05 % R_o / 100 m).

Spore fluorescence data agree well with vitrinite reflectance measurements. These data indicate the well is oil window mature (0.7% - 1.1% R_o), passing into gas condensate maturity (>1.3% R_o) by the approximate depth of 10,250 ft within the Shublik formation. From a projected maturity profile, the dry gas maturity threshold will probably be passed at approximately 12,300 ft., some 300 ft below the base of the analyzed section.

iii) Lisburne well - bitumen extraction data Additional parameters calculated from the Lisburne well are shown in Table B1.

C. Design and set-up of hydrous pyrolysis apparatus A hydrous pyrolysis set-up has been designed, as shown schematically in Figs C1 and C2, and is in the process of being assembled and tested. Some of the factors taken into account in the design are:

- i) Design of apparatus and procedures suitable for quantifying isothermal rates of gas generation and expulsion at high pressures in the presence of liquid water. Many smaller scale set-ups have been designed to run at low pressure, so that water is no longer liquid - ie Monthioux, et al, 1986; 1988; Horsfield, unpublished results. However, none of these has included studies of gas generation, to the best of our knowledge. Based on experience with oil generation and expulsion, the lower pressure experiments probably do not mimic the natural system as well as Lewan's hydrous pyrolysis experiments. A crucial factor seems to be water remaining as a liquid in the presence of the source rock because of the higher pressures which can be maintained

Figure B1: ikpikpuk well, Alaskan North Slope, nC_{17}/nC_{18} ; pristane/ nC_{17} ; phytane/ nC_{18} ; and pristane/phytane, including new data for Torok formation

Figure B2: Ikpikpuk well, Alaskan North Slope, ratio of tri- to (tri- plus mono-) aromatic steranes versus depth, including Torok samples, as determined by CI-IB-GCMS.

Figure B3: Ikpikpuk well, Alaskan North Slope, plots of methyl naphthalene ratio (MNR), ethyl naphthalene ratio (ENR), and dimethyl naphthalene (DNR) ratios versus depth, including Torok samples.

Figure B4: Ikpikpuk well, Alaskan North Slope, plots of methyl phenanthrene ratio (MPR), dimethyl phenanthrene index (DPI), methyl phenanthrene index 1 (MPI 1) and methyl phenanthrene index 2 (MPI 2) versus depth, including Torok samples.

Figure B5: Ikpikpuk well, Alaskan North Slope (petrology data): Vitrinite reflectance versus depth plot.

Figure B6: Ikpihpuk well, Alaskan North Slope, (petrology data): Vitrinite reflectance histograms; 9,500 - 10,310 ft.

Figure B7: Ikpikpuk well, Alaskan North Slope, (petrology data): Vitrinite reflectance histograms; 10,820 - 11,730 ft.

Pristane/nC17	Phytane/nC18	Pristane/Phytane
0.66	0.37	1.57
0.34	0.18	1.41
0.37	0.36	1.11

Table B1: Lisburne well, Alaskan North Slope, NC17/nC18; pristane/nC17; phytane/nC18; and pristane/phytane.

Depth (ft.)	% R _o	# Readings
9,500	0.78	3
9,800	0.75	1
9,950	1.31	5
10,010	1.46	3
10,280	1.39	6
10,310	1.56	6
10,820	1.67	2
11,210	1.58	19
11,660	1.52	21
11,730	1.67	17

Table B2: Vitrinite reflectance values, Alaskan North Slope Ikpikpuk well (determined by L. Buxton, Chemistry Department, Woods Hole).

in the larger vessels (Lewan, unpublished results). Because the gas window extends to considerably higher temperatures than the oil window, our equipment is being designed and tested so that it can eventually be taken to supercritical temperatures and pressures, which may be encountered in some gas generation zones in geological systems.

- ii) Ability to sample aliquots of compounds produced in both gas and liquid phases "on-line" without depressurization during the course of each experiment.
- iii) Trying to reach a compromise between large-scale, high pressure, time-consuming Parr bomb-type hydrous pyrolysis experiments used in the past to quantitate both oil generation and expulsion curves (Lewan, 1985; Lewan, in press) and the more convenient smaller scale lower-pressure reaction tubes mentioned above. In addition, we wanted a system in which some constituents could be measured during the course of the experiment, rather than only at the end as has been the case with the larger scale experiments in the past. Therefore, a small, relatively inexpensive, 20 ml "pipe-bombs" (which are rated for a maximum of 400°C and 500 bars of pressure) are being utilized. Quantitation of components present in both gas and liquid phases as a function of time will be carried out using internal standards and an automated "step-down" valving system to allow direct injection of aliquots of the reaction mixture onto a GC (Fig C1). The reaction vessels are small enough and cheap enough, so that vessels of different materials can be tested (eg, titanium for carboxylic acids, carburized stainless steel for hydrogen sulfide and hydrocarbon gases). The vessels can also be easily replaced if they are "wrecked" during an experiment (for example, if supercritical fluids cause solidification and bonding of sediment to vessel walls). An inexpensive vessel will also provide flexibility of designing special vessels for special experiments at a later time - e.g. to monitor changes in solid phases during the course of each experiment.
- iv) For following more polar water-soluble compounds which cannot be easily analyzed by GC, such as dicarboxylic acids, aliquots of liquid can be collected prior to reaching the GC and analyzed "off-line" by other procedures, such as HPLC, or derivatized prior to GC.

- v) All monitoring of temperatures and pressures as well as automated valve turning and GC analysis will be microprocessor controlled in order to provide maximum precision and operator safety.
- vi) The design minimizes dead volumes and allows all lines to be subjected to good vacuum for purging (MFP @ 0.1 torr = 5ul/linear inch) to eliminate potential background problems originating from sampling lines and valves.
- vii) The GC is equipped for both packed and capillary columns which can be run either parallel or in series though either (or both) an FID and a TC detector. Columns to be utilized will handle separations of gas and light hydrocarbons, mono-carboxylic acids, and some sulfur compounds.

