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EDITED BY JO ANNE KELLOGG

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This collection of papers continues the series begun in 1967 as a part of the *Reports of Studies* in the Bulletin. The papers present scientific and economic results of work by members of the State Geological Survey of Kansas and others during the calendar year 1971.

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Organic Geochemistry of a Pennsylvanian Black Shale (Excello) in the Midcontinent and the Illinois Basin

ABSTRACT

Organic geochemical studies of a widespread Pennsylvanian black shale (the Excello) indicate the portion of the shale present in the Midcontinent contains greater amounts of extractable hydrocarbons and has much higher hydrocarbon yields and higher saturate-to-aromatic hydrocarbon ratios than does the Excello present in the Illinois basin, which contains greater amounts of organic carbon.

These differences suggest that the Excello deposited in the Illinois basin incorporated greater amounts of terrestrial plant debris, although the predominant source of organic material in both areas is believed to have been marine plankton.

This interpretation is valid only if the organic material incorporated in the Excello Shale in both the Illinois basin and the Midcontinent has been subjected to maturation processes with similar thermal histories. The distribution of intermediate and heavy n-paraffins in the saturated hydrocarbon fractions of samples from both areas suggests maturation effects are quite similar in both the Midcontinent and the Illinois basin.

INTRODUCTION

The purpose of this investigation is to determine the nature and distribution of the extractable hydrocarbons present in a widespread Pennsylvanian black shale (the Excello) of the Midcontinent and the Illinois basin.

Although the bulk of the organic material present in ancient sediments is apparently in the form of a complex high molecular weight polymer (kerogen), the results of studies of the extractable hydrocarbons may reflect not only hydrocarbon generation and maturation processes, e.g., Philippi (1965), but also primary source variations in the type of organic material (i.e., marine vs. terrestrial) originally incorporated in the sediment. Previous organic-geochemical studies by Baker (1962) and Baker et al. (1969) of the Midcontinent Cherokee cyclothems indicate that Pennsylvanian rock units composed predominantly of terrestrial plant debris (coals) can be characterized by low hydrocarbon yields and have low saturate-to-aromatic hydrocarbon ratios, while rock units incorporating organic material derived predominantly from marine plankton (marine shales and limestones) have

much higher hydrocarbon yields and tend to display higher saturate-to-aromatic ratios. As all these rock units have been subjected to equivalent thermal histories, the differences in hydrocarbon yields among the various lithologic units must reflect primary organic source variations.

Presumably the organic material present in Pennsylvanian sediments in both the Midcontinent and the Illinois basin has been subjected to post-depositional maturation processes with similar thermal intensities; therefore regional studies of the extractable hydrocarbons present in the Excello Shale should indicate whether or not differing proportions of marine and terrestrial organic material were originally incorporated in the shale.

GEOLOGIC SETTING

The regional stratigraphic relationships of the Excello Shale are well known; the unit, which lies at the top of the Cherokee Group of the Des Moines Series of the Midcontinent, has been mapped as a member of the Summum cyclothem by Weiner (1961), Gamble (1967), and Wanless (1969). As is schematically shown in Figure 1, the Excello overlies marine carbonates (the Breezy Hill Limestone), gray mudstones, and coals (the Mulky and Summum) progressively from Oklahoma and Kansas to Indiana. It is in turn overlain by normal marine shales and carbonates of the basal Marmaton Group (the Blackjack Creek-Hanover limestones) over most of the Midcontinent and portions of the Illinois basin, but is overlain by a deltaic sequence (the Summum Shale) over most of the Illinois basin. The lithologic characteristics of the Excello have been described by James (1970); the unit averages 4 feet in thickness and generally consists of three major lithologic zones: a thin basal shell coquina, a thick middle zone of phosphatic dark gray-black clay-shale, and a thin upper zone of lighter colored mottled and burrowed claystones which grades into the overlying calcareous normal marine gray claystones and carbonates. As is shown in Figure 2, the Excello Shale, despite erosion

MIDCONTINENT   MISSISSIPPI   ILLINOIS
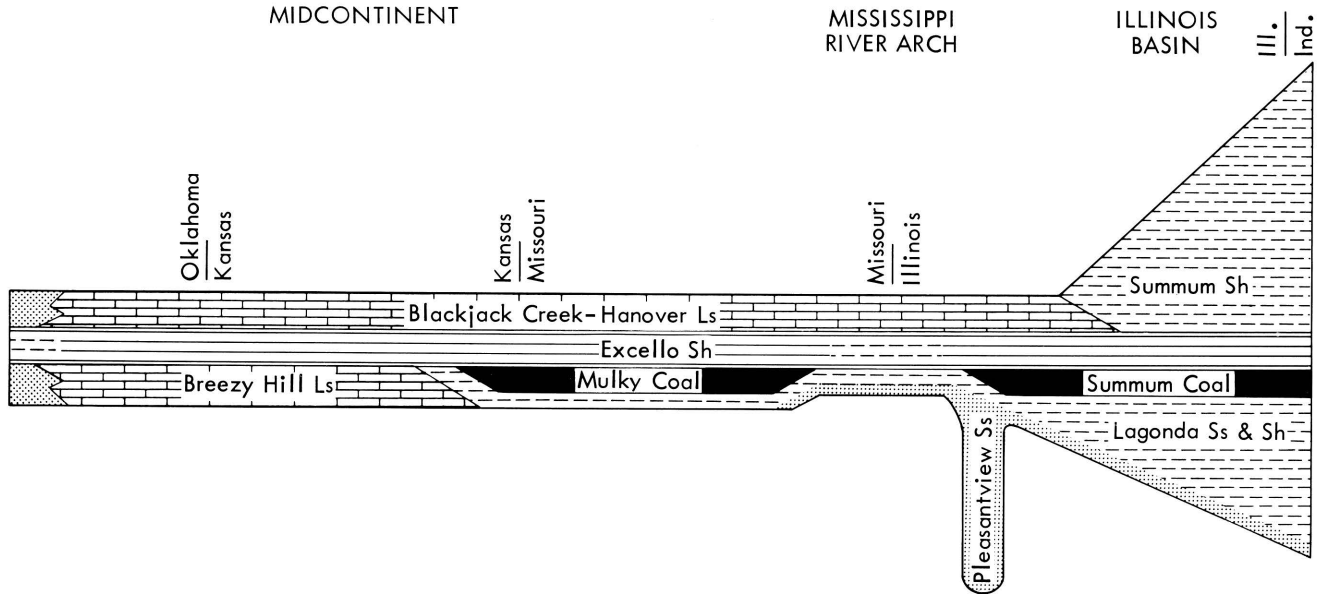   RIVER ARCH   BASIN

FIGURE 1.—Generalized lateral variations of Summum cyclothem.

from structural highs, covers an area of well over 100,000 square miles and grades laterally into more oxidized greenish-gray facies as it onlaps structural highs such as the Ozark uplift and the Mississippi River arch. The gross physical characteristics of the thinly laminated, organic-rich Excello Shale are amazingly uniform throughout the Midcontinent and the Illinois basin.

The environmental conditions which allowed the accumulation and preservation of organic material in the Excello have been interpreted by James (1970) and are summarized as follows:

1. A eustatic rise in sea level resulted in the gradual transgression of marine waters across the Midcontinent into the Illinois basin.

2. The development of a widespread density gradient (thermocline), due to high surface-water temperatures, prevented normal marine circulatory processes from replenishing the dissolved oxygen in the bottom waters which was utilized in the decomposition of organic material (produced primarily in the oxygenated surface waters).

3. Anoxic conditions then prevailed in the bottom waters over the Midcontinent and the Illinois basin as a result of subsequent denitrification and sulfate reduction. The use of nitrate and sulfate ions as reducible substrate by decaying organic material led to the introduction of toxic sulfides (H_2S and HS^-) into the poorly circulated bottom waters. Organic-rich sediments thus tended to accumulate as (1) lack of available oxygen inhibited biochemical decay processes, and as (2) bottom-dwelling fauna, which ingest and break down organic debris, were eliminated from the

ecosystem. The distribution of the sulfide-bearing bottom waters in the stratified epicontinental Excello sea, and hence the distribution of the organic-rich bottom sediments, was controlled by submarine topographic highs and basinal depressions.

4. Sedimentation was restricted to the slow influx of clay minerals (possibly clad with films of organic material), detrital plant and animal remains, and minor amounts of clay-sized quartz grains.

5. Return to the normal marine and clastic environments was brought about as the Excello sea shallowed, thus breaking up the thermocline and destroying the anoxic bottom-water conditions.

ANALYTICAL PROCEDURE

The organic-geochemical procedures used in this study were based on methods of hydrocarbon extraction and separation described by Ferguson (1962).

All samples prepared for analysis were first jaw crushed to ¼-inch pieces and then passed once through a hammer mill (Metals Disintegrating Co., "Mikro-Pulverizer"[2]). The resultant median particle size ranged from 8 to 16 microns.

Organic carbon was determined by combustion of an acid-treated portion of each sample in a Leco induction furnace with the resultant CO_2 being measured volumetrically in a Leco carbon analyzer.

"Hydrocarbon" extracts were obtained from the pulverized rock samples in Soxhlet extractors using redistilled reagent grade benzene as the solvent. Original sample weights ranged from 10 to 750 g. Depending on the estimated sample size needed to

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[2] Mention of companies or products is not to be considered an endorsement.

obtain approximately 150 mg of residue, the samples were extracted with either 750 ml or 2000 ml of benzene for 24 hours; cycle time was adjusted to 20 minutes. The benzene extracts were concentrated by distilling under partial vacuum at 40°C using a Buchler flash-evaporator. The extracts were isolated in a nitrogen evaporator by drying to constant weight (within 2.0 mg) in tared 2-dram vials. If necessary, the residues were dissolved in 100 ml of benzene, aliquoted, and redried to yield a final residue weight ranging from 120 to 170 mg.

The sediment extract was separated into a "saturated hydrocarbon" fraction and an "aromatic hydrocarbon" fraction by elution chromatography. The chromatographic columns (8 mm I.D. by 26 cm) were packed with two layers of silica gel slurried in cyclohexane; 13 cm of code 950 gel, used as a bottom layer to effect the analytical separation, were overlain by 13 cm code 70 gel (pulverized and sieved to produce a 40 to 60 mesh fraction) used to provide adsorption capacity for very large molecules. The sediment extracts were loaded on the columns with 2 ml of cyclohexane and were successively eluted with 30 ml cyclohexane and 30 ml benzene. The saturate and aromatic fractions collected were isolated by means of the rotary and nitrogen evaporators.

The analytical data obtained and calculated from the organic carbon determinations and the extraction and chromatographic procedures include: (1) organic carbon weight percent, (2) "saturated hydrocarbons" in ppm, (3) "aromatic hydrocarbons" in ppm, (4) "total hydrocarbons" in ppm (summation of 2 and 3), (5) the ratio of saturate-to-aromatic hydrocarbons, and (6) the ratio of total hydrocarbons-to-organic-carbon (hydrocarbon yield) in each rock sample.

The molecular size distribution of the intermediate and heavy (C_{13} – C_{33}) n-paraffins present in the saturated hydrocarbon fractions was determined by gas-liquid chromatography. The total alkane fractions were analyzed with a programmed temperature run from 115°C to 265°C at 6°/minute (held isothermally at 115° for 2 minutes and at 265° for 12 minutes) on a Perkin-Elmer Model 990 Gas Chromatograph equipped with dual flame ionization detectors and 8′ x ⅛″ copper columns coated with SE-30 silicone gum. Peak identities were determined by a series of co-injections with reference n-paraffin standards. All patterns were obtained by injecting a 4 μl of sample
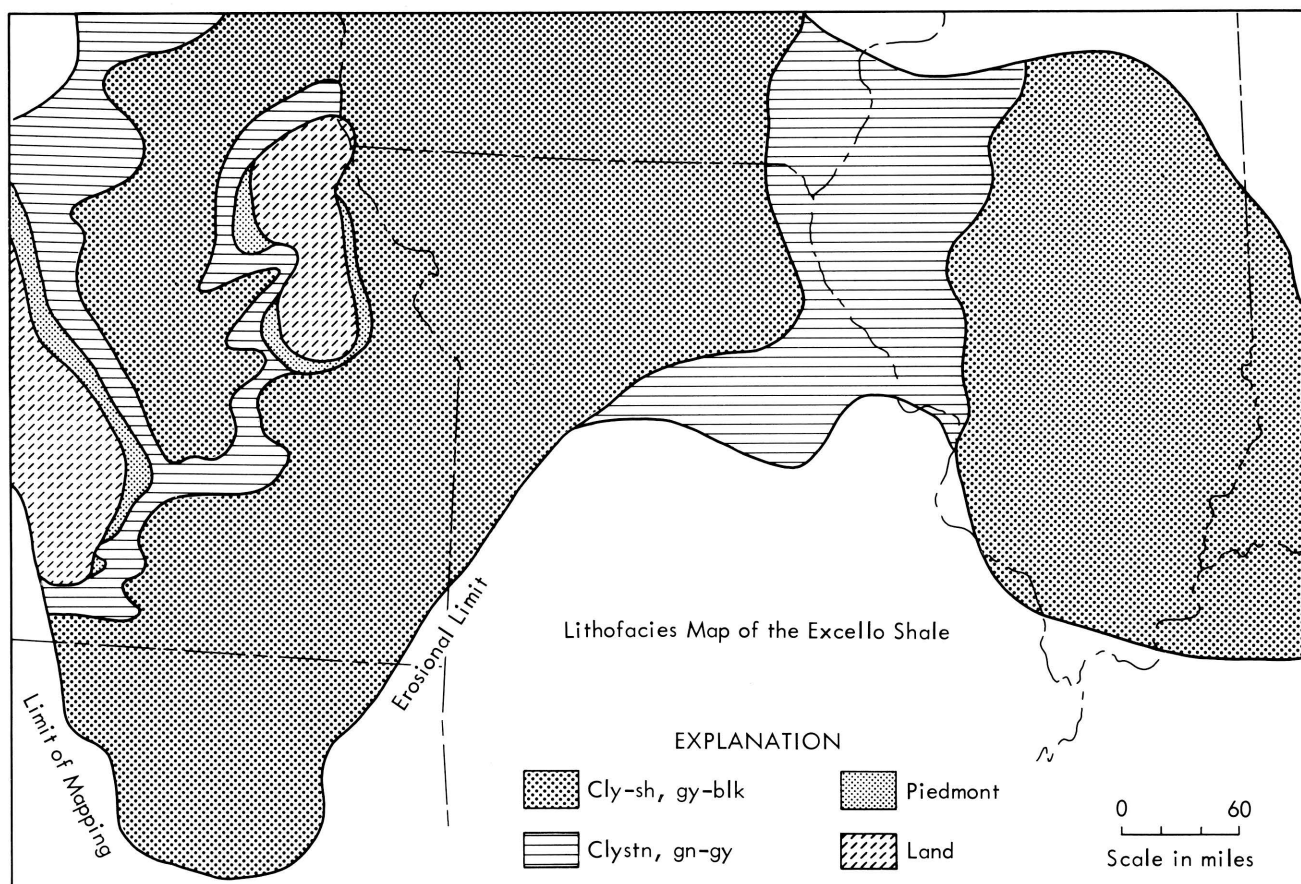
FIGURE 2.—Lithofacies map of Excello Shale in Midcontinent and Illinois basin. Modified from Weiner (1961) and Gamble (1968).

(solvent/extract = 1 ml hexane per 20 mg extract) and attenuating by a factor of 200. Comparison of the patterns from the total alkane fractions with patterns obtained by urea adduction and molecular sieving indicated resolution was such that the branched and cyclic compounds did not interfere with the peaks from the straight chain normal paraffins. No identities of the iso-paraffins and cyclo-paraffins were determined.

It has not been possible to establish the accuracy of the results of the procedure for the determination of sediment hydrocarbons because there are no suitable standards available. However, the procedures utilized in this investigation parallel those used by Baker (1962) and Baker *et al.* (1969), so that the data obtained in each of these investigations may be directly compared. Ferguson (1962) discussed the problems of making these measurements and presented precision data for the extraction and elution chromatographic procedures; the analytical errors (expressed as coefficient of variation[3]) for the organic carbon analyses and the hydrocarbon determinations are expected to be less than 5 percent and

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[3] Coefficient of variation (V) = (S/X) x 100%, where S = the standard deviation, X = the mean.

10 percent, respectively, at the concentration levels present in the Excello.

SAMPLING

Composite samples of the Excello from 12 widespread localities were prepared for analysis to provide regional data: 5 from core sections in the Midcontinent which overlie marine limestone, 3 from outcrop sections in the eastern portion of the Midcontinent which overlie coal, and 4 from core sections in the Illinois basin which also overlie coal. The distribution of these samples in the Midcontinent and the Illinois basin with respect to Middle Pennsylvanian structural features is shown in Figure 3.

RESULTS

The results of the organic carbon and hydrocarbon analyses are shown in Table 1. Organic carbon analyses are presented in weight percent; extraction and elution chromatographic data are shown as total hydrocarbons (ppm), saturated-hydrocarbons (ppm), aromatic-hydrocarbons (ppm), and as the ratios of saturated-to-aromatic hydrocarbons and hydrocarbons-to-organic carbon (times 10^{-2}). The relationship between the odd-carbon-numbered normal-par-

FIGURE 3.—Middle Pennsylvanian structural features and distribution of samples in Midcontinent and Illinois basin. Sample location index letters refer to samples listed in Table 1.

