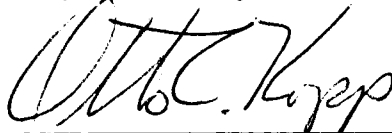


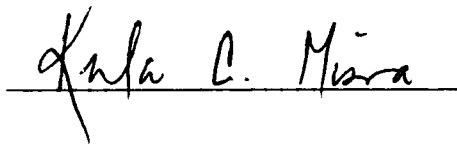
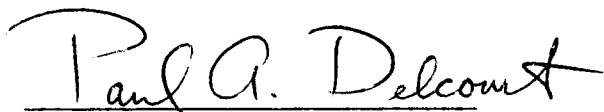
To the Graduate Council:

I am submitting herewith a thesis written by Anne E. Dorsey entitled "Elemental Distributions and Relationships between the Pewee Coal and Associated Sediments, Wartburg, Basin, Tennessee." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.



Otto C. Kopp, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the Council:



Vice Chancellor
Graduate Studies and Research

ELEMENTAL DISTRIBUTIONS AND RELATIONSHIPS BETWEEN
THE PEWEE COAL AND ASSOCIATED SEDIMENTS,
WARTBURG BASIN, TENNESSEE

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Anne E. Dorsey

December 1982

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ABSTRACT

It has been shown that the elemental concentrations in some coals increase adjacent to the upper and lower contacts with the clastic sedimentary rocks. This increase is possibly influenced by the character of the overlying sediments. The purpose of this study was to determine whether the chemical character of a coal remained relatively unchanged or whether the coal underwent significant changes in petrologic and/or chemical character as a result of the lithologic character of the adjacent sediments.

The Pewee coal, which outcrops in the Wartburg Basin in northeast Tennessee, was chosen for this study. The Pewee coal is early Pennsylvanian in age and is the uppermost member of the Redoak Mountain group.

The X-ray fluorescence data show that most elemental concentrations decrease upwards within the coal, from the base to the top. At the very top of the coal, most elemental concentrations show a significant increase. Correlation coefficients for elements within the sediments and within the coal reflect the typical compositions of clay minerals. The major mineral phases identified by X-ray diffraction were kaolinite, illite, chlorite, siderite and quartz.

Several conclusions have been reached concerning the Pewee coal and the sediments associated with the coal:

1. Although minor variations in chemical composition occur laterally, the Pewee coal is relatively homogeneous within the study area.

2. Elements which tend to be soluble in low pH solutions, (specifically Ca and Mn), may react with fluids coming from the peat and be transported away from the coal-sediment contact. Chlorite is absent from the coal due to its high solubility in such an acid environment. With these few exceptions, there is little direct evidence that diagenetic processes influenced the movement of elements from the coal into the sediment, or vice versa.

3. The decrease in elemental concentrations upwards in the coal is thought to result from a gradual decrease in the amount of detritus being brought into the Pewee swamp. The sudden increase in abundance of most elements at the top of the seam provides evidence for a sudden change in environmental conditions, perhaps as the result of the establishment of a new distributing system.

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CHAPTER I

INTRODUCTION

Barrett (1979) compared two coals, the Pewee and Grassy Spring, using petrologic and X-ray fluorescence analyses. Previous workers (Minkin, 1977; and Roberts, 1978) had studied these coals and determined their depositional environments. The Grassy Spring had been deposited in a lower delta plain environment and was influenced by one or more marine incursions. The Pewee had been deposited in an upper delta plain environment and had never been subjected to marine conditions. Barrett sampled both coals in their entirety. Full-face channel samples were taken in the field and split at 1 to 3 cm intervals. Barrett analyzed only one sample each from the underclay and the clastic sedimentary rocks overlying each seam.

The results of Barrett's analyses showed that the Grassy Spring was a rather impure coal, containing numerous shale beds and partings, and abundant pyrite. The Pewee, on the other hand, did not contain any visible shale beds or partings, nor did it contain much pyrite. In fact, the sulfur content of the Pewee ranged vertically from only 0.78% to 0.93%. By way of contrast, the sulfur content of the Grassy Spring ranged from 0.68% to 2.49%. When the analytical data for most elements were compared, the Grassy Spring contained significantly higher concentrations of each element and showed wider ranges of concentration for each. The Pewee was more homogenous throughout, at least in a relative sense.

Barrett did note that the concentrations of several elements appeared to increase near the top (and bottom) of the Pewee seam. Barrett's data suggested that the upper part of the Pewee coal was influenced by the character of the overlying clastic sedimentary rocks; however, there were insufficient samples to determine what kind of influence the sediments had. Also, Barrett's samples came from only one location each for the Grassy Spring and The Pewee. There was no way to determine what effect different kinds of sediment might have on the underlying coal.