D. Carbon isotopic composition of individual products from flash pyrolysis of kerogens - a preliminary study (Dr Timothy Eglinton)

Background Determination of the source of organic matter which ultimately is responsible for accumulations of oil and gas is a major goal in petroleum geochemistry. Petroleums may be derived from both terrestrial and marine organic matter and source rock kerogens reflect these differing inputs in a number of ways.

Stable carbon isotopes have the ability to distinguish carbon sources according to depositional environment (e.g. freshwater versus marine) as a result of the different fractionation effects related to atmospheric and dissolved CO₂ equilibria and uptake. The stable carbon isotopic compositions of kerogens and coals appear to be independent of the stage of thermal evolution (Schoell, 1984) and hence have potential applications for oil-source rock correlations. Typically the isotopic value of the gross kerogen is measured (i.e., $\delta^{13}\text{C}$ TOC). Since source rock kerogens are typically derived from a number of individual, and potentially separate, sources $\delta^{13}\text{C}$ TOC represents a composite value for the various constituents of which it is comprised. In order to resolve these separate contributions the isotopic compositions of each of the individual constituents must be determined. The integration of an established analytical approach (pyrolysis) with a newly developed technique (gas chromatography-combustion -isotope ratio mass spectrometry, GC-C-IRMS) now makes this possible. Pyrolysis of kerogens has been shown to provide important and useful information on kerogen structure. In combination with newly available mass spectrometers for on-line determination of the carbon isotopic composition

NOTES:

- (G) GAS PURGE LINE
- (M) MAKE-UP (FILL) GAS
- (P) UHP GAS PURGE LINE
- (W) WATER PURGE LINE
- FINAL CONFIGURATION CAN BE OPERATED UP TO LIMITS OF A.E. VALVES, i.e. > 5000psi @ 400°C.

Hydrous Pyrolysis
Essential Fluid Flows

REV. B

FINAL CONFIGURATION

4/10/90 CGJ / W H O I

Figure C1: Schematic diagram, hydrous pyrolysis apparatus: Essential fluid flows showing high pressure valve system on left and "step-down" lower pressure interface valves to the GC on the right.

	Represent a Controller.
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Top Box is power.
Middle Box is data out.
Bottom is control in.

Total Wob-HIP data $I_m = 97 \text{ Tcomp}$
 $= 1 \text{ Pass}$

Hydrous Pyrolysis
ELECTRONICS
REV B
FINAL CONFIGURATION
4/11/90 CGJ/WHOI

Figure C2: Schematic diagram, hydrous pyrolysis apparatus: Electronics of automatic valving, temperature and pressure controllers and monitors, and GC and data system.

of individual components eluting from a gas chromatograph, it is now feasible to determine the isotopic compositions of individual pyrolysis products. This study was designed to test the viability and use of this approach for the study of kerogens.

Summary of Results Six kerogens isolated from sediments representing a range of depositional environments (marine, estuarine, lacustrine) and ages (Recent to Carboniferous) were subjected to flash pyrolysis (800°C, 20s). "Aliphatic" fractions isolated from the pyrolysates were subjected to GC-C-IRMS. The bulk kerogens were also combusted and analyzed separately to provide $\delta^{13}\text{C}$ total organic carbon (TOC) values by conventional isotope mass spectrometry.

Fig D1 shows two representative m/z 44 mass chromatograms from GC-C-IRMS analysis. Four types of hydrocarbons were typically observed to dominate the chromatograms: n-alkenes, n-alkanes, acyclic isoprenoid and hopanoid hydrocarbons. The isotopic compositions (summed over the appropriate carbon number range) are listed in Table D1. Results from replicate analyses suggest that most values may be considered accurate to within ± 0.5 ‰; however, in the worst cases (i.e. for samples which display complex chromatograms, or for components which are incompletely resolved) the degree of error may be ± 1 ‰ or more. Marine kerogens typically proved more difficult to study than lacustrine samples. In Fig D2 the stable carbon isotopic compositions of these pyrolysis products are plotted with respect to carbon number for each of the kerogens. The data show that n-alkenes and n-alkanes generally display rather similar values to one another irrespective of carbon number, particularly for the lacustrine samples. The average values of these compounds also in several cases reflect the corresponding $\delta^{13}\text{C}$ TOC value, suggesting that they are derived from structurally important, or at least isotopically representative, components in the kerogen. The isotope compositions of normal hydrocarbons in the Messel kerogen pyrolysate showed the greatest difference compared to the $\delta^{13}\text{C}$ TOC value, being up to 10 ‰ lighter. Both the kerogen and the normal hydrocarbon pyrolysis products have been proposed to be derived predominantly from the cell-wall of the freshwater alga, *Tetradron minimum* (Goth et al., 1988). The discrepancy between the average n-hydrocarbon and TOC values may be due to several reasons. For example, other (non-aliphatic) components may strongly influence the $\delta^{13}\text{C}$ TOC value. Alternatively, $\delta^{13}\text{C}$ depletion in the lipid fraction of the contributing organisms may be significant. It is perhaps of note that the alkene/alkane values are very similar to that determined for an aliphatic hydrocarbon fraction previously isolated from the Messel shale extract (Hayes, et al., 1987).

The isotope compositions of the various compound classes vary substantially from one sample to another. Average values for normal hydrocarbons range from ca. -33 ‰

(Messel Shale) to ca. -14 ‰ (Westfield Shale). With the exception of the Westfield kerogen, non-marine lacustrine samples (i.e. Messel and Green River kerogens) give lighter average isotope values than the marine samples (Monterey, Peru, Spartina) in agreement with previous observations of gross isotopic compositions of organic matter derived from terrestrial versus marine systems. The Westfield Shale appears to represent a rather unusual and interesting case. The organic matter in the shale is almost exclusively comprised of the freshwater *B. braunii*-derived kerogens. Whilst the shale represents a freshwater lake deposit, the isotope values (both the normal hydrocarbons and the TOC) are unusually heavy. Two explanations may be forwarded: (1) isotopically heavier bicarbonate (HCO_3^-) was utilized as a carbon source by the algae; (2) free CO_2 utilization was restricted by either pH and temperature or by bio-physical-chemical limitations.