TABLE 1.—Organic composition of Excello Shale.

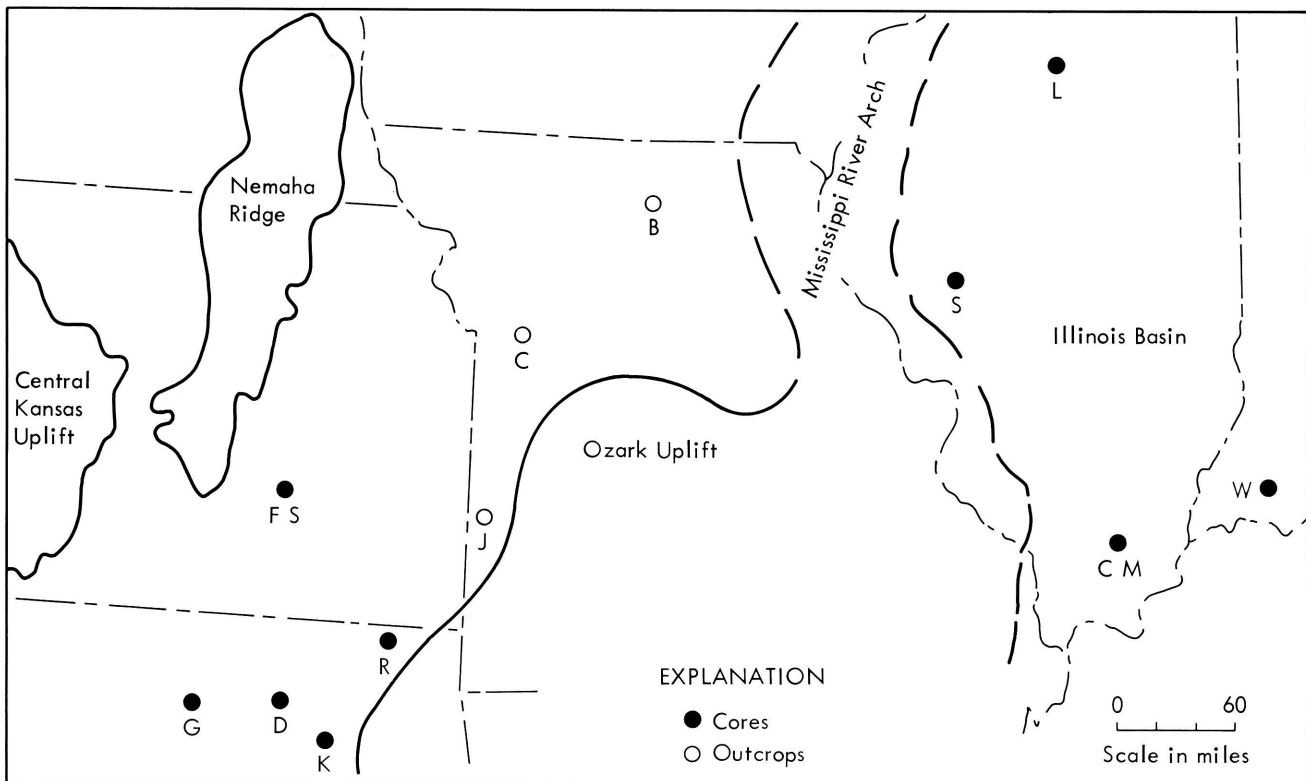|	Org C %	HC ppm	Sat ppm	Aro ppm	Sat/ Aro	HC/Org C(10^{-2})	CPI
Midcontinent							
Gross (G)	7.5	2750	1435	1315	1.09	3.66	1.02
Ft. Scott (FS)	6.6	2115	965	1150	0.84	3.20	1.00
Kelly (K)	11.0	3415	1450	1965	0.74	3.10	1.00
Drummond (D)	10.4	3060	1310	1750	0.75	2.94	1.03
Rexwinkle (R)	11.0	3250	1475	1775	0.83	2.95	1.05
Jones Quarry (J)	15.4	4215	1600	2615	0.61	2.74	1.15
Concordia (C)	7.8	1535	615	920	0.67	1.97	1.16
Bevier (B)	12.5	2430	1000	1430	0.70	1.94	1.08
Illinois Basin							
Carrier Mill (CM)	15.2	3260	1365	1895	0.72	2.14	1.15
Warrick (W)	18.5	2455	985	1470	0.67	1.33	1.08
Sangamon (S)	17.0	1945	795	1150	0.69	1.14	1.05
LaSalle (L)	7.0	625	250	375	0.67	0.89	1.13

affins and the even-carbon-numbered normal-paraffins is characterized by the carbon preference index (CPI) value, calculated according to Kvenvolden (1966).[4] Table 2 summarizes the data by averaging the results obtained from samples in the Midcontinent and the Illinois basin; the data from one coal analysis are included for comparative purposes.

Statistically, the differences of the mean values for the organic carbon and hydrocarbon contents of the Excello Shale samples in the Midcontinent and the Illinois basin do not appear to be significant; however, the following observations may be made from the data in Tables 1 and 2:

1. The organic carbon content of the dark-gray/black phosphatic Excello Shale is quite high throughout the Midcontinent and the Illinois basin. Although it ranges from 6.6 to 18.5 percent, it appears to be higher in the Illinois basin than in the Midcontinent region (averaging 14.4 percent vs. 10.3 percent).

2. The total hydrocarbon content of the Excello is also quite high throughout the Midcontinent and

[4] $\mathrm{CPI} = \frac{1}{2} \left(\frac{\Sigma \text{ conc. odd } C_{17} \text{ to } C_{31}}{\Sigma \text{ conc. even } C_{16} \text{ to } C_{30}} + \frac{\Sigma \text{ conc. odd } C_{17} \text{ to } C_{31}}{\Sigma \text{ conc. even } C_{18} \text{ to } C_{32}} \right)$

the Illinois basin (ranging from 625 to 4215 ppm), but, unlike the organic carbon, appears to be higher in the Midcontinent than in the Illinois basin (averaging 2845 ppm vs. 2070 ppm).

3. The saturate-to-aromatic hydrocarbon ratios of the Excello throughout both the Midcontinent and the Illinois basin are fairly low (ranging from 0.61 to 1.09) and are not quite as variable as the organic carbon and hydrocarbon values. However, as is illustrated in Figure 4, the ratios tend to be somewhat higher in the Midcontinent, especially throughout the western portion where the Excello overlies marine carbonates.

4. The hydrocarbon/organic carbon ratios ("hydrocarbon yield"), as illustrated in Figure 5, are quite variable (ranging from 0.89 to 3.66), but are particularly high in the western portion of the Midcontinent and tend to decrease progressively eastward across the Midcontinent into the Illinois basin.

5. The carbon preference index (CPI) values of the n-paraffins from C_{16} to C_{32} approach unity and are extremely uniform (ranging from 1.00 to 1.16) throughout the Excello.

TABLE 2.—Average regional organic composition of Excello Shale.

	Org C %	HC ppm	Sat/Aro	HC/Org C ($\times 10^{-2}$)	CPI
Midcontinent					
8 samples	10.3	2845	0.78	2.81	1.06
s.d.	3.0	835	0.14	0.61	0.06
Illinois Basin					
4 samples	14.4	2070	0.69	1.38	1.10
s.d.	5.1	1060	0.02	0.44	0.05
Warrick Coal	65.5	8890	0.30	1.35	

The average molecular weight distributions of the n-paraffins in the Midcontinent and the Illinois basin are illustrated in Figure 6. The n-paraffins occur predominantly in the C_{15} to C_{20} range and tail off in a somewhat smooth distribution curve to C_{33}. The overall distribution curves of the n-paraffins are fairly similar throughout the Excello. It should be noted that the extraction and isolation techniques utilized in this study prohibit quantitative recovery of the n-paraffins with molecular weights less than C_{15}.

INTERPRETATION

The data obtained from this investigation indicate that the Excello Shale contains varying amounts of organic carbon which can be characterized by differ-
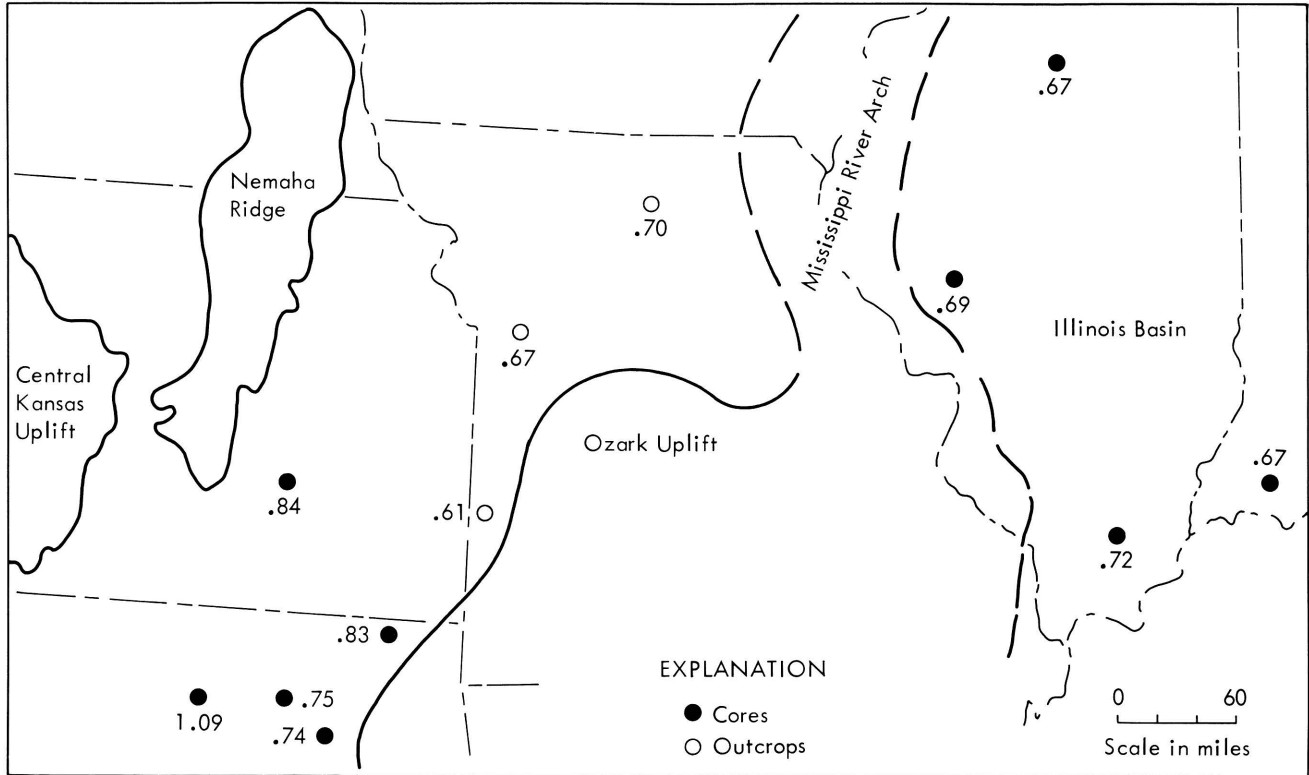
FIGURE 4.—Distribution of saturated-to-aromatic hydrocarbon ratios of Excello Shale in Midcontinent and Illinois basin.
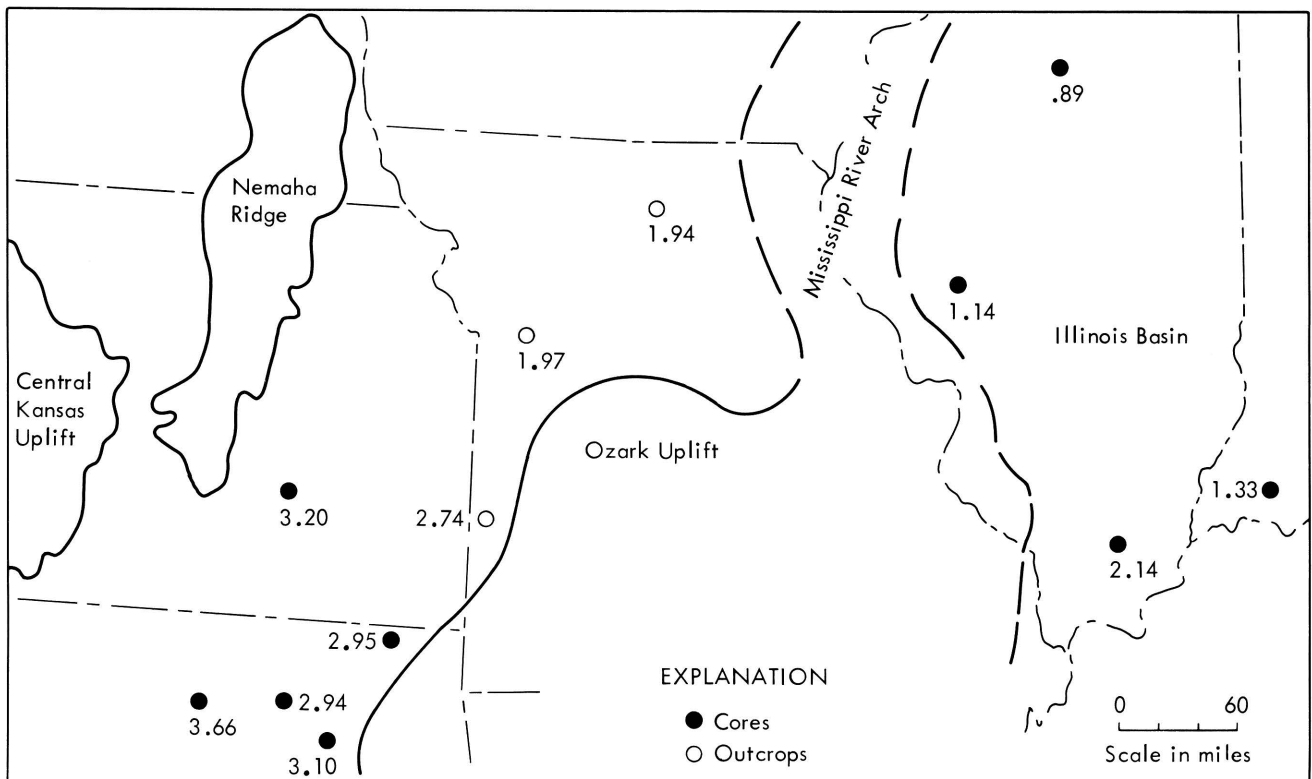

FIGURE 5.—Distribution of hydrocarbon-to-organic carbon ratios (times 10^{-2}) of Excello Shale in Midcontinent and Illinois basin.
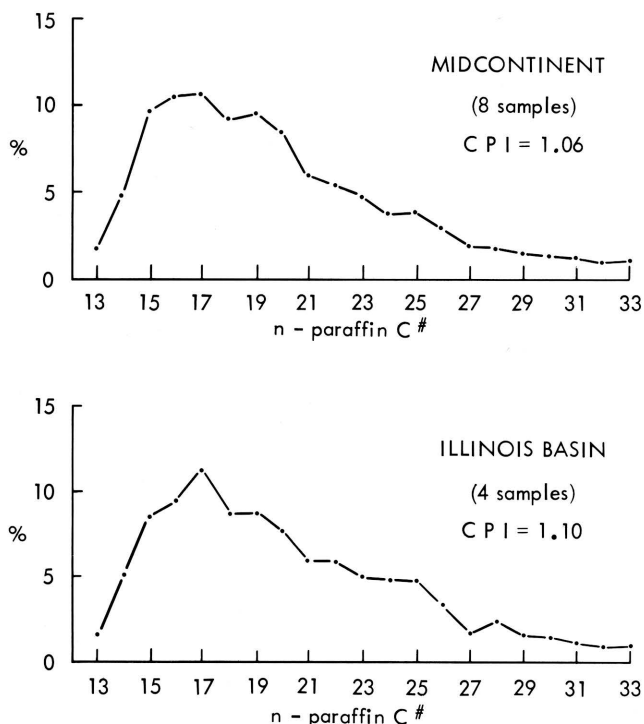
FIGURE 6.—Average n-paraffin distribution of Excello Shale in Midcontinent and Illinois basin.

ences in hydrocarbon yields and, to a limited extent, saturate-to-aromatic ratios. These differences appear to be regional in nature; i.e., the Excello present in the Illinois basin tends to contain greater amounts of organic carbon than does the Excello in the Midcontinent, but has lower hydrocarbon-to-organic carbon ratios and slightly lower saturate-to-aromatic ratios. The differences in the amounts of organic carbon incorporated in the shale reflect source supply, as the relatively large amounts of organic carbon (greater than 6 percent) indicate highly reducing environmental conditions were prevalent in both the Midcontinent and the Illinois basin. The variations in the hydrocarbon yields and the saturate-to-aromatic ratios, however, may be due to (1) differences in the original organic source material (i.e., marine vs. terrestrial) or (2) differences in the maturation history of the Excello in the Midcontinent and the Illinois basin, or a combination of both.