Purpose

The primary purpose of this investigation is to determine vertical and lateral chemical variations within a coal seam with respect to different kinds of sedimentary rocks (hereafter referred to as sediments) which overlie the seam in several locations.¹ To approach this problem, the vertical and horizontal distribution of major and several minor elements have been determined in the Pewee coal and sediments above the coal. If the effects of the overlying sediments were to be considered it was necessary to use a coal that had not suffered drastic environmental changes (such as had taken place for the Grassy Spring coal).

No attempt was made in this study to determine more detailed or specific depositional environment(s) for this coal. Previous

¹ Although coal is a combustible sedimentary rock composed predominantly of plant material, in the text, the term "sediments" will be restricted to sedimentary rocks composed of clastic, inorganic material.

workers (Minkin, 1977; Roberts, 1978) proposed a westwardly prograding delta system with the Pewee coal deposited in the upper delta plain regime. The dominance of fluvial processes led to the development of distributory channel, point bar, levee, overbank and backswamp deposits as the most characteristic lithofacies units in the Pewee interval. The laterally shifting fluvial system produced the juxtaposition of lithofacies in response to subsidence, infilling of basins and variation in sediment supply.

The Pewee coal is early Pennsylvanian in age. It is the uppermost member of the Redoak Mountain group, which is part of the Pottsville series (Luther, 1959). Because of its uniformity and extent the Pewee coal seam is easily recognized and extensively mined in the study area. Barrett (1979) showed that the Pewee coal is relatively low in sulfur content (avg. = 0.83% S) and uniform compositionally in an outcrop on Ash Log Mountain.

Regional Setting

The Wartburg Basin is a structural low in the northern portion of the Cumberland Plateau in northeast Tennessee (Figure 1). The basin is bounded by the Cumberland Plateau overthrust system to the southwest and by a northern extension of Walden Ridge to the southeast. To the northeast, the Jacksboro fault delineates one boundary of the study area, while to the northwest the basin merges with the Northern Cumberland Plateau subprovince (Luther, 1959).

The Wartburg Basin lies in an area known as the "dissected plateau" or the Cumberland Mountains region. Here, rugged mountainous

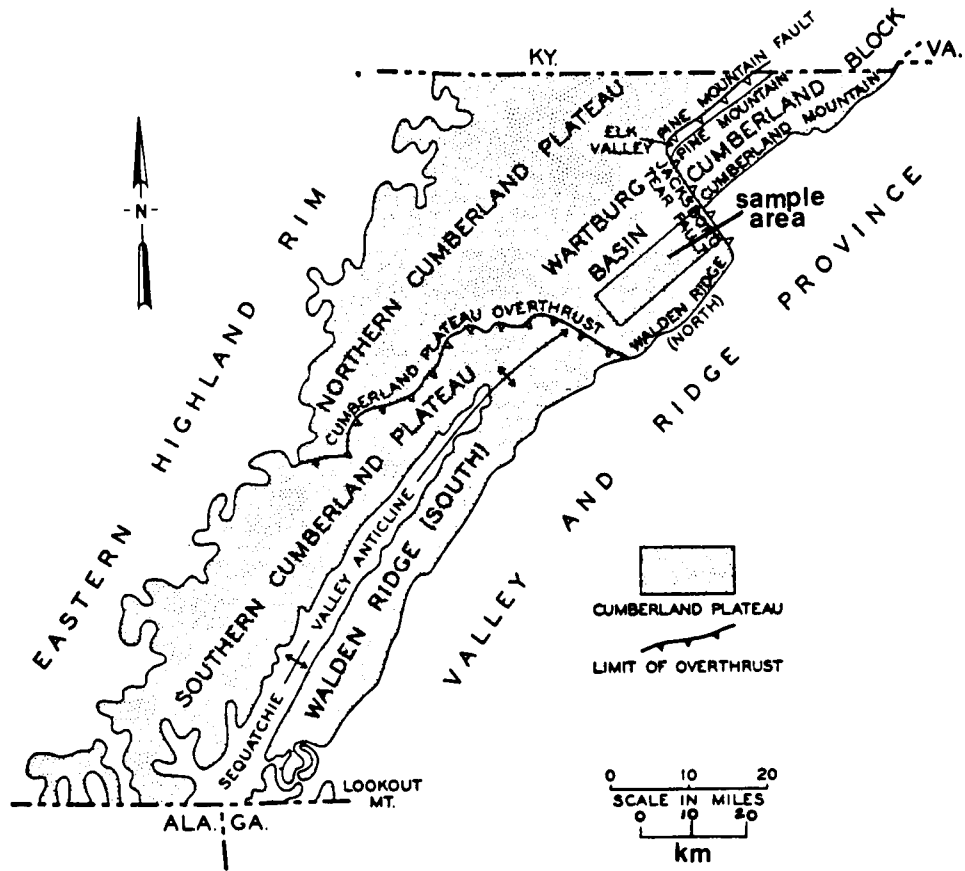


Figure 1. Structural features of the Cumberland Plateau (after Luther, 1959).