Differences in isotopic composition are apparent between the compound classes studied. Isoprenoid hydrocarbons (when present) were found to be heavier (Messel), lighter (Green River) or similar to the n-hydrocarbons. In contrast, the hopanoids were in each case substantially lighter than both the $\delta^{13}\text{C}$ TOC and n-hydrocarbons, with values as light as 50 ‰ recorded for hopanoids in the Messel kerogen pyrolysate. These latter values show good agreement with those reported by Freeman et al. (1990) for hopanoids in solvent extracts of the same shale, indicating a contribution by methanotrophs to the kerogen.

From this very preliminary investigation a number of conclusions may be drawn which would have not been previously possible from conventional analyses. It was found that normal hydrocarbon pyrolysis products displayed rather homogeneous values suggesting a common origin in keeping with a biopolymeric source. The isotopic compositions of these pyrolysis products generally showed a strong similarity to the overall TOC, indicating that they either influenced, or were representative of, the latter. In instances where isotopic compositions of the pyrolysis products did not closely match the $\delta^{13}\text{C}$ TOC (e.g. Messel), then alternative components must be considered. Regarding this point it should be born in mind that the present investigation has only dealt with aliphatic pyrolysis products. Isotopic evidence of bacterial contribution to kerogen was found in isotopically light hopanoids. The variable isotopic compositions of isoprenoid hydrocarbons suggest that they may have both separate and common biological origins.

Whilst this study contrasts geochemically very different kerogens, the results demonstrate that isotopic compositions may be readily determined for individual pyrolysis products by GC-C-IRMS. The data allow several new deductions to be made regarding the source of these components and their importance in dictating the overall $\delta^{13}\text{C}$ TOC value of kerogen. The approach holds much promise, therefore, for assessing the various

sources of the separate biological components comprising the kerogen, and also for interpreting the overall TOC value in terms of these components.

E. Global Basin Research Network (GBRN) - progress to date

Over the last two years, a group of geoscientists from Woods Hole, MIT, Lamont, Cornell, and LSU have worked informally to establish a research network to better understand subsurface fluid flow processes over geologic time in sedimentary basins and their relation to resource accumulation (ie, petroleum and metal ores). Our group at Woods Hole has been responsible for co-ordinating organic geochemical data, measurements, and expertise, considered to be a crucial part of the overall effort. The network will hook scientists from the different institutions and disciplines together via computer and graphic work stations. Such a network, co-ordinated by a central management council, allows flexibility in institutions and scientists participating at any particular time. For example, since formation of the initial Global Basin Research Network (GBRN) involving the "core" institutions listed above, groups from the University of Texas, Texas A & M, the Colorado School of Mines, and elsewhere have become involved in the work. Significant industrial support, in the form of data input as well as computer hardware and software, has been obtained in the initial stages of the project. Participating companies currently include three computer hardware and software companies (IBM, Landmark Graphics, and Computational mechanics), and nine major oil companies (AMOCO, ARCO, BP, Chevron, Exxon, Mobil, Shell, Texaco, and Union). In addition, at the time when the first GBRN Quarterly report was issued in May of 1990 (summarized later in this section), negotiations were in progress with Pennzoil, Schlumberger, and Conoco.

The rationale for establishing this network is that diverse basin phenomena, treated today by quite separate academic specialties, need to be viewed in a new way: as large-scale coupled processes in subsurface sedimentary basins which act as giant thermochemical-structural reactors. These "reactors" deform and break as organic matter in them matures, generates fluid overpressures, and causes (often episodic) fluid movement that chemically alter the host sediments. These processes produce, under favorable conditions, economically valuable mineral deposits and hydrocarbon accumulations. Mineral deposits in basins are often related to hydrocarbon accumulation and sediment alteration because both are produced by fluid movements, often using common permeability channels at different times. Organic and inorganic chemical alterations interact with the basin stratigraphy and structure which control local permeability. Thus, it is the

Figure D1: M/Z 44 " Combustograms" from GC-C-MS of kerogen
pyrolysates

Figure D2: $\delta^{13}\text{C}$ of individual hydrocarbons from pyrolysates of: c) Monterey Shale d) Peru upwelling.

Figure D2: $\delta^{13}\text{C}$ of individual hydrocarbons from pyrolysates of: a) Green River Shale, b) Messel Shale

Figure D2: $\delta^{13}\text{C}$ of individual hydrocarbons from pyrolysates of: d) Spartina
e) Westfield

Figure D2: $\delta^{13}\text{C}$ of individual hydrocarbons from pyrolysates of: c) Monterey Shale d) Peru upwelling.

Kerogen	Age	Env.	TOC*	$\delta^{13}\text{C}$ Value (‰)			
				Σane^2	Σisop^3	Σhop^4	
Westfield, Scotland	Carb.	Lacustrine	-14.26	-15.43	n.d.	-23.15	
Messel. FRG	Eocene	Lacustrine	-27.69	-33.13	-30.83	-45.47	
Green River, UT, USA	Eocene	Lacustrine	-29.00	-29.96	-31.27	-41.66	
Peru, S. America	Contemp.	Marine	-20.47	-23.82	-22.90	n.d.	
Monterey, CA, USA	Miocene	Marine	-22.17	-24.88	-24.64	n.d.	
"Spartina", GA, USA	Contemp.	Estuarine	-18.54	-23.30	-24.71	n.d.	

*Determined by conventional sealed-tube combustion and MS.

¹n-alkenes; ²n-alkanes; ³isoprenoids; ⁴hopanoids.

n.d. = not detected

Table D1: Carbon isotope data for kerogen samples.

interaction of the overall basin geology and geochemistry that ultimately determine fluid migration pathways. Understanding how these subsurface fluid flows affect basin resources is similar to many of today's major scientific and societal challenges in requiring the effective joining of many observations and processes that have previously been addressed by separate and largely non-communicating disciplines.