The maturation history of organic material in a sediment is primarily related to the duration and intensity of its thermal history. Two of the more important effects of the maturation process are the generation of additional hydrocarbons in the sediment and the gradual disappearance of the odd-carbon-number predominance in the normal paraffins (straight chain saturated hydrocarbons with the formula C_nH_{2n+2}).

These changes increase the hydrocarbon-to-organic carbon ratio and cause the CPI value to approach unity. The similarities of the CPI values and the distribution curves of the C_{16}-C_{32} normal paraffins of the Excello indicate that the post-depositional maturation history of the Excello present in the Illinois basin has been essentially equivalent to that of the Excello in the Midcontinent region. Since the thermal history of a sediment is dependent on two factors, geothermal gradient and depth of burial, it seems likely that the organic material in the Excello in both areas should be in the same maturation stage, as the Excello has been subjected to relatively shallow burial depths and as it is not unreasonable to assume that the Midcontinent and the Illinois basin have had similar geothermal gradients since late Paleozoic time.

The interpretation of the results from this study in terms of organic source differences may be aided by first examining the summary of similar data obtained by Baker *et al.* (1969) on different lithologic units present in the Cherokee cyclothems of the Midcontinent. Such a comparison is warranted since these units were deposited during Middle Pennsylvanian time and hence the original organic source material, whether terrestrial plants or marine algae, presumably had similar components which yielded saturated and aromatic hydrocarbons similar to the hydrocarbons generated from the organic material which contributed to the formation of the Excello Shale.

As is shown in Table 3, the extractable organic material present in the different Cherokee rock types displays a fairly wide range of saturate-to-aromatic ratios and hydrocarbon yields. Limestones, deposited in warm, shallow, oxygenated waters free from terrestrial influx, contain very little organic carbon, but have very high saturate-to-aromatic ratios and hydro-

TABLE 3.—Organic composition of the Cherokee lithologic units.

Lithology	Org C %	HC ppm	Sat/Aro	HC/Org C ($\times 10^{-2}$)
Limestone	0.19	423	2.1	30.8
s.d.	0.14	239	0.6	33.6
Foss. Shale	1.17	384	1.5	3.4
s.d.	0.15	78.5	0.1	1.0
Blk PO₄ Shale	10.85	3695	1.4	3.4
s.d.	1.04	849	0.4	0.8
Cly-Slt Shale	1.05	211	0.9	2.1
s.d.	0.30	78.1	0.2	0.6
Coal	58.3	2648	0.4	0.5
s.d.	3.6	733	0.1	0.1

Data from Baker *et al.*, 1969; published with permission of the Marathon Oil Co.

carbon yields. At the other extreme, with very low saturate-to-aromatic and hydrocarbon yields, are the carbon-rich coals which accumulated primarily from the decay of terrestrial plants. The clay-silt shales, with visible carbonized plant remains, have fairly low saturate-to-aromatic ratios and hydrocarbon yields. The calcareous fossiliferous shales, generally deposited in slightly oxidizing marine waters, and the phosphatic black shales, deposited in highly reducing marine environments, have similar saturate-to-aromatic ratios and hydrocarbon yields, despite the fact that the black shales contain approximately ten times the amount of organic carbon that is present in the calcareous shales. Presumably the organic material present in these shales, as in most modern shales, represents the remains of marine plankton somewhat diluted by the remains of terrestrial plants carried to the site of deposition.

While the hydrocarbon yields and the saturate-to-aromatic ratios of the Excello Shale in the Midcontinent are lower than the average values reported by Baker _et al._ (1969), the hydrocarbon yields and the saturate-to-aromatic ratios of the Excello present in the Illinois basin are much lower, and are only slightly higher than the average values of the coals. This difference suggests that in addition to the high-yield, saturate-rich "sapropelic" type of organic material derived principally from phytoplankton and zooplankton and the fatty tissues of animals, greater amounts of low-yield, aromatic-rich "humic" material derived from the woody parts of plants (cellulose and lignin) were incorporated into the Excello Shale present in the Illinois basin.

ACKNOWLEDGMENTS

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APPENDIX: Section Locations

Illinois Basin

Warrick (W) core	35-4S-8W	Warrick Co., Ind.
Carrier Mills (CM) core	4-10S-5E	Saline Co., Ill.
Sangamon (S) core	17-13N-5W	Sangamon Co., Ill.
LaSalle (L) core	15-30N-2E	LaSalle Co., Ill.

Midcontinent

Bevier (B) outcrop	24-56N-15W	Macon Co., Mo.
Concordia (C) outcrop	35-49N-25W	Lafayette Co., Mo.
Jones Quarry (J) outcrop	7-34N-32W	Vernon Co., Mo.
Fort Scott (FS) core	31-23S-10E	Greenwood Co., Kan.
Rexwinkle (R) core	30-29N-18E	Craig Co., Okla.
Drummond (D) core	4-23N-10E	Osage Co., Okla.
Gross (G) core	34-25N-14E	Osage Co., Okla.
Kelly (K) core	23-20N-14E	Rogers Co., Okla.

JOHN C. HALEPASKA
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Numerical Solution of the 3-Dimensional Heat Flow Equation

ABSTRACT

A numerical differencing scheme is outlined that gives the investigator a fast, accurate research tool. The scheme uses an extrapolation routine coupled with a line solution technique to solve the heat flow equation. The technique applies equally well to line or plane symmetry: 2-dimensional as well as fully 3-dimensional problems.

Heat flow problems are commonly handled in an analytical fashion, e.g., as in Carslaw and Jaeger (1959) and Ingersoll, *et al.* (1954). However, many problems in heat flow cannot be handled in a classical fashion and various finite difference techniques must be used. Explicit, successive over relaxation and alternating direction implicit (ADI) techniques are commonly employed differencing schemes used in the solution of heat or fluid flow problems (e.g., see Smith, 1965; Zienkiewicz, 1967; Carnahan, *et al.*, 1969; Von Rosenberg, 1969). Depending upon the problem, various differencing forms are superior to others in terms of computer time, accuracy, or general ease of programming.

The primary purpose of this investigation was to develop a differencing scheme that is fast, has a high order of accuracy, and is simple to iterate provided that the non-linear form of the heat flow equation is the solution objective.

The differential equation of heat flow can be expressed as

$$\frac{\partial}{\partial x}\left(\kappa\frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(\kappa\frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial z}\left(\kappa\frac{\partial T}{\partial z}\right) + Q = C_p\,\rho\,\frac{\partial T}{\partial t} \qquad (1)$$

where

  T = temperature ($^\circ$F)
  t = time T
  Q = heat generation rate per unit volume
      Btu/L^3-T
  C_p = specific heat Btu/lb-$^\circ$F
  ρ = density lb/L^3
  κ = thermal conductivity Btu/T-L-$^\circ$F

The Crank-Nicholson differencing scheme is used to approximate (1). This scheme is unconditionally

stable and has an error of

$$e = O\,(\Delta x^2) + O\,(\Delta y^2) + O\,(\Delta z^2) + O\,(\Delta t^2).$$

The resulting system of linear equations forms a tridiagonal matrix that is solved using the Thomas algorithm (see, for example, Von Rosenberg, 1969). The linear equations require two unknown values of temperature at the n+1 time step, the unknown values of temperature are extrapolated and the equations solved for the n+1 time. The extrapolation routine used is

$$T_{i,j,k}^{n+2} = T_{i,j,k}^{n+1} + \frac{\Delta t^{n+\frac12}}{\Delta t^{n-\frac12}}\,(T_{i,j,k}^{n+1} - T_{i,j,k}^{n})$$

The computed value of temperature is compared to the extrapolated value and if the differences are greater than some epsilon, the computed value replaces the extrapolated value and the computer solves the linear equations again. This iterate term is compared again and the iterations continue until the difference between two successive iterates is below epsilon.

The difference equation is:

$$\frac{1}{\Delta x_i}\left[K_{i+\frac12}\frac{(T_{i+1,j,k}^{n+\frac12} - T_{i,j,k}^{n+\frac12})}{\Delta x_{i+\frac12}} - K_{i-\frac12}\frac{(T_{i,j,k}^{n+\frac12} - T_{i-1,j,k}^{n+\frac12})}{\Delta x_{i-\frac12}}\right] +$$

$$\frac{1}{\Delta y_j}\left[K_{j+\frac12}\frac{(T_{i,j+1,k}^{n+\frac12} - T_{i,j,k}^{n+\frac12})}{\Delta y_{j+\frac12}} - K_{j-\frac12}\frac{(T_{i,j,k}^{n+\frac12} - T_{i,j-1,k}^{n+\frac12})}{\Delta y_{j-\frac12}}\right] +$$

$$\frac{1}{\Delta z_k}\left[K_{k+\frac12}\frac{(T_{i,j,k+1}^{n+\frac12} - T_{i,j,k}^{n+\frac12})}{\Delta z_{k+\frac12}} - K_{k-\frac12}\frac{(T_{i,j,k}^{n+\frac12} - T_{i,j,k-1}^{n+\frac12})}{\Delta z_{k-\frac12}}\right] = \qquad (2)$$

$$\frac{(T_{i,j,k}^{n+1} - T_{i,j,k}^{n})}{\Delta t^{n+\frac12}}\,(C_p\,\rho)_{i,j,k}$$

and K_i, K_j, K_k are $\kappa_{x(i,j,k)}$, $\kappa_{y(i,j,k)}$, and $\kappa_{z(i,j,k)}$ respectively; and κ_x, κ_y, κ_z are the thermal conductivities for the x, y, and z directions in node (i,j,k). $(C_p\,\rho)_{i,j,k}$ is the specific heat times the density in node (i,j,k). Defining:

$$T_{i,j,k}^{n+\frac12} = \tfrac12\,(T_{i,j,k}^{n+1} + T_{i,j,k}^{n}) \qquad (3)$$

and assuming (in this development) equal spacing in each layer ($\Delta x = \Delta y$) and constant spacing in all

directions, then:

$$\Delta x_i = \Delta x_{i+1}$$
$$\Delta y_j = \Delta y_{j+1}$$
$$\Delta z_k = \Delta z_{k+1}$$

$$\frac{1}{\Delta x_i \Delta x_{i+\frac{1}{2}}} = \frac{1}{\Delta x^2} = \frac{1}{\Delta y^2} = \frac{1}{\Delta z^2} \tag{4}$$

and similar equations can be developed for spacing, i−½, j+½, j−½, k−½, k+½. We also can define:

$$K_{i+\frac{1}{2}} = \frac{2\,K_{i+1}\,K_i}{K_{i+1} + K_i} \tag{5}$$

and here also similar equations can be developed for conductivities at i−½, j+½, j−½, k+½, k−½.

For simplicity let

$$A_i = \frac{1}{\Delta x^2} = \frac{1}{\Delta y^2} \tag{6}$$

$$B_k = \frac{1}{\Delta z^2} \tag{7}$$

$$AX_{i+1,j,k} = K_{i+\frac{1}{2}} = \frac{2K_{i+1}\,K_i}{K_{i+1} + K_i} \tag{8}$$

$$BX_{i-1,j,k} = K_{i-\frac{1}{2}} = \frac{2K_{i-1}\,K_i}{K_{i-1} + K_i} \tag{9}$$

$$CX_{i,j+1,k} = K_{j+\frac{1}{2}} = \frac{2K_{j+1}\,K_j}{K_{j+1} + K_j} \tag{10}$$

$$DX_{i,j-1,k} = K_{j-\frac{1}{2}} = \frac{2K_{j-1}\,K_j}{K_{j-1} + K_j} \tag{11}$$

$$EX_{i,j,k+1} = K_{k+\frac{1}{2}} = \frac{2K_{k+1}\,K_k}{K_{k+1} + K_k} \tag{12}$$

$$FX_{i,j,k-1} = K_{k-\frac{1}{2}} = \frac{2K_{k-1}\,K_k}{K_{k-1} + K_k} \tag{13}$$

$$E_{i,j,k} = \frac{2(Cp\ \rho)_{i,j,k}}{\Delta t} \tag{14}$$

$$Q'_{i,j,k} = \frac{2Q_{i,j,k}}{\Delta x^2 \Delta z} \tag{15}$$

Substituting into equation (2), collecting like terms, and simplifying yields:

$$A_i AX_{i,j,k} (T^{n+1}_{i+1,j,k} - T^{n+1}_{i,j,k}) - A_i BX_{i,j,k} (T^{n+1}_{i,j,k} - T^{n+1}_{i-1,j,k})$$

$$+ A_i CX_{i,j,k} (T^{n+1}_{i,j+1,k} - T^{n+1}_{i,j,k}) - A_i DX_{i,j,k} (T^{n+1}_{i,j,k} - T^{n+1}_{i,j-1,k}) +$$

$$B_k EX_{i,j,k} (T^{n+1}_{i,j,k+1} - T^{n+1}_{i,j,k}) - B_k FX_{i,j,k} (T^{n+1}_{i,j,k} - T^{n+1}_{i,j,k-1}) =$$

$$\tag{16}$$

$$- A_i AX_{i,j,k} (T^n_{i+1,j,k} - T^n_{i,j,k}) + A_i BX_{i,j,k} (T^n_{i,j,k} - T^n_{i-1,j,k})$$

$$- A_i CX_{i,j,k} (T^n_{i,j+1,k} - T^n_{i,j,k}) + A_i DX_{i,j,k} (T^n_{i,j,k} - T^n_{i,j-1,k})$$

$$- B_k EX_{i,j,k} (T^n_{i,j,k+1} - T^n_{i,j,k}) + B_k FX_{i,j,k} (T^n_{i,j,k} - T^n_{i,j,k-1})$$

$$+ E_{i,j,k} (T^{n+1}_{i,j,k} - T^n_{i,j,k}) - Q'_{i,j,k}$$

Letting $G_{i,j,k}$ equal all the terms on the right-hand side except $E_{i,j,k}$, equation (16) can be rewritten as follows:

$$- T^{n+1}_{i,j,k} (A_i AX_{i,j,k} + A_i BX_{i,j,k} + A_i CX_{i,j,k} + A_i DX_{i,j,k}$$

$$+ B_k EX_{i,j,k} + B_k FX_{i,j,k} + E_{i,j,k}) + A_i CX_{i,j,k}$$

$$\tag{17}$$

$$T^{n+1}_{i,j+1,k} + A_i DX_{i,j,k}\ T^{n+1}_{i,j-1,k} = G_{i,j,k} - E_{i,j,k}\ T^n_{i,j,k}$$

$$- A_i AX_{i,j,k}\ T^{n+1}_{i+1,j,k} - A_i BX_{i,j,k}\ T^{n+1}_{i-1,j,k} - B_k EX_{i,j,k}\ T^{n+1}_{i,j,k+1}$$

$$- B_k FX_{i,j,k}\ T^{n+1}_{i,j,k-1}$$

If we let all terms to the right of the equal sign equal $H_{i,j,k}$ and define the coefficient of $T^{n+1}_{i,j,k}$ as Del′, then:

$$- T^{n+1}_{i,j,k}\ Del' + A_i CX_{i,j,k}\ T^{n+1}_{i,j+1,k} + A_i DX_{i,j,k}\ T^{n+1}_{i,j-1,k} = H_{i,j,k}$$

$$\tag{18}$$

The system of equations as presented in the form of equation (18) is then solved using the Thomas algorithm for tridiagonal matrices. (For explanation of the algorithm, see Smith, 1965; Von Rosenberg, 1969.)

Introducing X and Y as coefficients in the Thomas algorithm, we obtain:

$$T^{n+1}_{i,j-1,k} = X_{j-1}\ T^{n+1}_{i,j,k} + Y_{j-1} \tag{19}$$

and substituting equation (19) into equation (18) we obtain:

$$- Del'\ T^{n+1}_{i,j,k} = H_{i,j,k} - A_i CX_{i,j,k}\ T^{n+1}_{i,j+1,k} - A_i DX_{i,j,k}\ X_{j-1}\ T^{n+1}_{i,j,k}$$

$$- A_i DX_{i,j,k}\ Y_{j-1} \tag{20}$$

solving for $T^{n+1}_{i,j,k}$ yields:

$$T^{n+1}_{i,j,k} = - \frac{(H_{i,j,k} - A_i DX_{i,j,k}\ Y_{j-1} - A_i CX_{i,j,k}\ T^{n+1}_{i,j+1,k})}{Del' - A_i DX_{i,j,k}\ X_{j-1}} \tag{21}$$

letting $\quad Del = Del' - A_i DX_{i,j,k}\ X_{j-1}$

then:

$$T^{n+1}_{i,j,k} = \frac{A_i CX_{i,j,k}\ T^{n+1}_{i,j+1,k} + A_i DX_{i,j,k}\ Y_{j-1} - H_{i,j,k}}{Del} \tag{22}$$

since

$$T^{n+1}_{i,j,k} = X_j\ T^{n+1}_{i,j+1,k} + Y_j \tag{23}$$

$$X_j = \frac{A_i CX_{i,j,k}}{Del} \tag{24}$$

$$Y_j = \frac{A_i DX_{i,j,k}\ Y_{j-1} - H_{i,j,k}}{Del} \tag{25}$$

After a solution for T^{n+1} is obtained in a given row, the next row in the same layer is solved. After a solution is produced for each layer, the routine proceeds to solve the next lower layer in the same manner. This procedure continues until a complete block of space is solved at the n+1 time step (see Fig. 1 and 2). When a T^{n+1} time level is solved (the entire grid is satisfied for some sigma), the time step is increased as: $\Delta t^{n+2} = \phi \Delta t^{n+1}$ where ϕ ranges from 1. to about 6. depending upon the boundary conditions and spacing. Time is advanced as: $\text{Time}^{n+2} = \text{Time}^{n+1} + \Delta t^{n+2}$. The T^{n+1} values are substituted into the T^n array and new T^{n+2} values are solved. This procedure continues until either a predetermined time span is satisfied or until the number of computation cycles is satisfied.
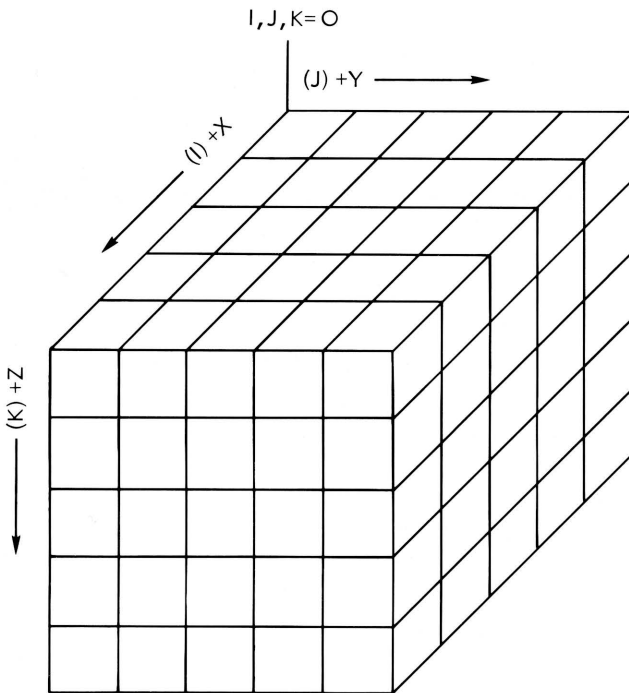
FIGURE 1.—Coordinate and grid system used in the analysis.