terrain has been produced through stream erosion of the relatively flat lying strata (Luther, 1959). This region has afforded excellent coal exposures resulting from extensive contour strip mining; however, in recent years, new strip mining laws have resulted in relatively rapid covering of the exposed seams.

Selection of Sample Sites

The Pewee coal was chosen for this study because it is relatively homogeneous, accessible and deposited within freshwater deltaic-plain environments (Minkin, 1977; Roberts, 1978). Four stratigraphic sections of the Pewee seam were sampled in this study. The samples were collected along a general northeast-southwest line, approximately 12 km (7.5 miles) long (Figure 2).

Several criteria were used for selecting samples in the field. Obtaining a range of sedimentary rock types overlying the coal was the major factor influencing where samples would be collected. Ideally, unweathered samples were sought, but this was not always possible. Older, but accessible, strip mines showed depositional sequences with weathering. Active strip mines were being mined, then rapidly buried to satisfy current mining regulations. The sample sites were chosen with the help of Mr. Larry Knox of the Tennessee Department of Conservation, Division of Geology (Knoxville office).

At site A, the Pewee and overlying sediments were sampled at the entrance to a drift mine operated by the Rainbow Mining Company. The site is located at an elevation of 762 m (2500 feet), 0.4 km (0.25 miles) northwest of Ash Log Gap. Map coordinates on the Block,