The overall goal of the GBRN is to develop a general methodology which is applicable to any sedimentary basin, as shown schematically in Figure E2. The philosophy of the approach is straightforward - i) to develop means of collecting and viewing in three-dimensions large amounts of diverse data (basin observations, placed in a "data cube" in a computer workstation, Fig E2), and ii) to develop and test integrated process models that describe diverse basin phenomena as products of operation of a single thermo-chemical-structural reactor ("model cube" in Fig E2A). The computer will be the major tool in all phases of the work, with heavy utilization of 3-dimensional color graphics on modern computer workstations which will allow comparison "snapshots" of the subsurface from the actual data (the data cube) versus that generated by the computer model. Thus, our approach is conceptually similar to the way science is usually done for less complex problems: a conceptual model is continuously tested and modified to fit observational data (Fig E2A).

To date, modern Landmark Graphic computer workstations have been installed and are being used for the GBRN at Lamont, Cornell, and LSU in order to store and visualize voluminous and diverse types of data covering large geographic areas, as summarized later in this section. Work is in progress to obtain additional workstations for other participating institutions, including Woods Hole and MIT. The "data cube" required to visualize the possible connections between different types of geological and geochemical data is built by overlaying well log, temperature, pressure, organic and inorganic geochemical, sedimentological, etc., data on seismic profiles via stacked cubes in the work station (Fig E2B). Various parameters can be overlain and visualized on a variety of scales as shown for a 20x40 km area of the Louisiana Gulf Coast (Fig 8 in the accompanying proposal) in the highly productive area of the S. Marsh Island-Eugene Island Fields (Lewis, et al, 1982; Holland, et al, 1980; Powell, 1988). For example, Fig E3 shows the relation of the smaller 20x40 km area where a wealth of detailed geological and geochemical data has been made available to us, to a N-S transect covering a larger section of the basin.

The goal of the numerical modeling, which has also been started on the supercomputer at Cornell, is to carry out realistic modeling of single or multiphase fluid

flows in the subsurface. FEM (finite element modeling) software working on today's supercomputers permit, for the first time, realistic fluid flow modeling of the subsurface (Cathles, private communication). A number of FDMs (finite difference models) and FEMs have already been developed to model single or multiphase flow in porous media on a reservoir or regional scale. Natural flow can be driven by a number of processes (as reviewed by Cathles, in press) including variations in hydraulic head under geopressed conditions, by pressures induced by compaction, by gas and oil maturation reaction with positive volume changes (DV), and/or by thermal- or salinity-induced buoyancy (e.g. Cathles, in press; Cathles and Smith, 1983; Yukler and Kokesh, 1984; Evans and Nunn, 1989 and refs cited). An example of FEM modeling working on a supercomputer is shown for the thin Permian age Kupfershiefer shale of Europe in Fig E4. Permeability, the key parameter in describing fluid flow, is difficult to measure accurately or to map. Fig E4 shows a model of the horizontal flow velocity across the Kupfershiefer and underlying Weisliegendes sand (see "shark fin" in Fig E4). With no tuning of the finite element code from Computational Mechanics, only a few CPU seconds of computer time were required on the supercomputer at Cornell to obtain the steady-state solution shown in Fig E4 which describes permeability contrasts to three orders of magnitude and defines flow in a 4-element 150m thick layer. Reservoir models have been developed that show clearly how methods of grid refinement can be used to address geological variations in permeability (Espedal and Ewing, 1987). Effective methods for tracking chemical fronts have also been developed (Ewing, et al., 1984). Most important, realistic permeability contrasts and geometries can be addressed by FEM in 3-D.

The logical next step for the GBRN is to superimpose the available organic geochemical data on the geological information in the data cube. This work, together with developing realistic 3-dimensional fluid flow models and testing in detail how they compare to the "real world", follows logically and builds on one- and two-dimensional organic maturation modeling work begun at IFP in France (Ungerer, et al, 1984) and KFA in Germany (Yukler and Kokesh, 1984). The initial GBRN efforts have focused on the Gulf of Mexico because of its obvious importance to United States domestic oil and gas production and because a wealth of data is available, because of oil and gas exploration, to build and test the methodology.

Work to date to demonstrate the basic approach of the GBRN has focused on the 20x40km area of the Eugene Island-S. Marsh Island data cube (Figs E2 & Fig 8 from the accompanying proposal) containing productive oil and gas fields. The images in Fig 8 (of the proposal) were generated by Dr Roger N. Anderson of Lamont working together with Bryce Crawford of Landmark Graphics, both principal collaborators in the GBRN. Raw

data provided by AMOCO together with surface heat flow (obtained by Dr Roger Anderson, Lamont) were placed in the workstation. Figure 8A shows the top of the salt topography and surface heat flow, with locations of oil and gas reservoirs superimposed in green and red respectively. Figure 8B shows a three dimensional view of salt topography displayed beneath the surface heat flow and oil and gas fields at the surface. Note the apparent location of oil and gas fields over the tops of the salt structures. This association could be caused either by thermal anomalies over salt domes sufficient to cause oil and gas generation from Tertiary sediments or by fluid circulation from depth through permeability channels associated with salt structures. Figure 8C shows the positions of two major fault systems, superimposed as the vertical red and blue grids running vertically through the system. These could be acting as conduits for gas and oil migration (although "locked" faults where migration can occur only episodically are also a possibility). Note the high heat flow anomaly 'C' and a gas field which appear at the terminus of the blue fault.

The obvious next question is to ask whether the compositions of the fluids in this area in relation to the images in Fig 8 provide information on sources of oil and gas (ie deep marine vs Tertiary), timing of expulsion, and migration conduits. Recent research and contract exploration work carried out by Texas A & M's Geochemical and Environmental Research Group (GERG) has generated a wealth of organic geochemical data related to these questions. All four phases of a 5.5 year oil correlation study, which focused on the organic geochemistry of the Gulf of Mexico and was funded by a consortium of several oil companies, are now complete. The select sets of data from the first three phases of the study, including compositions of 557 oils and 257 rock extracts covering both on-shore and off-shore portions of the Texas and Louisiana Gulf Coast, are available for inclusion in the GBRN data cube. Phase IV of the Texas A & M oil correlation study includes the quantitative analyses of compositions of 212 oils, 63 gases, and 3 condensates in the S. Marsh Island-128/Eugene Island-330 areas, which are within the first GBRN data cube. A computer tape of the organic geochemical data has been sent to Roger Anderson at Lamont and will be inserted in the data cube.