A simple program using the preceding developed coefficients is available (Halepaska and Hartman, 1971) upon request.

The heat flow equation in rz geometry is

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\kappa\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial y}\left(\kappa\frac{\partial T}{\partial y}\right) + Q = Cp\,\rho\,\frac{\partial T}{\partial t} \qquad (26)$$
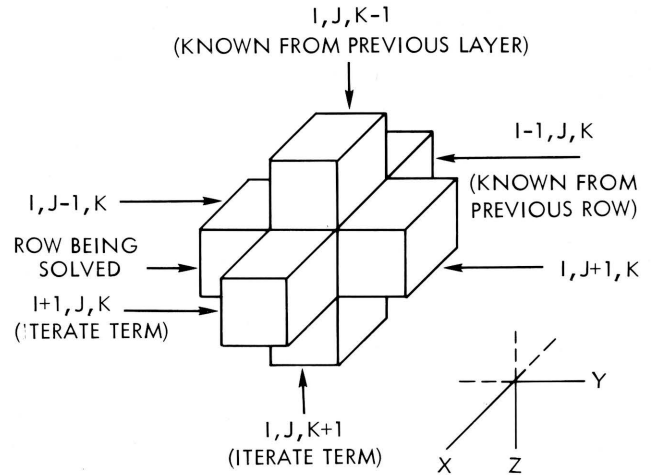
FIGURE 2.—Solution block and coordinate system used in the analysis.

Let $u = \ln\frac{r}{r_w}$, then equation (26) takes the form

$$\frac{e^{-2u}}{r_w^2}\frac{\partial}{\partial u}\left(\kappa\frac{\partial T}{\partial u}\right) + \frac{\partial}{\partial y}\left(\kappa\frac{\partial T}{\partial y}\right) + Q = Cp\,\rho\,\frac{\partial T}{\partial t} \qquad (27)$$

where u = dimensionless length

r_w = some basic dimension (radius of the source or sink term for example).

Use of the transformation on the radial part of the differential equation allows the investigator to go from line symmetry (r,y) to plane symmetry (x,y) in an efficient manner. It also provides for equal grid spacing in either plane or cylindrical symmetry.

The same procedures outlined in the differencing of the 3-dimensional equation hold for equation (27).

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Brine Leaching of the Heebner Shale (Upper Pennsylvanian) of Kansas

ABSTRACT

Leaching studies on samples of the Heebner Shale indicate the mobilization of trace elements such as Ni, Co, Mn, and Zn in the presence of chloride brines. The length of time the brines were in contact with the shale as well as the effect of increased temperature was studied. Increased temperature and the presence of SO_4^{-2} improved leaching ability for the chloride brines. Tabulated results show that when some Kansas oil field brines were left in contact with the Heebner Shale for 3 days at a temperature of 80°C, as much as 2.94 ppm Mn, 2.26 ppm Fe, 0.20 ppm Co, 0.53 ppm Ni, 0.10 ppm Cu, and 8.98 ppm Zn was extracted.

INTRODUCTION

Black shales represent large volumes of potential sources of a variety of trace elements. The geochemical mobility of trace elements associated with black shales is determined by the extent to which these elements are fixed in the shales compared to the ability of reacting fluids to produce soluble species of these elements. Many of the trace elements associated with black shales have the ability to form chloride complexes which are soluble in aqueous solutions. This study represents an effort to determine the solubility behavior, and thus mobility, in chloride brines of some of the trace elements (Cr, Mn, Fe, Co, Ni, Cu, Zn, and Pb) which are associated with the black shale of the Heebner. A suitable method for the determination of trace elements in chloride brines has been described by Galle (1971) and this method has been employed here to determine the trace element concentrations in the brine leach solutions.

EXPERIMENTAL METHOD

Samples of the Heebner Shale Member of the Oread Limestone used in this study were taken from a road cut at the SE corner of Lone Star Lake (NE NW sec. 23, T 14 S, R 18 E), Douglas County, Kansas. Large pieces of apparently unweathered shale were rinsed with distilled water, dried at 110°C, pulverized in a titanium carbide shatter box and mixed

together. Solutions used consisted of three synthetic chloride brines, distilled water, and three oil field brines—R. Hays #1 (upper "Squirrel sandstone"), R. Hays #2 (upper "Squirrel sandstone"), and Kerr-Magee ("Cherokee sand").

In the leaching studies 20 g of shale per 100 ml of brine solution were placed in stoppered flasks and allowed to stand, with occasional shaking, for periods of 1-9 days. The flasks were maintained at either room temperature (24°C) or 80°C during the leaching period. After an appropriate length of time, the samples were centrifuged and then filtered through a 0.45μ filter. The pH of the filtrates was adjusted to 4.5 and separation of the trace elements in 100-ml aliquots of the filtrates was achieved using columns of Dowex A-1 chelating resin adjusted to a pH of 4.5. Elemental analyses were achieved by atomic absorption.

A 1-g sample of shale for the determination of total trace element concentration in the shale was treated three times with 5 ml of 48 percent HF and 5 drops H_2SO_4, and taken to dryness after each treatment. Next, 150 ml of 10 percent H_2O_2 was added, stirred, and left overnight. The solution was treated with 20 ml of concentrated HCl, warmed, and filtered. The filtrate volume was reduced to 100 ml, using a flash rotary evaporator, and analyzed directly by atomic absorption.

One 20-g sample of shale was treated with four 100-ml portions of brine to determine effect of successive leachings upon a single sample. Each time the brine and shale were in contact for 24 hours.

The compositions of the synthetic brines are given in Table 1. Brine A corresponds to a synthetic sea water. The oil field brines were found to be low in SO_4^{-2} and had Cl^- concentrations of 50,000-70,000 ppm.

RESULTS AND DISCUSSION

The concentrations of trace elements found in the leach solutions under varying conditions are given in

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TABLE 1.—Ionic composition of synthetic brines.

Brine	Na+, ppm	Mg+2, ppm	Ca+2, ppm	K+, ppm	Cl-, ppm	SO_4^{-2}, ppm	Br-, ppm	Total solids g/l
A	10,900	1,300	410	390	19,600	2,700	70	33.58
B	19,900	40	260	_____	30,700	710	____	52.06
C	23,400	466	990	_____	33,100	8,400	____	69.46

Tables 2-4. For comparison, the concentrations of trace elements solubilized by HF-H₂O₂-HCl treatment are listed in Table 5. Coefficients of variation for the various elements determined in the leach solutions are given in Table 6.

TABLE 2.—Leaching data for synthetic brines.

Distilled Water

Trace element	Brine only	Concentration in solution, ppm			
		3 days 24°C	6 days 24°C	9 days 24°C	3 days 80°C
Cr	_____	N.D.*	N.D.	N.D.	N.D.
Mn	_____	0.14	0.18	0.25	1.42
Fe	_____	0.14	0.19	0.27	0.38
Co	_____	N.D.	N.D.	N.D.	0.06
Ni	_____	0.10	0.11	0.26	0.33
Cu	_____	0.03	0.03	0.09	0.09
Zn	_____	0.18	0.59	0.98	2.96
Pb	_____	N.D.	N.D.	N.D.	N.D.

Brine A

Cr	N.D.	N.D.	N.D.	N.D.	N.D.
Mn	0.02	2.38	2.61	3.79	5.29
Fe	0.11	0.18	0.12	0.22	2.99
Co	N.D.	0.13	0.08	0.18	0.25
Ni	0.07	0.45	0.44	0.65	0.80
Cu	0.04	0.05	0.04	0.13	0.10
Zn	0.43	13.0	6.86	4.09	9.72
Pb	N.D.	N.D.	N.D.	N.D.	N.D.

Brine B

Cr	N.D.	N.D.	N.D.	N.D.	_____
Mn	0.02	2.04	2.06	3.42	_____
Fe	0.10	0.18	0.14	0.14	_____
Co	N.D.	0.08	0.11	0.18	_____
Ni	0.06	0.38	0.36	0.65	_____
Cu	0.06	0.04	0.10	0.10	_____
Zn	0.17	4.20	3.40	3.71	_____
Pb	N.D.	N.D.	N.D.	N.D.	_____

Brine C

Cr	N.D.	N.D.	N.D.	N.D.	N.D.
Mn	0.01	2.52	2.79	4.21	5.70
Fe	0.11	0.14	0.16	0.18	3.90
Co	N.D.	0.11	0.10	0.26	0.27
Ni	0.07	0.50	0.56	0.91	0.82
Cu	0.04	0.05	N.D.	0.10	0.11
Zn	0.20	6.46	8.57	6.36	12.80
Pb	N.D.	N.D.	N.D.	N.D.	N.D.

* Not detected.

TABLE 3.—Leaching data for oil field brines.

R. Hays #1 Brine

Trace element	Concentration in solution, ppm		
	Brine only	3 days 24°C	3 days 80°C
Cr	N.D.*	N.D.	N.D.
Mn	0.18	3.02	4.94
Fe	0.11	0.12	2.26
Co	N.D.	0.13	0.20
Ni	0.07	0.43	0.53
Cu	N.D.	N.D.	0.10
Zn	0.19	8.58	8.98
Pb	N.D.	N.D.	N.D.

R. Hays #2 Brine

Cr	N.D.	N.D.	N.D.
Mn	0.02	2.82	4.89
Fe	0.09	0.14	2.02
Co	N.D.	0.14	0.19
Ni	0.07	0.50	0.69
Cu	0.03	0.02	0.12
Zn	0.19	4.07	7.99
Pb	N.D.	N.D.	0.48

Kerr-Magee Brine

Cr	N.D.	N.D.	N.D.
Mn	0.03	2.30	4.12
Fe	0.12	0.14	0.71
Co	N.D.	0.11	0.17
Ni	0.08	0.30	0.47
Cu	0.05	0.02	0.09
Zn	0.16	2.23	2.95
Pb	N.D.	N.D.	N.D.

* Not detected.

TABLE 4.—Effect of successive leaching on a single shale sample at 24°C.

R. Hays #2 Brine

Trace element	Successive leachings, concentration, ppm			
	1st	2nd	3rd	4th
Cr	N.D.*	N.D.	N.D.	N.D.
Mn	1.25	1.22	0.77	0.48
Fe	0.20	0.14	0.08	0.09
Co	0.10	0.11	0.07	0.06
Ni	0.45	0.38	0.35	0.33
Cu	0.17	0.12	0.09	0.08
Zn	2.13	1.87	1.93	1.79
Pb	N.D.	N.D.	N.D.	N.D.

* Not detected.

TABLE 5.—Trace element concentrations from HF-H₂O₂-HCl-treated shale sample.

Cr ppm*	Mn ppm*	Fe ppm*	Co ppm*	Ni ppm*	Cu ppm*	Zn ppm*	Pb ppm*
133	35.0	8080	3.92	39.0	18.1	226	18.7

* Equivalent to 20 g shale dissolved in 100 ml brine.

TABLE 6.—Coefficients of variation.

Trace element	%
Cr	5
Mn	5
Fe	11
Co	14
Ni	7
Cu	15
Zn	4
Pb	16

The elemental analyses for synthetic brines A, B, and C indicate low background concentrations of Mn, Fe, Ni, Cu, and Zn which are probably due to traces of these elements in the reagents used to achieve the ion-exchange separation of the trace elements from the leach solutions. This background was assumed to be relatively constant throughout the leaching studies, and increases in concentrations above these levels are assumed to be indicative of the effectiveness of the leaching process.

At both 24°C and 80°C, the synthetic and natural chloride brines were found to be more effective than distilled water in leaching trace metals from the Heebner Shale. As noted in Tables 2 and 3, Cr was not detected in leach solutions under any conditions, and Pb was observed in only one 80°C oil field brine extract. The concentration of Fe found in the 24°C extracts is fairly constant (range 0.09-0.27 ppm) and not greatly different from the background values obtained for the three synthetic brines (range 0.10-0.11 ppm). An increase in temperature appears to improve the effectiveness of the brines as well as that of distilled water in leaching Fe from the shale. Copper does not appear to be mobilized to any great extent by the brines at 24°C or 80°C and distilled water is observed to be about as effective as the chloride brines in removal of Cu under the conditions of temperature and shale-brine contact time used in this study.

Chloride brines appear to mobilize Mn, Co, Ni, and Zn, and are generally found to be much more effective than distilled water under similar conditions of temperature and shale-brine contact time. Increasing the temperature of the brine again is found to improve the effectiveness of the leaching process.

Maturation studies using distilled water and synthetic brines A, B, and C for periods of 3, 6, and 9 days of shale-brine contact at 24°C suggests an increase in the extent of leaching with time for Mn, Fe, Co, Ni, and Zn. The data for Fe and Co are not extensive enough to verify this trend. The data for Zn in the brines show no clear-cut trend, whereas a trend toward greater leaching with greater shale-solution contact time is noted for distilled water extracts. Factors such as non-uniform shaking of the shale-brine mixtures during the maturation studies and slight variations in the bulk of the mixed shale powder used could be responsible for some variation in the general trend established by the maturation studies.

The effect of repeated leaching upon a single shale sample is shown in Table 4. The concentrations of Mn, Fe, Co, and Cu in the fourth extract are about one-half or less of the concentration of those elements in the first extract. The value of Fe appears to reach the background level with the third leaching. The concentrations of Ni and Zn are found to remain relatively high even after four extractions.

A feeling for the general efficiency of the brines in the leaching studies can be obtained by comparing the data of Tables 2-4 with that of Table 5. Table 5 shows the concentrations of the various trace elements expected in 100 ml of brine leach solution if the entire trace element content was extracted from the 20 g of shale used in each experiment. Considering the 80°C runs of the chloride brines to be the most effective in removing the trace elements from the shale, the leaching yields range from about 0.05 percent for Fe to about 14 percent for Mn. It appears that Cr, Fe, and Pb are tightly fixed in the black shale and not easily removed. Increasing the temperature beyond 80°C would presumably increase the effectiveness of the leaching process for Pb and other less mobile elements.

The data for the synthetic brines A, B, and C also provide an indication of solubility trends as a function of brine composition and salinity. The salinity of brine B is nearly 70 percent greater than that of brine A, and the chlorinity of brine B is nearly 50 percent greater than that of brine A, yet, brine A and brine B show about the same effectiveness in leaching except for Mn and Zn where brine A appears to be somewhat more effective. Brine C also has a fairly high salinity and a chlorinity similar to that of brine B and about 4 times as much SO_4^{-2} as brine A. Brine C appears to be somewhat more effective than brine A in leaching Mn, Ni, and Zn from the shale as compared to brine A.

It appears the most effective combination of chlorinity and salinity has been reached or exceeded in brine A. Compositional changes in the brine do appear to alter the geochemical behavior of chloride brines. This suggests the need to determine the leaching behavior of brines rich in ions such as SO_4^{-2} and

CO_3^{-2}. Studies at extended temperature ranges are also desirable in order to determine how firmly the trace elements are fixed in the black shales.

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Organic Geochemistry of Some Upper Pennsylvanian and Lower Permian Kansas Shales: Hydrocarbons

ABSTRACT

A comparative organic-geochemical study has identified some of the extractable hydrocarbon components of ten Upper Pennsylvanian and Lower Permian Kansas shales, and has applied criteria for biogenicity of such compounds.

The lithologies of the shale samples examined ranged from organic-rich black shales to red shales which contain very low amounts of extractable organic material.

The extractable organic material present in these shales includes normal alkane hydrocarbons, isoprenoid and sterane hydrocarbons, and more polar compounds, including aromatic hydrocarbons.

Organic-geochemical separation techniques and identification methods utilized in this study include thin-layer, liquid, and gas chromatography, ultraviolet and infrared spectroscopy, and mass spectrometry.

INTRODUCTION

The purpose of this investigation is to examine the nature of extractable hydrocarbon components present in Upper Pennsylvanian and Lower Permian Midcontinent (Kansas) shales, and to relate these components to biologic precursors.

Although the use of organic-geochemical methods endeavors to detect "chemical fossils" in natural samples in order to trace the evolution of life or life-supporting compounds, the extractable organic material present in ancient rocks today represents not only the remains of plants and animals originally incorporated in the sediment, but biogenic and abiogenic modifications which occurred during diagenesis and burial of the rock. Superimposed on these modifications are possible effects of weathering and/or migration of hydrocarbons.

Criteria for biogenicity are therefore extremely important for organic-geochemical research. Eglinton (1969) has summarized these criteria and has presented structural and presumed causal relationships between biologic precursors and compounds found in sediment extracts. Certain hydrocarbons, fatty acids, and porphyrins appear to be stable throughout geologic time, and therefore serve as criteria for biogenicity. The ability of certain compounds to rotate plane polarized light because of enzymatic activity in the original organism is, for example, another test for biogenicity.

In this study, three groups of hydrocarbons (alkanes, isoprenoids, and steranes) will be used as criteria for biogenicity.

Alkanes are generally derived under geologic conditions from fatty acids produced by living organisms. Only three types of alkane hydrocarbons are found in natural samples: normal, iso-, and anteisoalkanes. For example, over one million isomers are possible for $C_{31}H_{64}$, yet only three are found in sediments (see Fig. 1); those isomers could be predicted because of biochemical pathways in present organisms.
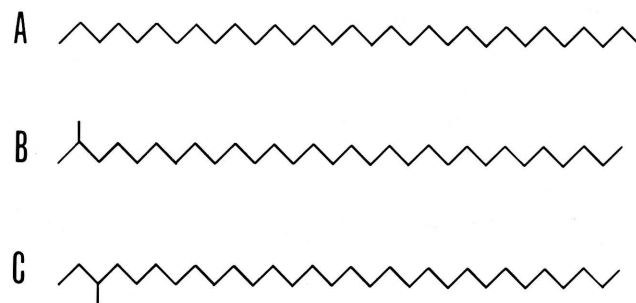
FIGURE 1.—Skeletal formulations of isomeric alkanes, $C_{31}H_{64}$. A, n-hentriacontane (n-alkane); B, 2-methyltriacontane (isoalkane); C, 3-methyltriacontane (anteisoalkane). The zig-zag portrayal is for convenience of representation; the molecules are flexible and are free to take up an almost unlimited number of shapes (after Eglinton, 1969).

Chlorophyll from green plants degrades to several pigments, and the phytol side chain to isoprenoid hydrocarbons (Fig. 2). Recent sediments contain
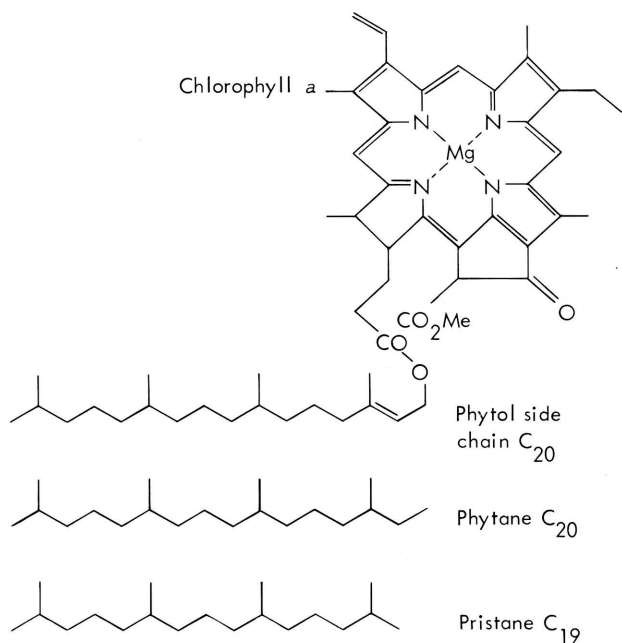
FIGURE 2.—Degradation of chlorophyll *a*, giving rise to two kinds of isoprenoid molecules, phytane and pristane (diagrammatic representation; after Eglinton, 1969).

phytane and some pristane, and other isoprenoids of C_{18}, C_{17}, C_{16}, C_{15}, C_{14}, if the organic matter has been well preserved. With geologic age, the phytane degrades, and pristane often becomes the major component of the isoprenoid compounds (Robinson, *et al.*, 1965).

Steranes, which result from the plant and animal steroids such as cholesterol, often indicate the type of organism deposited in the sediment (Hills, *et al.*, 1966; Speers and Whitehead, 1969). Both plants and animals contribute the steroid ring nucleus which in the sediment becomes reduced and saturated, and as a result remains very stable in sediments. Cholestane and sitostane are the most abundant triterpenes in sediments. Again, enzyme activity accounts for the specificity that only 2 out of 256 possible isomers for

cholesterol have ever been detected in natural samples. Cholestane and coprostane are presumably derived from cholesterol (Fig. 3).

SAMPLING

The stratigraphy and lithologic characteristics of the Pennsylvanian and Permian rocks of Kansas have been described by Moore (1949) and Moore and Mudge (1956). Ten shales from the Upper Pennsylvanian and Lower Permian of Kansas were selected for this investigation; their stratigraphic positions are illustrated in Figure 4. All samples were collected from outcrops, and every effort was made to obtain fresh samples. Gloves were used to prevent hand contamination of the shales. A brief description of the location and lithology of the shales is presented in Table 1.

ANALYTICAL METHODS

The analytical scheme employed for the isolation and identification of organic matter in the Kansas shales is illustrated in Figure 5.

The shale samples were ground or pulverized to less than 200-μ size in a motor-driven mortar and pestle or an Angstrom grinder using a stainless steel sample holder. The powdered shales were extracted ultrasonically with benzene-methanol (4:1, v/v) for an hour; three such extractions were completed with fresh solvent for a total extraction time of three hours. After the mixture was centrifuged, the solvent was removed by flash evaporation. The last traces of solvent were evaporated under a stream of dry nitrogen. Once the weight of the extract was obtained, the general distribution of classes of components in the extract was revealed by a thin layer chromatogram on Silica Gel G developed in hexane and visualized with 0.0005% Rhodamine 6G. Information from thin layer chromatography determined the conditions for column chromatography and solvent
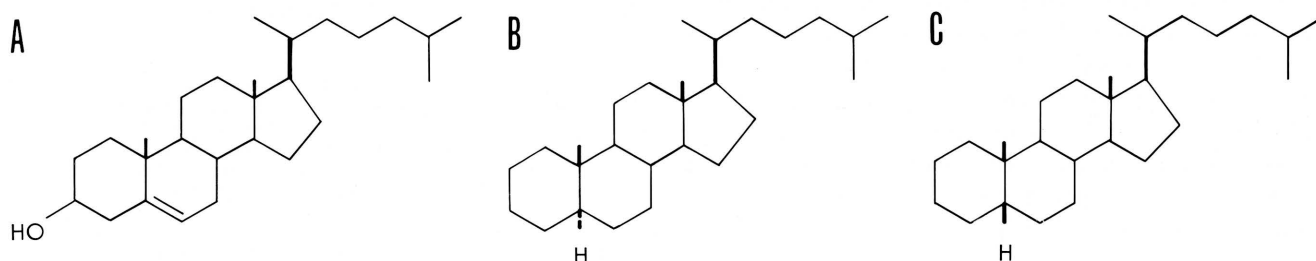
FIGURE 3.—Cholesterol and its diastereomeric, $C_{27}H_{48}$ cycloalkanes. *A*, cholesterol; *B*, 5α-cholestane (cholestane); *C*, 5β-cholestane (coprostane). Heavy lines indicate bonds directed above the plane of the ring and dashed lines indicate bonds below the ring (after Eglinton, 1969).
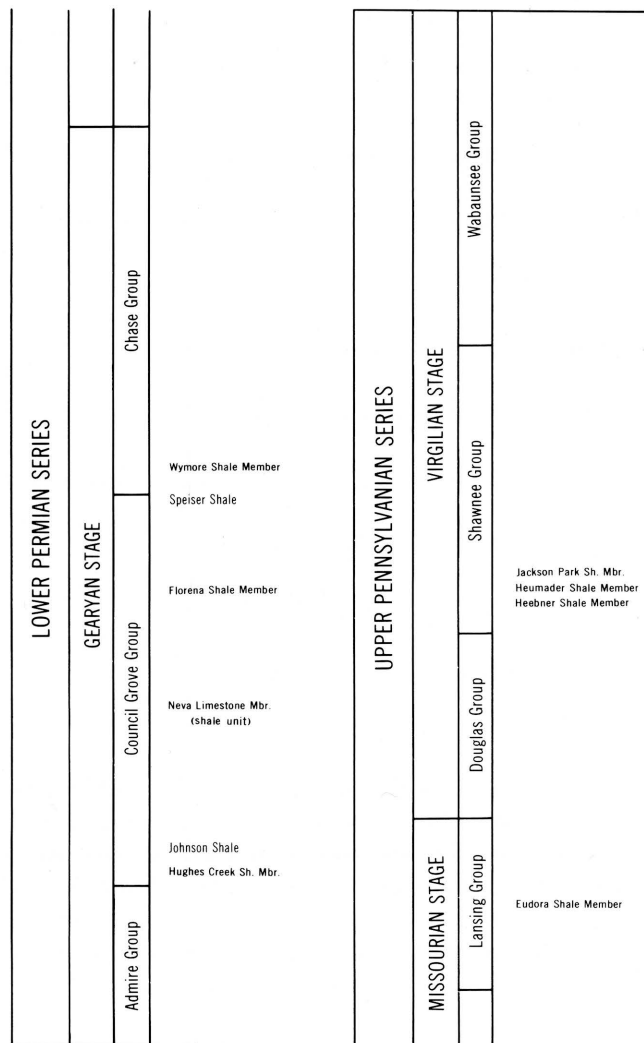
FIGURE 4.—Stratigraphic position of the Upper Pennsylvanian and Lower Permian shales sampled for this study.

volumes. A ratio of 1:100 sample to alumina adsorbent was always employed for optimum separation. The columns were eluted first with hexane, then hexane-ether (8:2 and 1:1), ether, and methanol.

The hexane fraction, collected in 25-ml portions, was checked for elemental sulfur using ultraviolet absorption maxima at 262 mμ and 283 mμ, as well as for aromatic hydrocarbons, using a Beckman DK-2A Ratio Spectrometer (Murphy, *et al.*, 1965). Organic sulfur, if suspected from thin layer chromatography, was tested for with N-ethylmaleimide. The ultraviolet absorption and thin layer migration values determined which classes of hydrocarbons were in the individual fractions.

The other solvents used for elution were collected as single fractions from the column. Thin layer chromatograms confirmed the effectiveness of the column

separations. The separation of classes of compounds present in the Heebner shale hexane fractions and other column eluates is illustrated in Figure 6.

The chain and sterane ring fractions eluted prior to sulfur were separated into normal and branched and cyclic fractions with 5A molecular sieves (Thomas and Mays, 1961). These fractions were separated into individual components by gas chromatography (Perkin-Elmer 226 with an SE-30 S.C.O.T. column, 50′ x 0.02″, and equipped with a flame ionization detector). Many of the peaks were identified from retention time data on standard hydrocarbons with an average deviation of less than 0.25 min. A comparison of the

FIGURE 5.—Analytical procedure.

TABLE 1.—Sample location and description.

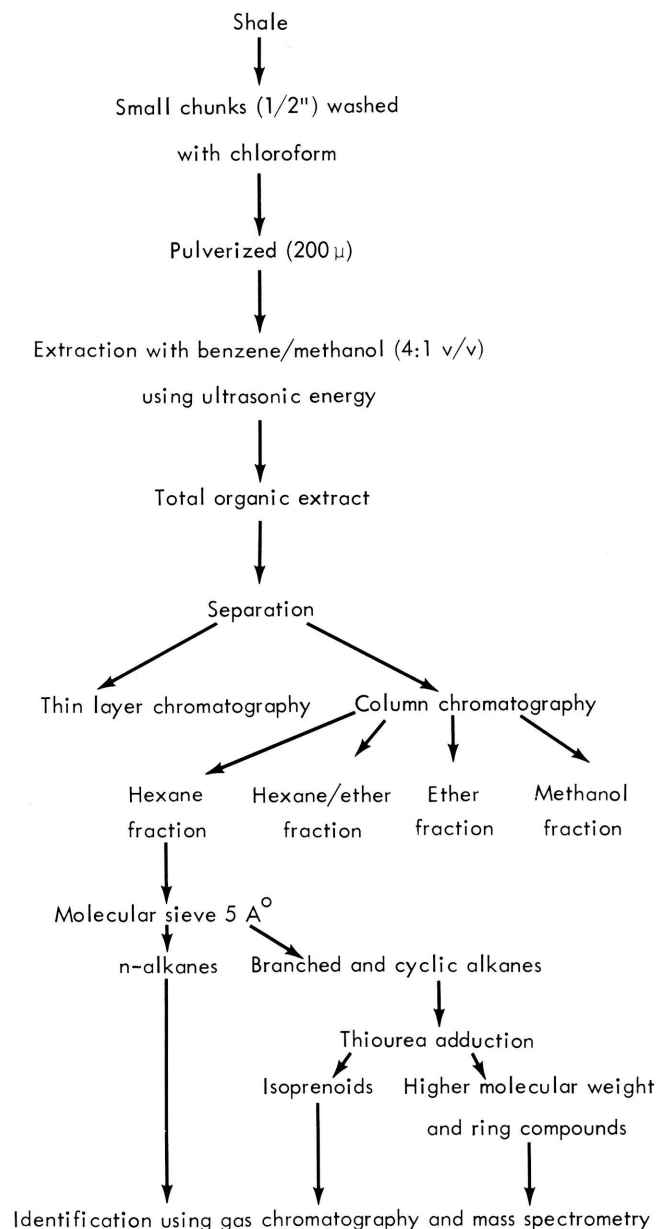| Shale	Location	Description
Wymore	Road cut, W side of K-113 cen., W ½, 26-9S-7E, Riley Co.	Mudstone, silty, gray-red (10R 4/2)
Speiser	Road cut, S side of I-70 cen., 34-11S-6E, Geary Co.	Claystone, greenish-gray (5G 6/1), calcareous
Florena	Quarry cut, top of Prospect Hill, W of K-177 NW ¼, 20-10S-8E, Riley Co.	Claystone, medium light-gray (N6), calcareous
Neva	Road cut, base of Prospect Hill, W of K-177 NW ¼, 20-10S-8E, Riley Co.	Clayshale, dark gray (N3), fossiliferous
Johnson	Road cut, base of Bluemont Hill, N of Water Works SE ¼, 7-10S-8E, Riley Co.	Claystone, greenish-gray (5GY 6/1)
Hughes Creek	Road cut, base of Bluemont Hill, NW of Water Works SE ¼, 7-10S-8E, Riley Co.	Clayshale, dark gray (N3)
Jackson Park	U.S. storage cave, above Gate 1 SE ¼, 7-6S-21E, Atchison Co.	Claystone, light olive-gray (5Y 6/1), calcareous
Heumader	U.S. storage cave, inside cave SE ¼, 7-6S-21E, Atchison Co.	Claystone, medium-gray (N5)
Heebner	Road cut, SE intersection U.S. 40 and U.S. 59 NE ¼, NE ¼, 36-12S-19E, Douglas Co.	Clayshale, dark gray (N3), phosphatic
Eudora	Quarry cut SE ¼, 27-16S-20E, Franklin Co.	Clayshale, dark gray (N3)

gas chromatographic traces for the total extract, branched-cyclic fraction, and the normal alkanes for the Neva shale is illustrated in Figure 7.

Further identification of several compounds was obtained from mass spectra derived from combination GC/MS analyses (Hitachi RMU-6 Mass Spectrometer).