Even cursory comparison of the Texas A & M oil compositions with the Eugene Island-S. Marsh Island geological and thermal profiles shows some interesting relationships. The source rocks and maturity of oils in geographically adjacent SMI-128 and EI-330 fields are different, with the more northerly South Marsh Island oils being more "terrigenous", ie lower in sulfur and heavy metals, and the more southerly Eugene Island oils, closer to the shelf break being more "marine" or slightly higher in sulfur and heavy

metals and isotopically slightly different from the SMI oils (Fig E1). These different signatures of oils in this small data cube, together with detailed compositions in biomarkers and light hydrocarbons available in the Texas A & M data, once superimposed on data cube, should allow us to track in detail the maturities, sources, and migration paths of these fluids.

Some other major conclusions of the Texas A & M oil correlation study as described in various manuscripts based only on organic geochemical data are:

- 1) The compositions of the oils on the Louisiana shelf are most remarkable for their gross similarity, both isotopically and compositionally (Thompson et al, in press). The properties of these shelf oils are quite different from those of the Smackover oils which are sourced in on-shore carbonate rocks (Sasson, et al, 1987); some Florida shelf oils; and most oils from deeper water near the shelf-break (such as the Eugene Island oils), all of which contain higher levels of sulfur and metals and appear to be more marine.
- 2) Detailed biomarker studies suggest that the onshore sources of eight major shelf oil types are from very near their containing reservoirs, suggesting that oil migration has been predominantly vertical rather than lateral, with the offshore oils being more complex. However, the possibility of contamination of a migrated oil with traces of indigenous bitumen may apply in certain onshore cases.
- 3) A mechanism is required to explain the presence of biodegraded oils, as delineated by both C15(+) analyses and light hydrocarbon ratios, at much deeper than normal depths - to about 12,000 ft in some cases.
- 4) The C15(+) data and the light hydrocarbon ratios have been used to define the degree of alteration of the various Gulf Coast oils: about 74% appear to have been compositionally altered by the process of evaporative fractionation (ie, alteration by formation and upward migration of a gas phase), 64% have undergone some degree of biodegradation, and only about 5% appear to be unaltered.

- 6) Detailed geochemical studies suggest that various volatility ranges (i.e. gases, gasoline, oil, etc) of a single fluid may have separate and distinguishable sources, with younger less mature oils mixed with older more mature gases being a common pattern (Thompson, et al 1990; Comet, et al, submitted). This pattern could be explained either by multiple sources from different maturities and depths or a single source experiencing multiple phases of expulsion or both.
- 7) Geological maps delineating source (i.e. genetic oil typing), maturity, and secondary alteration have been prepared at Texas A & M.

Other progress of the GBRN, as reported in the first quarterly report issued in May of 1990, focuses on making the first steps toward: a) synthesis of the Louisiana Transect Data Volume; b) development of a user-friendly, integrated fluid, thermal, compactive FEM model, and c) setting priorities within the project for data and model image transmission and networking. Specific work described in that report, in addition to the organic geochemical work described above and in the attached proposal, includes:

1. South Eugene Island Data Cube (in addition to data described above):

- a) Amoco has provided five chronostratigraphic horizons, including top of sand/shale and top of geopressured shales, and top of salt. They have also provided reservoir information (e.g. production data and well logs) from S. Marsh Island Block 130 and S. Eugene Island Block 301.
- b) Halliburton Geophysical Services has donated a 2-D seismic coverage (at two mile grid-spacing) that expands the S. Eugene Island Data Cube from 60 blocks to 105 blocks. The data is being loaded onto the Landmark workstation at LSU and will then be ported to Lamont for merging with the Amoco horizons already in this data cube.
- c) Chevron has donated the Gulf Oil Heat Flow Survey of the S. Marsh Island Data Cube, consisting of over 700 surface heat flow measurements to the GBRN. A new analysis of these valuable data will be entered into the Lamont GEOBASE by the end of 1990. Lamont has entered the preliminary heat flow numbers into the Landmark Data Cube, and combined these with depths to top-of-salt, to predict subsurface heat fluxes between these horizons. From these data,

material properties will be defined for three-dimensional, finite-element, fluid flow modeling at Cornell.

- d) Though we are still overwhelmed by the dataset itself, the Shell 3-D seismic survey from the South Eugene Island Data Cube area (SMI 128) is being loaded into a Landmark at the Colorado School of Mines, for eventual transfer to LSU. If we can obtain subsurface pressures, temperatures, structure, and well logs from this field, we will have reservoir information from three producing fields in the Data Cube (Fig E 5).

2. Regional Data

- a) Top of salt and chronostratigraphic horizons interpreted by a Minerals Management Service Study (1987) extend from Western Louisiana to Eastern Texas offshore. These lines and wells are being put into the Landmark workstation at Cornell, where they are defining the three-dimensional litho- and chronostratigraphy. Time sections are being converted to depth. Lithofacies are being defined from well log data to help define the regional permeability structure.
- b) Halliburton has donated a long north-south line from Rabbit Island onshore to the Sigsbee Escarpment offshore that ties the S. Eugene Island Data Cube into its regional setting (Fig E5). In addition this study ties into the E-W grid of land wells presently being input into the LSU Landmark (a corporate gift from Mobil) (Fig E1). Mobil's data comprise detailed inorganic geochemical studies of these wells.
- c) We have also acquired top-of-geopressure and thickness-of-the-transition-to-normal-pressure maps of the Sabine Pass/W. Cameron area (Fig E5) from ARCO. We are seeking top-of-salt, top-of-geopressure and gravity maps from on- and offshore Louisiana from several other participating companies.
- d) Texaco is requesting release to the GBRN of SEG-Y tapes of their northern Louisiana segment of the AAPG Gulf Coast cross-section (Fig E5). Organics from four wells within this transect provide a section through gulf coast strata.