The more polar fractions obtained by elution column chromatography require further separation and identification. The aromatic hydrocarbons often have characteristic fluorescence spectra, thin layer migration values, and gas chromatographic retention times; however, mass spectrometry is required for confirmation of individual compounds.
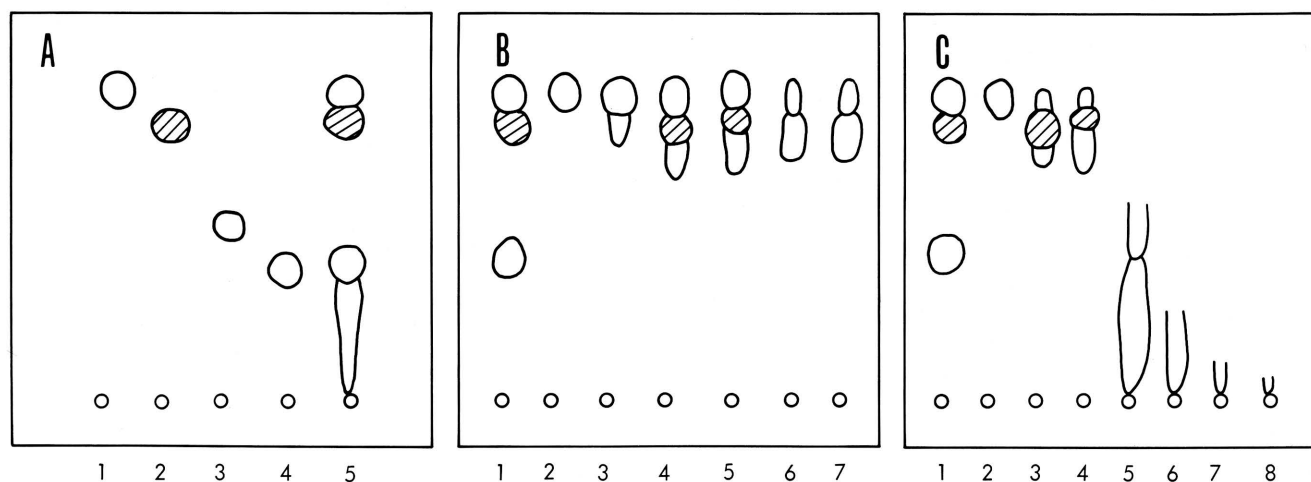
FIGURE 6.—Thin layer chromatograms of Heebner shale extract. Conditions: Silica Gel-G; n-hexane developer, 0.0005% Rhodamine 6-G visualizer; observed under ultraviolet light 254 and 365 mμ. A, standards and total extract: (1) n-octadecane, (2) elemental sulfur, (3) 2,7-dimethyl naphthalene, (4) phenanthrene, (5) total extract; B, hexane fractions: (1) standards—octadecane, 2-methylnaphthalene, phenanthrene, and sulfur, (2) fractions 1 and 2, (3) fractions 3 and 4, (4) fractions 5 and 6, (5) fraction 7, (6) fractions 8, 9, and 10, (7) fraction 11. Fractions 2-11 are the successive 25-ml portions eluted from the column; C, other column fractions: (1) standards—octadecane, 2-methylnaphthalene, phenanthrene, and sulfur, (2) hexane fractions 1 and 2, (3) hexane fraction 7, (4) hexane fractions 8, 9, and 10, (5) hexane/benzene fraction, (6) benzene fraction, (7) ether fraction, (8) methanol fraction.

RESULTS

The total lipid content of the ten Upper Pennsylvanian and Lower Permian shale samples is listed in Table 2. The results of the hydrocarbon analyses of each of these extracts are summarized in Table 3.

TABLE 2.—Lipid content of the shales.

Shale	Lipid-mg/1000 g shale
Wymore	27
Speiser	16
Florena	700
Neva	3,930
Johnson	27
Hughes Creek	35
Jackson Park	180
Heumader	645
Heebner	5,000
Eudora	1,059

TABLE 3.—Comparison of hydrocarbons in shale extracts.

Shale	n-Hydro-carbons	Isoprenoid, diterpenes	Steranes, triterpenes	Carotane, tetraterpene	Aromatic hydro-carbons	Sulfur
Wymore	+	?	?	?	?	—
Speiser	+	?	?	?	—	—
Florena	+	+	?	?	+	+
Neva	+	+	+	?	+	—
Johnson	+	?	?	?	?	—
Hughes Creek	+	+	?	?	+	+
Jackson Park	+	+	+	?	+	+
Heumader	+	+	+	—	+	+
Heebner	+	+	+	—	+	+
Eudora	+	+	+	?	+	+

Chase Group (Lower Permian)

The reddish Wymore shale of the Chase Group, as expected, contains very little extractable organic material; however, some normal alkane hydrocarbons were identified by gas chromatography.

Council Grove Group (Lower Permian)

Of the five shales examined from the Council Grove Group, only the gray-black Neva and Florena shales contain appreciable amounts of extractable organic material. The reddish-green Speiser shale contains very low amounts of extractable organic material. The greenish-gray to black Johnson and Hughes Creek shales contain surprisingly low amounts of extractable material; the extent to which the lipid content of these shales may have been modified by weathering processes, as compared to the other samples, is not known.

The Florena and Hughes Creek shales contain elemental sulfur; the extract of the latter contained nearly 50 percent sulfur. No other shales studied in this investigation released such large amounts of sulfur.

Hydrocarbons were present in all examined members of the Council Grove Group. The extracted normal alkanes generally exhibit a single smooth distribution from C_{12} to C_{26} with a maximum around C_{17}; the Neva shale has a slight, but definite, odd- over even-numbered carbon atom preference (Fig. 7,C). The original preference of odd-numbered hydrocarbons, characteristic of recent sediments, disappears with geologic age, resulting in a more Gaussian distribution (Meinschein, 1969).

Phytane ($C_{20}H_{42}$) and pristane ($C_{19}H_{40}$) are the two most abundant isoprenoid hydrocarbons present in these shales (See Fig. 7,B). Pristane is present in somewhat greater concentrations than phytane, which is characteristic of older sediments. Farnasane ($C_{15}H_{32}$) frequently appears in these shales in relatively high concentrations. Steranes, such as cholestane ($C_{27}H_{48}$), are definitely present in moderate concentrations, but identification of individual components requires mass spectrometric analyses, as do the aromatic hydrocarbons and more polar compounds present in the ether and methanol column eluates.

Shawnee Group (Upper Pennsylvanian)

The three gray-black shales from the Shawnee Group have been investigated previously by Gould (1969), Noonan (1971), and Prentice (1971). The Heebner shale contains a large amount of extractable organic material, while the Jackson Park and the Heumader shales contain only modest amounts of lipid material. Both the Heumader and Jackson Park extracts form a "pitch-like," black, semi-solid material which does not redissolve in methanol. All three shales contain elemental sulfur.

These shales also exhibit a single distribution of normal alkane hydrocarbons with a maximum at C_{17}, although the Jackson Park sample has a predominant odd-over-even carbon preference. Isoprenoids and steranes present in the extracts are characteristic of sediments deposited under reducing conditions. The less common C_{18} isoprenoid is present in the Heumader shale, while in the Heebner shale phytane is somewhat unexpectedly more abundant than pristane. Retention times of peaks obtained by capillary gas chromatography indicate the presence of cholestane ($C_{27}H_{48}$), and possibly ergostane ($C_{28}H_{50}$) and sitostane ($C_{29}H_{52}$), in these samples. These compounds

A

Steranes

Isoprenoid & n-alkanes

84   56   28   0

B

Steranes

Phytane   Pristane

84   56   28   0

C

n-C$_{21}$ n-C$_{19}$ n-C$_{17}$ n-C$_{15}$ n-C$_{13}$

56   28   0

Time (min)
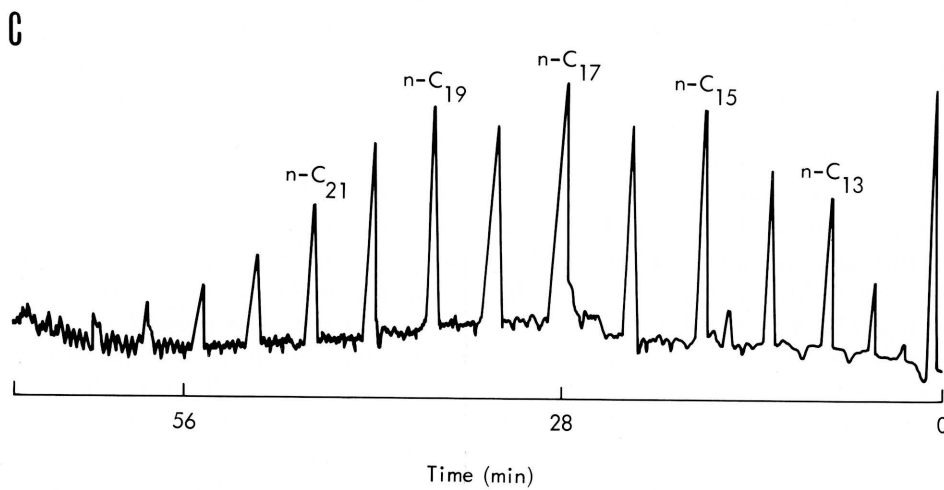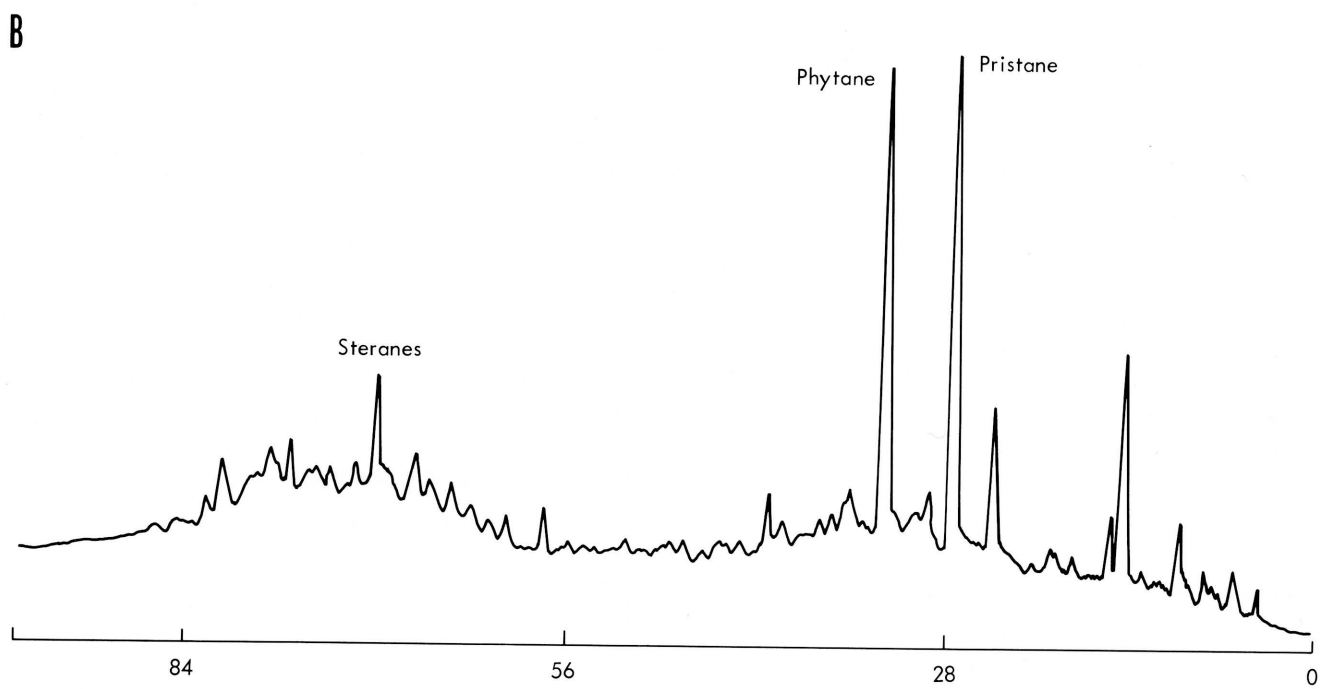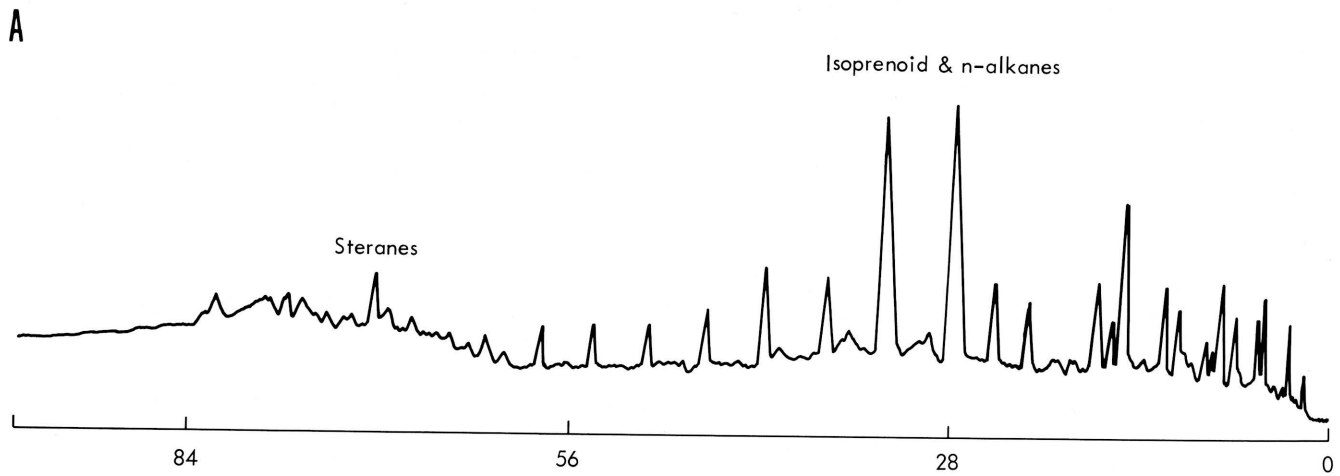
result from saturation of steroid ring compounds. Perhydrocarotene ($C_{40}H_{78}$), which is present in the Green River (Colorado) oil shale (Murphy, *et al.,* 1967), is not detectable in the Heebner and Heumader extracts, and was not determined in the other extracts.

Lansing Group (Upper Pennsylvanian)

The black Eudora shale, the only member of the Lansing Group studied, is relatively rich in lipids. The analysis of the organic extract reveals the presence of sulfur, normal alkanes from C_{15} to C_{27}, isoprenoid hydrocarbons, steranes, and aromatic hydrocarbons.

DISCUSSION

In general, the lipid compositions of the shales examined are not unexpected, and represent compounds formed by biologic synthesis and modified over geologic time. The contribution of green plants in the original organic source material is well established by the prominent isoprenoid and sterane components. However, some differences do exist among the extractable organic materials present in these shales. The distributions of the normal alkane hydrocarbons and the concentrations of the isoprenoid hydrocarbons may vary somewhat. Further work on the nature of the steranes, the aromatic fraction, and the fatty acids will provide information that may help determine differences in environment during deposition and temperature conditions after incorporation of the organic matter into the sediment.

ACKNOWLEDGMENTS

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FIGURE 7.—Gas chromatograms of hexane fractions of Neva shale. Conditions: P-E 226, gas chromatograph; Column SE-30, S.C.O.T. 50' x 0.02"; temperature program, 80-240°, 2°/minute; final time, 20 minutes; chart speed 15"/hour; block temperature, 280°C; detector temperature, 180°C; carrier gas, helium. *A,* total hexane fraction; *B,* non-adduct of 5A molecular sieve; *C,* adduct of 5A molecular sieve.

DORIS E. NODINE-ZELLER

Endothyroid Foraminifera from Subsurface Mississippian in Kansas

ABSTRACT

A survey of a core from the Atlantic Oil Company No. 1-A Mark well (C SE SE sec. 28, T 20 S, R 33 W), Scott County, Kansas, has revealed endothyroid foraminifera of Meramecian (late Mississippian) age. *Endothyra symmetrica, E. spiroides,* and *E. macra* have been identified from a foraminiferal limestone at 4991 feet. *E. spiroides* is a zone marker for rocks equivalent in age to the Salem Limestone.

Preliminary studies reveal that endothyroid foraminifera are plentiful and sufficiently well preserved to be used for stratigraphic correlation of subsurface rocks in Kansas. Specimens of endothyroids, both free and in thin sections, have been obtained from a core from the Atlantic Oil Company No. 1-A Mark well in Scott County, Kansas. The endothyroids present indicate a Meramecian (late Mississippian) age for that part of the core in which they occur. The Meramecian Stage is made up, in ascending order, of the Warsaw Limestone, Salem Limestone, St. Louis Limestone, and Ste. Genevieve Limestone. Heretofore, correlation of the subsurface Mississippian in Kansas was made on the basis of lithology or electric logs, and the presence of the key Salem Limestone (oolitic) was universally based upon the occurrence of "*Endothyra baileyi*," which is prolific in the oolite of the type section of the Salem (=Bedford, Spergen) Limestone in Washington County, Indiana. The No. 1-A Mark was chosen for this investigation because Lee (1940) stated that fossils of definite St. Louis age were present in this well (see Girty, 1940), and because of subsequent age determination of part of this core by Thompson and Goebel (1969) on the basis of the occurrence of conodonts.

Members of the endothyroid group, to which "*E. baileyi*" belongs, are now known to range from middle and upper Devonian well into the Pennsylvanian. They comprise more than six genera occurring in rocks of equivalent age throughout the world—in Russia, China, Japan, England, Belgium, Canada, Australia, Indochina, France, Spain, Ireland, Germany, Brazil, Turkey, Wales, Rumania, Morocco, Algeria, Laos, and Alaska. Endothyroid foraminifera have become the valuable zone markers for Mississippian beds in world-wide stratigraphic correlation

that the fusulinids are for Pennsylvanian and Permian strata.