3. Modeling

Work is focused at Cornell on the supercomputer as well as at Lamont and LSU. Progress as of May 1990 was summarized as follows:

- a) The COMSYS 3-D Finite Element Code is running on AIX (the operating system for the Landmark workstation) at Cornell. Development at Cornell and Lamont has focused on expanding previous work on simple pressure driven flow problems and developing user-friendly input and output.
- b) Cornell has formulated the equations for integrated thermal, fluid flow and sediment compaction referenced to the sediment coordinate system. In conjunction with Computational Mechanics, they are developing and debugging the template of these equations for finite element modeling.
- c) At LSU, a salt-diapir-evolution Finite-Difference-Model (FDM) has been modified to include sloping layers. This code will be used to model flow in the Wilcox formation which appears to be driven by up-dip dense saline waters from northern Louisiana (Hanor and Nunn, unpublished results). Temperatures, pore fluid concentrations, and streamlines from numerical simulations of fluid flow have been successfully transferred to the Landmark for visualization.
- d) Efforts are underway to begin problem solving on the IBM3090 supercomputer at Cornell from both Lamont and Cornell. Several problems with the test version of AIX on the Supercomputer are being debugged to optimize communication between the Landmark work stations and the IBM3090. As of May, negotiations were in progress for porting COMSYS (the 3-D FEM code) to the IBM-KIngston supercomputer (at IBM) where an advanced version of the AIX operating system is operational.

4. Networking

The essential ingredient to the success of the GBRN will be the ability to network scientists from diverse locations together to produce scientific interchange, both with respect to the database and modeling sides of the project. To this end, the infrastructure of the GBRN communications and control network are being designed very carefully. The end product will be real time interactive control of a scientific problem being run on the supercomputer by experts residing at local workstations throughout the GBRN. They must be able to visualize the progress of the model, and compare the results with a vast database describing the true geological condition of the subsurface being modeled. To this end, the following progress had been made:

- a) X-windows visualization of COMSYS code (the FEM code) output is now possible throughout the network on any X-window equipped workstation

running UNIX. These images have also been successfully ported from the Cornell supercomputer to the Landmark at Lamont using OPENWORKS from Landmark Graphics Co.

- b) A Graphical Data Analysis Application (Scientist's Spreadsheet) has been developed which forms the structural basis of the database synthesis. This application is capable of executing commands on remote workstations.
- c) Network distributed-processing Control Applications have been developed for designing, executing, and monitoring processes on multiple hosts.
- d) A Network-Based retrieval scheme has been developed for accessing data at remote database serving computers.
- e) GBRN scientists have participated in the design and testing of the IRIS world seismological Data Management Center at the Center for High Performance Computing at UT Austin in order to gain experience in remote database query and retrieval of large data volumes.
- f) We are currently working on the control of the FEM code running on the IBM 3090 supercomputer at remote workstations, particularly the problem of where and how to visualize the output, and how to distribute animation.

Figure E1: Map, areas of different Gulf Coast oils and summary of properties of continental shelf (Type 1A) in northern part of Eugene Island-S. Marsh Island (EI-SMI) data cube vs more marine (Type 1B) oils in southern part of EI-SMI area.

Fig. 7. Building the Data Cube

Figure E2: Schematic diagram of overall methodology approach of GBRN. A) Schematic relationship of basin observations (i.e., data cube) and modeling; B) Building the data cube.

Figure E3: Scaling of S. Marsh Island-Eugene Island data cube with larger N-S Louisiana transect

Overpressuring of the Rotliegende hydrofractured the Kupferschiefer shale, making it the permeable pathway for fluids that deposited zones of copper, zinc and lead, respectively, from the basin margin toward the center.

Figure E4: Finite element modeling - permeability structure of the Kupferschiefer shale.

Fig. E5: A The GBRN Louisiana on- and offshore volumetric transect includes, from south to north: 1.) the South Eugene Island Data Cube, 2.) regional seismic and well data from the Minerals Management Service (expanded in B), 3.) Arco top-of-geopressure study, 4) east-west onshore geochemical, pressure and temperature grid from 50 wells, and 5.) the north-south Texaco/AAPG transect. B.) Detailed seismic and well data available through the Minerals Management Service.

5. REFERENCES

- Barker, C.E. (1989) Temperature and time in the thermal maturation of sedimentary organic matter. In: Thermal History of Sedimentary Basins, N.D. Naeser and T.H. McCulloh, eds, Springer-Verlag, New York, pp 73-98.
- Bird, K.J. (1985). The framework geology of the North Slope of Alaska as related to oil-source rock correlations. In: Alaskan North Slope Oil Rock Correlation Study, Magoon, L.B. & G.E. Claypool, eds, AAPG Studies in Geology No. 20, AAPG, Tulsa, OK, pp 3-29. Comet, P.A., J.K. Rafalska and J.M. Brooks (submitted) Sterane and triterpane fingerprinting as a tool in mapping of oils, condensates and source rocks of the Gulf of Mexico region, Organic Geochemistry.
- Cathles, L.M. (1990). Scales and effects of fluid flow in the upper crust. Science, in press.
- Cathles, L.M. and Smith, A.T. (1983). Thermal constraints on the formation of Mississippi Valley-type lead-zinc deposits and their implications for episodic basin dewatering and deposit diagenesis. Econ. Geol., v. 78, pp 983-1002.
- Durand, B., B. Alpern, J.L. Pittion, and B. Pradier (1986) Reflectance of vitrinite as a control of thermal history of sediments. In: Thermal Modeling in Sedimentary Basins, J. Burrus, ed., Editions Technip, Paris, France, pp 441-474.
- Durand, B. (1988) Understanding of HC migration in sedimentary basins (present state of knowledge). Org Geochem., v. 13, pp 445-459.
- Espedal, M. and R.E. Ewing (1987) Characteristic Petrov-Galerkin subdomain methods for two-phase flow. Comp. Meth. Appl. Mech. and Eng., v.64, pp 113-135.
- Evans, D.G., and Nunn, J.A. (1989). Free thermohaline convection in sediments surrounding a salt column. Jour. Geophys. Res.
- Ewing, R.E., T.F. Russel, and M.F. Wheeler (1984). Convergence analysis of an approximation of miscible displacement in porous media by mixed finite elements and a modified method of characteristics. Comp. Mech. Appl. Mech. Eng., v. 47, pp 73-92.
- Farrington, J.W., Davis, A.C., Tarafa, M.E., McCaffrey, M.A., Whelan, J.K., and Hunt, J.M. (1988b) Bitumen molecular maturity parameters in the Ikpikpuk well, Alaskan North Slope. Org Geochem., v. 13, pp 303-310.
- Freeman, K.H., J.M. Hayes, J.M. Trendel, and P. Albrecht (1990) Evidence from stable isotope measurements for diverse origins of sedimentary hydrocarbons. Nature, v.343, pp254-256.
- Goth, K., de Leeuw, J.W., W. Puttman, and E.W. Tegelaar (1988) Origin of Messel Oil Shale kerogen. Nature, v.336, pp759-761.
- Hanor, J.S. and R. Sasson (1989) Evidence for the large-scale vertical and lateral migration of formation waters, dissolved salt, and crude oil in the Louisiana Gulf Coast. Proc. 1988 Gulf Coast Section SEPM Research Conf., The Geochemistry of Gulf Coast Crude Oils and Gases, in press.
- Hayes, J.H., R. Takigiku, R. Ocampo, H.J. Callot, and P. Albrecht (1987) Isotopic compositions and probable origins of organic molecules in the Eocene Messel shale. Nature, v. 329, pp 48-51.
- Holland, D.S., W.E. Nunan, D.R. Lammlein, and R.L. Woodhams (1980) Eugene Island Block 330 Field, Offshore Louisiana. In: Giant Oil and Gas Fields of the Decade 1968-1978, M.T. Halbouty, ed, AAPG Memoir 30, pp 253-279.
- Huc, A.Y. and J.M. Hunt (1980) Generation and migration of hydrocarbons in offshore South Texas Gulf Coast sediments, Geochim Cosmochim Acta, v 44, pp 1081-1089.
- Hunt, J. M., 1979. Petroleum Geochemistry and Geology, W. H. Freeman and Co., San Francisco.

- Hunt, J.M., Lewan, M.K., and Hennen, R. (in press). Modeling oil generation with Arrhenius time-temperature index graphs. AAPG Bull.
- Jenden, P.D. (1983) Maturation of Organic Matter in the Paleocene-Eocene Wilcox Group, South Texas: Relationship to Clay Diagenesis and Sandstone, Ph.D. Thesis, University of California at Los Angeles.
- Johnson, C. and Whelan, J.K. (submitted). Determination of ratios of mono to triaromatic steranes in oils and sediments of high maturity by isobutane chemical ionization gas chromatography/mass spectrometry (IB-CI-GCMS).
- Kennicutt, M.C., and K.F.M. Thompson, A classification of offshore Gulf of Mexico oils and condensates, AAPG Bull, in press.
- Lewan, M.D. (1985) Evaluation of petroleum generation by hydrous pyrolysis experimentation, Phil. Trans R. Soc. Lond., v A315, pp 123-134.
- Lewan, M.D. (in press) Laboratory simulation of petroleum formation: hydrous pyrolysis. In: Organic Geochemistry, M.H. Engel and S.A. Macko, eds, Plenum Publishing Corp, New York.
- Lewis, R.L., H.J. Dupuy Jr., and D.S. Holland (1982) Eugene Island Block 330 Field - development and production history, Society of Petroleum Engineers Journal, pp 1-5.
- Magoon, L.B. & G.E. Claypool (1985). In: Alaskan North Slope Oil Rock Correlation Study, Magoon, L.B. & G.E. Claypool, eds, AAPG Studies in Geology No. 20, AAPG, Tulsa, OK, pp 31-46.
- Mineral Management Service, OCS Report MMS 87-0026 (1987). Correlation of Cenozoic sediments, Gulf of Mexico, outer continental Shelf, Part 1: Galveston Area, Offshore Texas through Vermillion Area offshore Louisiana. U.S. Department of the Interior Minerals Management Service.
- Nunn, J.A. and R. Sassen (1986) The framework of hydrocarbon generation and migration, Gulf of Mexico continental slope, Trans. Gulf Coast Assoc. Geol. Soc., v.36, pp 257-262.
- Pirkle, R.J., J.C. Williams, J.M. Brooks, and M.C. Kennicutt (submitted) Regional interpretive surface geochemical exploration parameters in the Gulf of Mexico.
- Powell, T.F. (1988) South Marsh Island Block 128 Field offshore Louisiana. In: Offshore Louisiana Oil & Gas Fields, J.R. J. Studlick, J.G. Bryant, J.A. Hartmen, and R.D. Shew, eds, Vol II, New Orleans Geological Society, New Orleans, LA, pp 159-162.
- Radke, M. (1988) Application of aromatic compounds as maturity indicators in source rocks and crude oils, Marine and Petroleum Geology, v.5, pp224-236.
- Sasson, R.C. C.H. Moore and F.C. Meendsen (1987). Distribution of hydrocarbon source potential in the Jurassic Smackover Formation. Org Geochem., v. 11, pp 379-383.
- Schoell, M. (1984) Stable isotopes in petroleum research. In: Advances in Petroleum Geochemistry, vol. 1, J. Brooks and D.H. Welte, Eds., pp. 215-245. Academic Press, London.
- Solkolov, V.A. and S.I. Mironov (1962) On the primary migration of hydrocarbons and other oil components under the action of compressed gases. In: The Chemistry of Oil and Oil Deposits, Acad. Sci. USSR, Inst. Geol. and Exploit. Min. Fuels, pp 38-91.
- Solkolov, V.A., T.P. Zhuse, N.B. Vassoevich, P.L. Antonov, G.G. Grigoryev, and V.P. Kozlov (1963) Migration processes of gas and oil, their intensity and directionality, World Petroleum Congress, June, Frankfurt, Maine.
- Solomon, P.R., M.A. Serio, R.M. Carangelo, R. Bassilakis, D. Gravel, M. Baillargeon, F. Baudais, and G. Vail (1990) Analysis of the Argonne Premium Coal Samples by Thermogravimetric Fourier Transform Infrared Spectroscopy, Energy and Fuels, v. 4, pp 319-333.