Three species have been identified among the free specimens extracted from a foraminiferal limestone from 4991 feet in the No. 1-A Mark well: *Endothyra symmetrica, E. macra,* and *E. spiroides,* all found in Mississippian rocks of the Great Basin (Zeller, 1957). The planispiral endothyroids make up about 75 percent of the limestone. Plectogyroid forms and the large planispiral *Tournayella* are not abundant. The microfauna from 4756 to 5111 feet contains *E. symmetrica, E. macra,* "*Plectogyra* sp.," *Tournayella* sp., *Ammodiscus* sp., *Archaediscus?* sp., and *Calcisphaera* sp.

E. symmetrica E. J. Zeller, illustrated in Figure 1, is approximately 0.83 mm in diameter, with a large proloculus of 80.16 μ. It has no hook in the final chamber and contains no secondary deposits. The coiling shows a nearly uniform rate of expansion, and the septa are strongly anteriorly directed. It has four volutions, the septal count per volution (from last to first) being 10, 10, 10, 7.

E. macra E. J. Zeller, illustrated in Figure 2,*A-B,* is approximately 1 mm in diameter and has a proloculus size of about 50 μ. It has a hook in the final chamber and secondary deposits are slightly devel-

FIGURE 1.—*Endothyra symmetrica* E. J. Zeller. A, Horizontal axial section (KUMIP 2,013,808); B, vertical axial section (KUMIP 2,013,809); X 68; 4991 feet, Atlantic Oil Company No. 1-A Mark core, C SE SE sec. 28, T 20 S, R 33 W, Scott Co., Kansas.
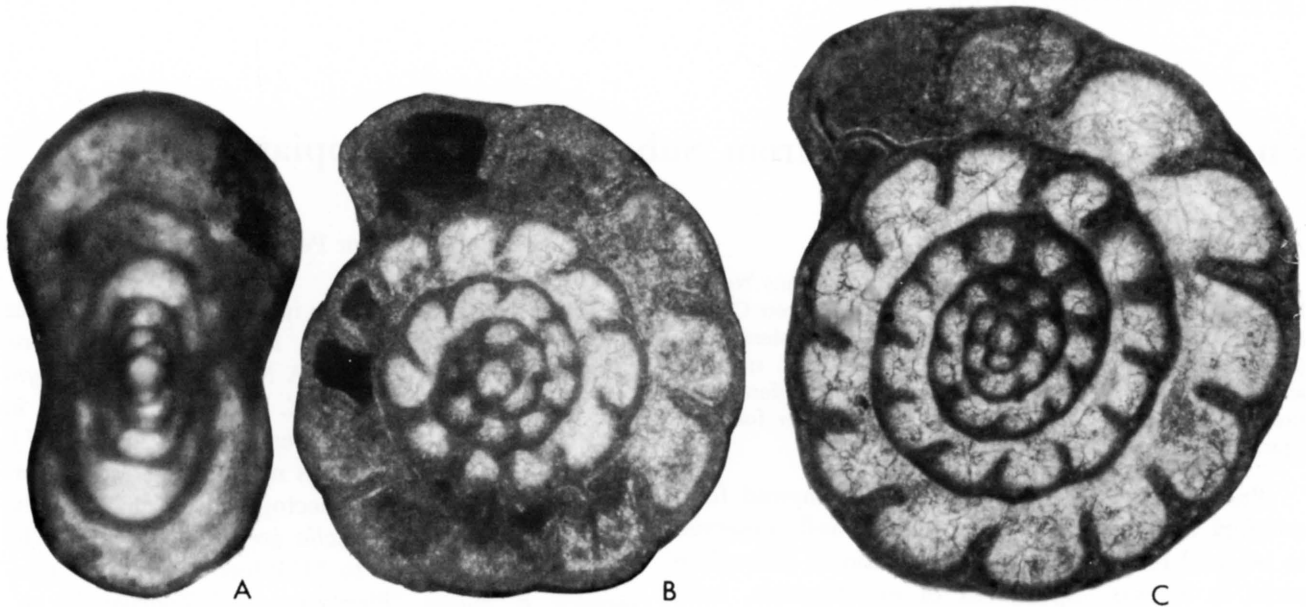
FIGURE 2.—*Endothyra macra (A-B)* and *E. spiroides (C)* from core at 4991 feet in Atlantic Oil Company No. 1-A Mark well, C SE SE sec. 28, T 20 S, R 33 W, Scott Co., Kansas. *A-B, E. macra* E. J. Zeller. *A,* Vertical axial section (KUMIP 2,013,810); *B,* horizontal axial section (KUMIP 2,013,811); X 68. *C, E. spiroides* E. J. Zeller. Horizontal axial section (KUMIP 2,013,812), X 68.

oped. The first two volutions are much more tightly coiled than the succeeding volutions. The septa are medianly directed and arching. One of the larger specimens of *E. macra* contains four and one-half volutions, and the septal count per volution is (last) 11, 10, 9, 6, 3.

E. spiroides E. J. Zeller, illustrated in Figure 2,*C,* is approximately 1.03 mm in diameter, with a relatively small proloculus of 46 μ, although it is not certain that this section is exactly through the proloculus. Distinctive characters of *E. spiroides* are its slightly ovoid method of coiling, which is rather rapidly expanding, and chambers that show almost no swelling between the sutures. There is a hook in the final chamber, but there are no other secondary deposits. The septa are slightly anteriorly directed. This species contains five volutions, and the septal count is (last) 12, 12, 10, 7, 4.

E. symmetrica is early Meramecian in age and may range upward into the Chesteran. *E. spiroides* is a valuable zone marker because of its widespread occurrence and short stratigraphic range. Zeller (1957) correlated the *Endothyra spiroides* Zone in the Cordilleran area with lower Meramecian beds in the Midcontinent region, stating that this Zone con-

tains a microfauna which is similar in many respects to that of the Salem Limestone of Indiana. The foraminiferal limestone at 4991 feet in the Mark No. 1-A well is equivalent in age to the Salem Limestone on the basis of the occurrence of these endothyroid foraminifera.

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WILLIAM KOVACIC[1]
RONALD G. HARDY

Progress Report: Utilization of Fly Ash in the Reclamation of Coal Mine Spoil Banks in Southeastern Kansas

ABSTRACT

This research project utilizes bituminous coal fly ash for neutralizing acid soil and/or water on leveled spoil banks. The study program included laboratory testing to determine the proper ratio of fly ash to soil and establishment of experimental test plots in Crawford County, Kansas. Factors such as temperature and rainfall were recorded and soils were tested for other chemicals that could also affect plant growth. In general it was concluded that fescue grew better on soil treated with fly ash rather than with lime, as long as rainfall was adequate.

INTRODUCTION

This paper is a progress report on a segment of continuing research involving mined-land reclamation in Cherokee and Crawford counties in southeastern Kansas. This segment concerns the utilization of coal fly ash for corrective measures in connection with agricultural uses of leveled spoil banks, i.e., neutralizing acid soil and/or water. Considerable work along this line has already been undertaken by staff of the U.S. Department of the Interior, Bureau of Mines, Energy Research Center, Morgantown, West Virginia. There are, of course, differences between West Virginia and Kansas reclamation; one of the most significant is that much of the strip-mining in West Virginia is contour mining, or stripping along the sides of hills. In Kansas, mining is done on an areal basis. Also, acid conditions in West Virginia are more frequent and severe than in Kansas, with the net result that stream pollution is more prevalent in West Virginia than in Kansas.

This study program proceeded along the following general lines. First, in the laboratory, by adding varying amounts of fly ash to the soil, a proper fly ash-to-soil ratio was estimated on the basis of change in pH. Second, suitably sized test plots were laid out to compare the necessary amounts and effects of fly ash versus pulverized limestone on the growth rate of several different types of plantings.

Temperature and rainfall measurements were taken at the plot site and observations were carried on to note growth rates and quality of plant growth. It was found that extremely variable weather affected plant growth. Planting took place in April, 1971, followed by a month of extremely dry weather and then a month of very wet weather.

DETERMINATION OF FLY ASH REQUIREMENT

Fly ash utilized in this study was unmodified, dry-collected ash obtained from the Montrose station of the Kansas City Power and Light Company at Clinton, Missouri. The chemical analysis of the fly ash (figures rounded) was as follows: SiO_2, 41.3%; Fe_2O_3, 32.1%; Al_2O_3, 16.7%; TiO_2, 0.8%; CaO, 4.3%; MgO, 0.6%; SO_3, 1.0%; K_2O, 2.1%; P_2O_5, 0.3%; Na_2O, 0.5%; undetermined, 0.2%. The fly ash pH was 9.8.

Representative samples of soil from the plots were treated in the lab with the fly ash. The fly ash was added in 5-gm increments to seven 100-gm samples of soil to produce soil-to-fly ash ratios of 100-5, 100-10, 100-15, 100-20, 100-25, 100-30, 100-35. Six days after the experiment began, the pH was recorded. The per-acre rate of treatment to produce the various pH levels as determined in the lab and the amount required to treat the 25 x 25-foot plots was then computed (Table 1).

TABLE 1.—Soil-fly ash ratios, pH values, and application rates.

Soil-fly ash ratio (gm)	pH after 6 days	Application rate per acre (tons)	Application rate per 25 x 25′ test plot (lbs)
100-35	8.8	285	8178
100-30	8.5	245	7031
100-25	8.2	204	5854
100-20	7.7	163	4677
100-15	7.3	129	3702
100-10	7.2	82	2353
100-5	6.6	41	1177

DETERMINATION OF LIME REQUIREMENT

The lime requirement was found by taking nine samples from the plot. These were tested to determine pH and buffer pH for each sample. The requirement for effective calcium carbonate (E.C.C.) was then determined. The nine values were averaged to determine the E.C.C. requirement per acre. This figure was reduced to the amount required for a 25 x 25-foot plot, 350 pounds (24,222 pounds E.C.C. per acre). At a lime composition of 65 percent E.C.C., 500 pounds of lime were required for the plot.

TEST PLOTS

The experimental tests plots for fly ash research are located in the northeast corner of a farm owned by Mario Nardelli, Sr., in sec. 15, T 28 S, R 25 E, Crawford County, Kansas (Fig. 1). The area was strip-mined for coal in the 1930's and was partially leveled in 1967 to allow a large power shovel from the Clemens Coal Company to move across the land to a new location. The general appearance of the area was extremely barren. A sterile pit of water borders the west edge of the area. The pH of the water in the pit was 3.1.

Three 25 x 25-foot plots were laid out in the area that had been leveled. The south plot was used for fly ash treatment with fescue as the crop. The middle

FIGURE 1.—Layout of experimental test plots, NW NW ¼ sec. 15, T 28 S, R 25 E, Crawford County, Kansas (not to scale).

TABLE 2.—Treatment of test plots.

Treatment	Application rate	
	per 25 x 25' test plot	per acre
South Plot (fly ash)		
Fly ash from KCP&L	3800 lbs	132.0 tons
Fertilizer (6-24-24)	46 oz	200.4 lbs
Seed—Kentucky 31 Tall Fescue	7 oz	30.48 lbs
Middle Plot (lime)		
Lime—65% E.C.C.	500 lbs	17.4 tons
Fertilizer (6-24-24)	46 oz	200.4 lbs
Seed—Kentucky 31 Tall Fescue	7 oz	30.48 lbs
North Plot (fly ash and lime)		
Strip A	(2½ x 25' test plot)	
Fly ash	600 lbs	209.1 tons
Crown vetch transplants	not determined	not determined
Strip B	(2½ x 25' test plot)	
Neutralizing agent	none	none
Crown vetch transplants	not determined	not determined
Strip C	(2½ x 25' test plot)	
Lime	50 lbs	17.4 tons
Crown vetch transplants	not determined	not determined
Fertilizer (6-24-24)	46 oz	200.4 lbs

plot was used for lime treatment with fescue as the crop. The north plot was used for both fly ash and lime treatment and crown vetch was the crop. The planting schedule is outlined in Table 2.

EFFECT ON SOIL pH: FLY ASH VERSUS LIME

Soil samples were taken and pH values were determined before any treatment was made. Nine samples were taken from each plot, each sample consisting of four probes taken approximately 6 inches deep. The effect of the addition of fly ash and lime on soil pH is given in Table 3. The average pH for the fly ash plot was raised from 3.5 to 4.5 and the average pH for the lime plot was raised from 3.6 to 4.4.

TABLE 3.—Change in soil pH of test plots with application of fly ash and lime.

Sample no.	South Plot (fly ash)		Middle Plot (lime)		North Plot (fly ash and lime)	
	Before	After	Before	After	Before	After
1	3.9	4.2	3.6	4.8	3.8	4.8
2	3.4	3.7	3.7	4.4	3.5	4.5*
3	3.5	4.6	3.9	4.0	3.6	4.7
4	3.4	4.2	3.4	4.9	3.8	5.3
5	3.4	4.2	3.4	4.8	3.9	4.5†
6	3.4	6.1	3.7	3.8	3.7	4.5
7	3.5	4.8	3.6	3.8	4.2	5.7
8	3.4	4.3	3.7	4.0	3.8	6.3‡
9	3.9	4.3	3.4	3.9	4.1	4.1

* Lime strip.
† No treatment strip.
‡ Fly ash strip.

TEMPERATURE AND RAINFALL

The weekly temperature range at the plot site was recorded, as indicated by a maximum-minimum thermometer. The minimum temperature, 37°F, was recorded during the first week of experimentation, April 12-18, 1971. The maximum temperature, 102°F, was recorded the week of August 23-29.

A record of rainfall during the plant-growing period was kept from April 15 to August 30, 1971. Total rainfall was: April, 2.8 in.; May, 4.7 in.; June, 4.7 in.; July, 9.5 in.; August, 0.7 in. By comparison, the ten-year (1961-1970) average rainfall for these months was: April, 4.7 in.; May, 6.4 in.; June, 5.9 in.; July, 3.4 in.; August, 3.1 in.

TRACE ELEMENT ANALYSIS

A qualitative analysis of trace element content of the acid soil of the test plots was made. The fly ash test plot was compared to the lime test plot for trace element content. They were the same, with the following exception: traces of chromium, cobalt, nickel, and zinc were found in the fly ash plot.[2]

RESULTS

Because of adverse weather immediately after planting, crop growth was not as vigorous as it could have been; however, all treated plots supported plant growth. There was no growth on the non-treated crown vetch plot.

As long as rainfall was adequate, fescue growth was better on soil treated with fly ash. During prolonged dry periods, fescue on the fly ash-treated plot appeared to be the most adversely affected and began to turn brown. However, it was evident from the appearance of the plots that moisture retention was greater in the soil-fly ash mix than in lime-soil mixes. When rainfall increased after the dry period, fescue planted on fly ash-treated soil again took on a normal green color. Samples of fescue from the fly ash-treated plot are being analyzed for mineral content.

Whether or not fly ash can be utilized in southeastern Kansas will depend largely upon the cost of its application compared to the cost of lime application. A cost analysis of fly ash versus lime application is planned in order to make this comparison.

The results of this segment of the continuing research on mined-land reclamation in southeastern Kansas definitely indicate that application of fly ash to acid spoil-bank soils can alter the soil pH to the extent that production of grasses and legumes is possible on otherwise useless soils.

[2] Testing was conducted in the Geochemistry laboratory of the Kansas Geological Survey. A detailed analysis is available.

RONALD G. HARDY

Industrial Profiles as an Aid in Expanding Economic Activity

ABSTRACT

Some relative industry characteristics are outlined in this paper to aid in developing a program for selecting new industries for a region. These characteristics are used to catalog industries to determine which would be the most suitable for a given community.

The strongest manufacturing industries in Kansas are determined to be the petroleum and coal products industries and the chemical-allied products industries.

To a community or region seeking to expand economic activity through industrial development, any industry not previously existing in that community may be considered "new." Shifting resource patterns, shifting and expanding markets, and development of new processes make familiar products proper objects for consideration as new ventures for area development. To be successful, any new undertaking must begin with process and product features that meet the anticipated market changes. Industrial development is a dynamic phenomenon and is constantly responding to changes in technology, to destruction or emergence of resources, and to changes in composition of the demand.

Rural communities predominate in Kansas except for the metropolitan areas of Kansas City and Wichita. However, rural areas provide natural locations for processing many farm, forest, fishery, and mineral raw materials. Actually, a rural area can be a highly attractive location for a wide range of products that have no rural origins or demands. If the area can provide good transportation, water, community facilities, and a trainable labor supply, it may support a profitable industry.

Those individuals or groups concerned with promoting industrial development have many factors to weigh. In the mineral industry, for example, there are a number of mineral industry profiles that are useful as take-off points for more detailed analysis.

It is important to note that Kansas industry, in general, is characterized by a fairly high percentage of labor engaged in agriculture and a less than average proportion of labor involved in manufacturing. This distribution is changing, in part at least, because

of a steady release of farm labor, yet no decrease of agricultural production is evident.

Kansas industry can also be characterized by the preponderance of industries employing fewer than 100 people. For example, almost 99 percent of manufacturing units have 100 or fewer employees and 57 percent have three or less employees. The same employment distribution is true in the mineral resource industries. The larger employment industries are the petroleum and coal products industries.

A quality profile of the manufacturing industry can be revealed through available ratios. For example, value added by manufacturing can be used as the measure of productivity from which comparisons of productivity per dollar of wages, productivity per employee, and productivity as a percent of shipment can be drawn. The first two ratios are measures of labor costs and the last one is an indirect indication of product marketability. The conclusion to be drawn is that products with a high ratio of value added to dollar wage require either fewer dollars, or less skilled labor, or high production per employee, or some combination of these factors. Similarly, a high ratio of value added per employee suggests that high product values can be generated with a minimum number of employees. Products having high ratios of value added in relation to value of shipment (i.e., percent) as compared with lower ratios have, in general, a history of being more restricted in marketing than those with lower ratios. Thus as a preliminary step in the assessment of the desirability of a manufacturing industry for any community, some broad characteristics can be assigned to them.

The ratios for the total United States manufacturing industry and the total Kansas manufacturing industry are listed in Table 1. Kansas industry is about par with U.S. industry with regard to value added per dollar of wages, and is somewhat lower in value added as percent of shipments. It would seem that the present Kansas manufacturing industry mix is less restricted in marketability than the national industry mix.

To obtain a closer look at the profile, the manufacturing industry classification can be disaggregated according to the Standard Industrial Classification

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TABLE 1.—Industry profiles for the United States and Kansas.

Year	Total employment		Production workers		
	Number of workers	Payroll, dollars	Number of workers	Man-hours	Wages, dollars
Total U.S. Industry					
1961	15,738,000	83,670,000,000	11,790,000	23,311,000,000	54,792,000,000
1963	16,235,000	93,289,000,000	---------------	---------------	-----------------
Total Kansas Industry					
1961	108,907	610,550,000	79,636	159,661,000	399,562,000
1963	114,288	684,449,000	84,599	176,971,000	463,229,000
1965	121,000	758,000,000	90,000	188,000,000	520,000,000
1966	135,548	880,816,000	102,647	215,188,000	610,096,000

Year	Value added, dollars	Value of shipments, dollars	Value added as percent of shipments	Value of shipments per production worker, dollars	Value added, dollars		
					per production worker	per dollar of wages	per man-hour
Total U.S. Industry							
1961	164,292,000,000	------------------------	------	---------	13,900	3.00	------
1963	192,103,000,000	420,528,000,000	45.6	34,000	---------	2.06	------
Total Kansas Industry							
1961	1,277,064,000	------------------------	------	---------	16,000	3.19	7.98
1963	1,460,374,000	------------------------	------	---------	17,300	3.15	8.25
1965	1,707,000,000	4,633,000,000	31.8	51,500	18,900	3.28	9.10
1966	1,955,579,000	5,102,757,000	38.3	49,500	19,100	3.20	9.10

Data from Survey of Manufacturers: U.S. Department of Commerce, Bureau of the Census, 1966.

(SIC). This examination shows characteristics of industry sectors which may be used to assess the most promising mineral resources users. In Table 2 these SIC factors have been arranged from maximum to minimum values for the U.S. data, and Kansas figures have been included for comparison. The excellent showing of petroleum and coal products and chemical-allied products, where Kansas figures are somewhat better than those on the national level, emphasizes the strength of these industries. The petroleum and coal products industry exhibits the lowest required productivity per unit of shipments as evidenced by the high value of shipments per production worker. Mineral-related industries, i.e., petroleum and coal products as well as stone, clay, and glass products, are in the upper range of value added per dollar of wages.

Another profile of Kansas industry is developed from its interindustry structure. The Kansas interindustry structure model, developed by the Kansas Office of Economic Analysis,[1] shows how the output of each industry is distributed among other industries and sectors of the economy. At the same time, it shows the input to each industry from other industries and sectors.

The distribution of the values of total purchases is given in Table 3. It is readily apparent that among Kansas mineral producers the petroleum industry is the heaviest purchaser of goods, services, labor, etc., exceeding $400 million annually. The majority of the mineral-related industries makes purchases of less than $100 million annually.

The top ten purchasing industries in the Kansas economy are given in Table 4. The petroleum and coal products industry ranked third, with the crude oil and natural gas production industry ranking sixth in total value of "purchases from governments," i.e., in taxes paid. Focusing on the mineral extraction industries and possible mineral-based industries, Table 5 was developed to show the ranking of purchases. Again, petroleum-related industries top the list in dollar value of purchases.

For comparative purposes, it is useful to determine how each dollar of an industry's purchases is distributed. Furthermore, for any region attempting to attract business, it is pertinent to ask how much labor is purchased, and how much is spent by various industries for taxes. This information is given in Table 6, which also shows the principal products purchased. For every dollar spent by the Kansas cattle industry, 20 cents was spent within the Kansas cattle

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[1] Emerson, M. Jarvin, The Interindustry Structure of the Kansas Economy: Kansas Department of Economic Development, 1965.

TABLE 2.—Productivity and marketability measures of selected industries for the United States and Kansas.

SIC*	Products	Value added as percent of shipments		SIC*	Products	Value of shipments per production worker	
		Kansas	U.S.			Kansas	U.S.
38	Instruments & Related Equipment	64.5	65.2	29	Petroleum & Coal Products	221.0	150.0
27	Printing & Publishing	66.0	64.8	28	Chemicals & Allied Products	68.0	60.5
39	Miscellaneous & Ordnance	57.5	57.1	21	Tobacco Manufacturers	------	59.0
32	Stone, Clay, & Glass Products	59.5	57.1	20	Food & Kindred Products	105.0	58.7
36	Electrical Machinery	------	57.0	37	Transportation Equipment	40.4	49.8
28	Chemicals & Allied Products	55.0	55.3	33	Primary Metal Industries	------	37.6
25	Furniture & Fixtures	51.0	52.2	26	Paper & Allied Products	33.6	33.6
35	Machinery Except Electrical	53.3	51.8	36	Electrical Machinery	------	28.8
34	Fabricated Metal Products	51.5	51.2	35	Machinery Except Electrical	29.6	28.7
30	Rubber & Plastics Products	------	51.0	30	Rubber & Plastics Products	------	28.2
31	Leather & Leather Products	------	49.5	27	Printing & Publishing	19.5	27.4
23	Apparel & Related Products	31.8	46.0	39	Miscellaneous & Ordnance	22.0	26.5
26	Paper & Allied Products	42.2	45.2	38	Instruments & Related Equipment	15.1	26.3
24	Lumber & Wood Products	49.5	43.8	34	Fabricated Metal Products	28.3	26.2
33	Primary Metal Industries	------	42.8	32	Stone, Clay, & Glass Products	32.7	25.4
37	Transportation Equipment	43.2	41.1	22	Textile Mill Products	------	19.8
22	Textile Mill Products	------	38.9	25	Furniture & Fixtures	21.8	18.2
21	Tobacco Manufacturers	------	37.2	24	Lumber & Wood Products	18.7	17.5
20	Food & Kindred Products	19.0	31.9	23	Apparel & Related Products	31.5	15.0
29	Petroleum & Coal Products	25.2	20.6	31	Leather & Leather Products	------	13.7

SIC*	Products	Value added per dollar wages		SIC*	Products	Value added per production worker	
28	Chemicals & Allied Products	3.9	3.5	28	Chemicals & Allied Products	37.3	33.5
29	Petroleum & Coal Products	5.6	3.2	29	Petroleum & Coal Products	55.6	31.0
20	Food & Kindred Products	2.1	2.5	21	Tobacco Manufacturers	------	22.0
32	Stone, Clay, & Glass Products	2.4	2.2	37	Transportation Equipment	17.9	20.5
21	Tobacco Manufacturers	------	2.2	20	Food & Kindred Products	19.9	18.7
26	Paper & Allied Products	1.9	2.1	27	Printing & Publishing	12.9	17.8
38	Instruments & Related Equipment	1.4	2.1	38	Instruments & Related Equipment	9.7	17.2
33	Primary Metal Industries	------	2.0	36	Electrical Machinery	------	16.5
30	Rubber & Plastics Products	------	2.0	35	Machinery Except Electrical	15.9	16.3
37	Transportation Equipment	1.9	1.9	33	Primary Metal Industries	------	16.1
27	Printing & Publishing	1.7	1.9	26	Paper & Allied Products	14.2	15.2
34	Fabricated Metal Products	2.4	1.8	39	Miscellaneous & Ordnance	12.7	15.1
36	Electrical Machinery	------	1.8	32	Stone, Clay, & Glass Products	19.5	14.6
35	Machinery Except Electrical	1.9	1.8	30	Rubber & Plastic Products	------	14.4
22	Textile Mill Products	------	1.8	34	Fabricated Metal Products	14.7	13.4
23	Apparel & Related Products	2.5	1.8	25	Furniture & Fixtures	11.2	9.5
25	Furniture & Fixtures	1.8	1.8	22	Textile Mill Products	------	7.7
24	Lumber & Wood Products	1.4	1.7	24	Lumber & Wood Products	9.3	7.6
39	Miscellaneous & Ordnance	2.3	1.7	23	Apparel & Related Products	31.6	6.9
31	Leather & Leather Products	------	1.7	31	Leather & Leather Products	------	6.8

* Standard Industrial Classification.
Data from Annual Summary of Manufacturers: U.S. Department of Commerce, Bureau of the Census, 1963.

industry itself, 14 cents was spent on labor (purchases from households), and nearly one cent was spent for state and federal government taxes (purchases from government). In the Kansas aerospace industry, of every dollar spent for purchases, about 1.5 cents was spent for machinery and equipment, 44.5 cents for labor, and 0.5 cent for taxes. Heavy purchases from other suppliers were made by the cattle, meat products, petroleum and coal products, and building construction industries. Aerospace, education, retail trade, and the construction industries were heavy pur-

chasers of labor. The building construction industry is a principal "purchaser" from government.

Table 7 shows the portion of each purchasing dollar spent by the mining industry and mineral-related industries on supplies, labor, and taxes. The petroleum and coal products industry is a heavy purchaser of supplies; the mining industry, other than nonmetallic, is also a fairly heavy purchaser. The oil and gas field service sector purchased over 50 cents of labor per total dollar of purchases. The stone and clay and cement and concrete sectors also have high labor pur-

TABLE 3.—Size distribution of industry purchases.

Range in value of annual industry purchases, millions of dollars	Number of industries or frequency occurring in range	Mineral industry or mineral industries products occurring in specified range
0-50	18	Agricultural chemicals; other mining; oil and gas field services
50-100	15	Cement and concrete products; other stone and clay; nonmetallic mining
100-150	8	
150-200	7	Industrial chemicals
200-250	5	Other chemicals
250-300	1	
300-350	5	
350-400	2	
400-450	2	Crude oil and natural gas production
450-500	0	
500-550	1	
550-600	4	Petroleum and coal products

Data from Emerson, M. Jarvin, The Interindustry Structure of the Kansas Economy: Kansas Department of Economic Development, 1965.

chases. Of the industries listed, the industrial chemical and the cement and concrete industries make the highest payments to state and local governments.

Another useful set of relationships that can be evolved from an interindustry structure table such as that developed for Kansas is the effect of an increase in final demand on all sectors.[2] For example, a change

[2] See Kansas Direct, Indirect and Induced Requirements Matrix *in* The Interindustry Structure of the Kansas Economy: Kansas Department of Economic Development, 1965.

TABLE 4.—Ten leading Kansas industries, based on purchase of labor, goods, and services, 1965.

Industry sector	Rank	Total purchases, thousands of dollars
Cattle	1	596,977
Meat Products	2	590,639
Petroleum and Coal Products	3	580,338
Aerospace	4	561,134
Education	5	541,826
Crude Oil and Natural Gas Production	6	441,761
Other Retail Trade	7	419,530
Building Construction	8	367,289
Special Trade Construction	9	344,804
Grain Mill Products	10	333,728

TABLE 5.—Ten leading Kansas mineral industries, based on purchase of labor, goods, and services, 1965.

Industry sector	Rank	Total purchases, thousands of dollars
Petroleum and Coal Products	1	580,338
Crude Oil and Natural Gas Production	2	441,761
Other Chemicals	3	229,897
Industrial Chemicals	4	153,654
Other Stone and Clay	5	96,544
Cement and Concrete Products	6	76,168
Nonmetallic Mining	7	73,132
Other Mining	8	46,902
Oil and Gas Field Services	9	46,443
Agricultural Chemicals	10	16,605

TABLE 6.—Purchases by ten leading Kansas industries and recreation-related industries per dollar of total purchase.

Industry sector	Principal supplier to industry	Purchases from principal suppliers, dollars	Purchases from households (i.e., labor), dollars	Purchases from government (i.e., taxes), dollars
Ten Leading Industries				
Cattle	Cattle	0.2021	0.1429	.0092
Meat Products	Cattle	0.5342	0.1022	.0018
Petroleum & Coal Products	Crude Oil & Natural Gas Products	0.4952	0.0660	.0018
Aerospace	Machinery & Equipment	0.0141	0.4449	.0048
Education	Maintenance & Repair	0.0389	0.6718	.0460
Crude Oil & Natural Gas Products	Insurance & Real Estate	0.1382	0.0836	.0036
Other Retail Trade	Communications	0.0177	0.7208	.0052
Building Construction	Special Trade Construction	0.3914	0.1561	.0181
Special Trade Construction	Special Trade Construction	0.0191	0.2532	.0156
Grain Mill Products	Wheat	0.3000	0.0659	.0079
Recreational Industries				
Eating and Drinking	Meat Products	0.0395	0.4085	.0060
Gasoline Service Stations	Other Wholesale Trade	0.0758	0.4776	.0077
Lodging Services	Electric, Gas, and Sanitary Service	0.0672	0.3168	.0395

Data from The Interindustry Structure of the Kansas Economy, 1965.

TABLE 7.—Purchases by Kansas mineral industries per dollar of total purchase.

Industry sector	Principal supplier to industry	Purchases from principal suppliers, dollars	Purchases from households (i.e., labor), dollars	Purchases from government (i.e., taxes), dollars
Petroleum & Coal Products	Crude Oil & Natural Gas Products	0.4952	0.0660	.0018
Crude Oil & Natural Gas Products	Oil Field Services	0.1036	0.0836	.0036
Other Chemicals	Other Chemicals	0.0613	0.1809	.0069
Industrial Chemicals	Crude Oil & Natural Gas	0.0472	0.1927	.0138
Other Stone and Clay	Railroad Transportation	0.0130	0.3795	.0053
Cement and Concrete	Cement and Concrete	0.1042	0.2744	.0153
Nonmetallic Mining	Other Stone and Clay	0.0404	0.0951	.0005
Other Mining	Other Mining	0.2260	0.0984	.0002
Oil and Gas Field Service	Machinery & Equipment	0.0388	0.5459	.0023
Agricultural Chemicals	Petroleum & Coal Products	0.0333	0.1669	.0117

Data from The Interindustry Structure of the Kansas Economy, 1965.

in final demand of crude oil and natural gas will affect the industries supplying the oil- and gas-producing industries. Each of these industries will in turn cause changes in industries supplying them. Thus a multiplier effect is generated via direct, indirect, and induced purchases.

If crude oil and natural gas production is increased by $1 million, there can be an expected increase of $1,000,000 x .1631 = $163,100 in the real estate and insurance trade in Kansas. On the other hand, the same increase in the aerospace industry gives an expected increase of only $1,000,000 x .008 = $8,000 in the real estate and insurance trade.

Another consideration is the type of industry growth that would have the most impact on existing local industries. If, for example, it is important to select an industry that will increase the local retail market, the following Kansas interindustry structure data shows the relative purchases by industries at the retail level.

Industry sector	Purchases from local retail establishments per dollar of total purchases, dollars
Nonmetallic Mining	.0183
Other Mining	.0172
Wholesale Grocery	.0095
Eating and Drinking	.0069
Heavy Construction	.0066
Communications	.0029
Building Construction	.0014

Thus, with the use of interindustry structure tables, a number of important questions can be analyzed. Such factors as how to increase employment, improve the tax base, or improve markets for local business can be scrutinized for ideas on proper regional development.

The difficult problem is matching a product with a profitable demand with a community that can pro-

duce it advantageously. The community pool of skills, capital, and natural resources defines the range of product possibilities. For example, a type of mineral product that could be produced in a small industry and have an excellent growth potential is filler for plastic products. The plastic products industry has already experienced a phenomenal growth and is expected to be among the highest of any industry, with some sources predicting 15 percent annual growth. Even the most conservative estimate indicates that the plastic materials industry should expand rapidly over the next decade.[3] Any supplier to this industry should enjoy the same growth benefits.

SUMMARY

The overall worth or potential worth of an industry to a community can be estimated from three measures: (1) total value of output, (2) wages and salaries paid households, and (3) tax payments at the state and local level. Overall the mineral industry of Kansas has a very significant impact on the community: first and primarily through the petroleum industry, second through construction-related minerals, and third through minerals used in the chemical industry.

According to 1965 figures, the petroleum industry alone had outputs of $1.067 billion which generated $1.804 billion of outputs in all other industries of Kansas. At the same time, the industry paid $1 billion in wages and salaries while generating $405 million in wages in the remaining Kansas industries. Unfortunately, tax figures for like comparisons are not available.

It is also worth noting that the Kansas mineral

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[3] Growth Pace Setters in American Industry 1958-68: U.S. Department of Commerce, Business and Defense Services Administration, Oct. 1968.

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industry ranked 10th out of 68 industry sectors in amount of total dollar purchases from all other Kansas industries.

Kansas minerals do offer opportunities for workable imaginative industries. In this connection the Kansas Geological Survey program is geared to maintenance of mineral resource capability, accommodation of minerals to changing end-use patterns, and resolution of problems related to environmental conflicts.