- Solomon, P.R.; Hamblen, D.G.; and Carangelo, R.M. (1982). Applications of Fourier Transform IR Spectroscopy in Fuel Science. In: *Coal and Coal Products: Analytical Characterization Techniques*; Fuller, E.L., Jr., Ed.; ACS Symposium Series 205; American Chemical Society, Washington, DC, pp 77-131.
- Strach, E., Mockowsky, M.T., Teichmüller, M., Taylor, G.H., Chandra, D., and Teichmüller, R. (1982) *Stach's Textbook of Coal Petrology*, 3rd ed, English Edition, Gebrüder Borntraeger, Berlin, p. 52.
- Tarafa, M.E., J.K. Whelan, and J.W. Farrington (1988) Investigation on the effects of organic solvent extraction on whole-rock pyrolysis: Multiple-lobed and symmetrical P2 peaks. *Organic Geochemistry*, v. 12, pp 137-149. Lewan, M.D. (1985). Evaluation of petroleum generation by hydrous pyrolysis experimentation; Phil. Trans. R. Soc. London, v. 315, pp 123-124.
- Tarafa, M.E., J.K. Whelan, and J.W. Farrington (1988). Investigation on the effects of organic solvent extraction on whole-rock pyrolysis: Multiple-lobed and symmetrical P2 peaks. *Org Geochem*, v. 12, pp 137-149.
- Thompson, K.F. (In press) Correlations of Gulf Coast petroleums on the basis of isoprenoid biomarkers, *Organic Geochemistry*.
- Thompson, K.F., M. & M.C. Kennicutt (in press) Nature and frequency of occurrence of non-thermal alteration processes in offshore Gulf of Mexico petroleums, 9th Annual GCS-SEPM Research Conference, December 1988, New Orleans, LA.
- Thompson, K.F.M. (1988) Gas-condensate migration and oil fractionation in deltalic systems, *Marine and Petroleum Geology*, v. 5, pp 237-246.
- Thompson, K.F.M. (submitted). Contrasting characteristics attributed to migration in petroleums reservoirs in clastic and carbonate sequences in the Gulf of Mexico region. *Petroleum Migration Symposium, 1989* Special Publication, Geological Society of London.
- Thompson, K.F.M., M.C. Kennicutt, and J. M. Brooks (1990) Classification of offshore Gulf of Mexico Oils and Gas-Condensates. AAPG Bull., in press.
- Tissot, B.P. and D.H. Welte (1984) *Petroleum Formation and Occurrence*, Springer Verlag, New York, 699 pp.
- Ungerer, P., F. Bessis, P.Y. Chenet, B. Durand, E. Nogaret, A. Chiarelli, J.L. Oudin, and J.F. Pertin (1984). Geological and geochemical models in oil exploration; principles and practical examples. In: *Petroleum Geochemistry and Basin Evaluation*, G. Demaison and R.J. Murtis, eds, AAPG Memoir 35, AAPG, Tulsa, OK, pp 53-78.
- Ungerer, P., J. Espitalie, F. Marquis, and B. Durand (1986) Use of kinetic models of organic matter evolution for the reconstruction of paleotemperatures. Application to the case of the Gironville Well (France). In: *Thermal Modeling in Sedimentary Basins*, J. Burrus, ed., Editions Technip, Paris, France, pp 531-546.
- Whelan, J.K. (1987) Organic geochemistry of continental margin and deep ocean sediments. A progress report to the U.S. department of energy, DOE Report No. COO-13466-2. U.S. Government Printing Office, Washington, D.C.
- Whelan, J.K., Carangelo, R.M., and Solomon, P.R. (in press) TG-FTIR - a pyrolysis method for following maturation of oil and gas generation zones using Tmax methane. *Org Geochem*, v. 16.
- Whelan, J.K., Farrington, J.W., and Tarafa, M.E. (1986) Maturity of organic matter and migration of hydrocarbons in two Alaskan North Slope wells, *Org. Geochem*, v. 10, pp 207-219.
- Whelan, J.K., J.M. Hunt, J. Jasper, and A. Hue (1984a). Migration of C1-C8 hydrocarbons in marine sediments, *Org Geochem*, v. 6, pp 683-694.
- Whelan, J.K., J.W. Farrington, and M.E. Tarafa (1986) Maturity of organic matter and migration of hydrocarbons in two Alaskan North Slope wells, *Org Geochem*, v. 10, pp 207-219.

- Whelan, J.K., Solomon, P.R., Deshpande, G.V. and Carangelo, R.M. (1988a) Thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR) of petroleum source rocks. Initial results. *Energy and Fuels*, v. 2, pp 65-73.
- Whelan, J.K., Hunt, J.M., Hennet, R., Tarafa, M.E., Dickinson, P.A., and Johnson, C. (1988b) Organic geochemistry of continental margin and deep ocean sediments. A progress report to the U.S. department of energy, DoE Report No. COO-13466-3. U.S. Government Printing Office, Washington, D.C., pp1-11.
- Whelan, J.K., Solomon, P.R., Deshpande, G.V., and Carangelo, R.M. (1988c) Thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR) of petroleum source rocks. Initial results. *Energy and Fuels*, v. 2, pp 65-73.
- Whelan, J.K., Yukler, A., Bird, K., and Magoon, L.B. (in preparation). One-dimensional modeling of Ikpikpuk well, Alaskan North Slope NPRA area: implications for timing of regional oil and gas generation and expulsion. *AAPG Bull.*
- Wood, D.A. (1988) Relationships between thermal maturity indices calculated using Arrhenius equation and Lopatin method. *AAPG Bull.*, v.72, pp 115-134.
- Yukler, M.A. and Kokesh, F (1984) A review of models used in petroleum resource estimation and organic geochemistry. In: Advances in Petroleum Geochemistry, vol 1, J. Brooks and D. Welte, eds, Academic Press, London, pp 69-114.

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