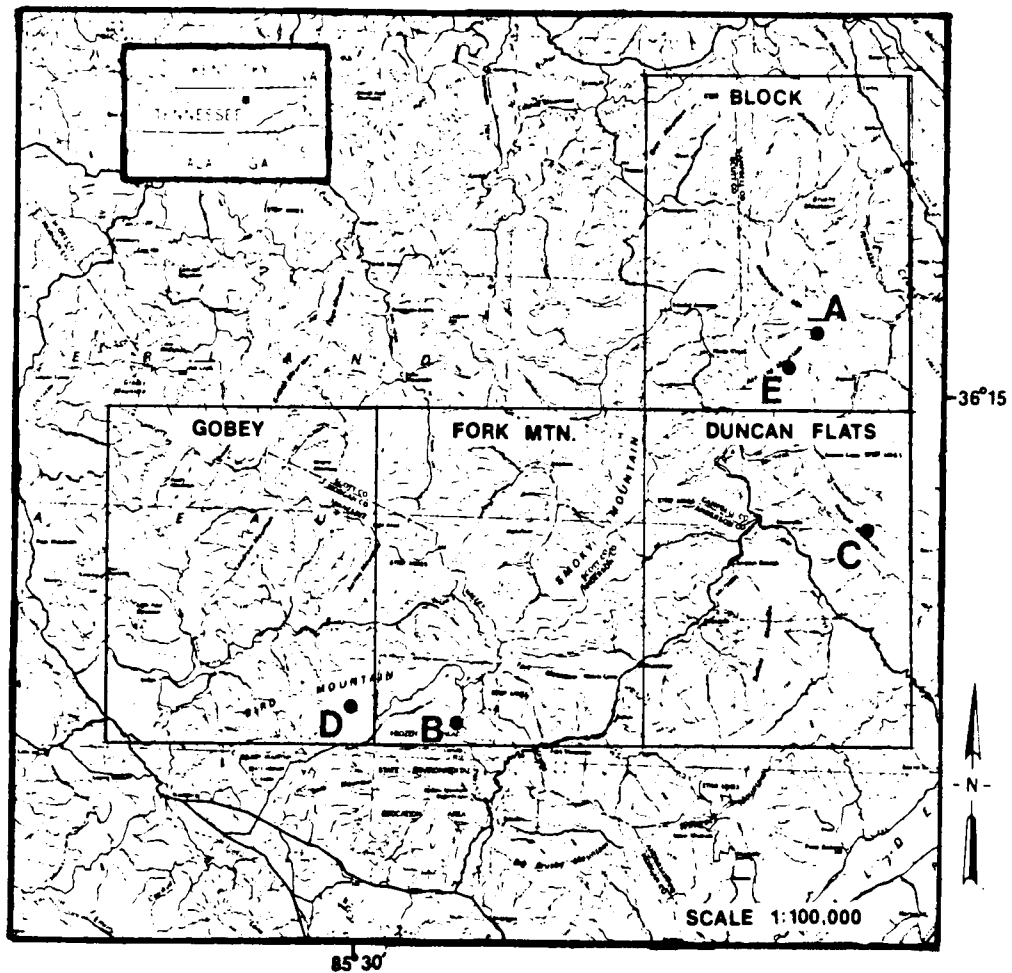


Figure 2. Sample sites (A-E) plotted on 1:100,000 topographic map of Oak Ridge, Tennessee. N3600-W8400/30X60

Tennessee 7.5 minute Quadrangle (No. 128-SE) for this location are 690,000' N and 2,519,000' E. 75 cm of Pewee coal was exposed, then sampled. The total thickness of the Pewee coal at this location is unknown. Although coal in this section was badly weathered, care was taken to eliminate as much altered material as possible by removing the weathered rind from coal samples.

Samples from site B were collected at an active strip mine, owned by C.L.&C. Company. The exposure was at an elevation of about 823 m (2700 feet), 1.08 km (0.67 miles) southeast of Peach Orchard Gap. The map coordinates on the Fork Mountain 7.5 minute Quadrangle (No. 129-NW) are 640,000' N and 2,457,950' E. The uppermost 63.5 cm of Pewee coal was exposed and sampled at this location. The material sampled had been exposed by mining activities for less than one year.

The coal and sediments designated from site C are from a 335 cm (132 in.) long core supplied by Mr. Larry Knox of the Tennessee Division of Geology. The core was drilled for West Coal Company on Red Oak Mountain. The Pewee coal was encountered at an elevation of 675 m (2215 feet). The core was drilled 2000 m (6550 feet) southeast of the town of Clinchmore. The map coordinates on the Duncan Flats Quadrangle (No. 129-NE) are 663,450' N and 2,508,750' E. At site C, the Pewee coal is 71 cm (28 in.) thick. Sediments stratigraphically above and below the coal were sampled for chemical and petrographic analysis. These core samples had not experienced any surficial weathering.

The fourth section was collected at an active strip mine owned and operated by G & F Coal Company. The Pewee outcrops at an elevation

of approximately 853 m (2800 feet). Site D is located at coordinates 641,200' N and 2,439,500' E on the Gobey 7.5 minute Quadrangle (No. 122-NE). The sample column was collected from a bench where 51 cm (20 in.) of coal was exposed. Coal was being mined at the sample locality. It is probable that the overlying sediments and coal were exposed for less than a month before sample collection.

Barrett's section of the Pewee coal (1979) outcrops within the present study area. This section is referred to as site E on Figure 2. Barrett's detailed chemical analysis for the Pewee coal provides information on vertical changes within that coal at a single site. The Pewee coal horizon and one sample each from the underclay and overburden were collected at a drift mine operated by the Dan Branch Mining Company. The mine is located at the 768 mm (2520 feet) elevation on Ash Log Mountain, 915 m (3000 feet) southeast of Ash Log Gap. Map coordinates on the Block, Tennessee 7.5 minute Quadrangle (No. 128-SE) are 687,000' N and 2,495,000' E. The Pewee coal is 100 cm (39 in.) thick at this location.

The elevation of the Pewee coal systematically drops within the study area from a high of 853 m (2800 feet) in the west to a low of 675 m (2215 feet) in the east. Roberts (1978) determined that structural deformation (in the form of broad anticlines and synclines) occurred after the deposition of the youngest deltaic sediments preserved in the Wartburg Basin. Apparently, that deformation exerted no control on deposition of deltaic facies in northeastern Tennessee.

CHAPTER II

METHODS

Sample Selection and Collection

The procedures for sample selection differ from those generally used. Coal is commonly collected and combined before chemical tests are run (ASTM D346-78). Such results provide only a gross chemical identity. More recent studies (Nichols, 1968; Gluskoter, et al., 1973; Barrett, 1979) have shown that the concentrations of elements change vertically through a coal section. The greatest changes in composition appear near the top or at the base of the coal and in the vicinity of intracoal shaly partings, etc.

In this study, an accurate stratigraphic position and distance (± 1.0 cm) to the coal-sediment contact was maintained for all samples. Adjacent to the contact, samples were more closely spaced while away from the contact, larger intervals were selected. The sample intervals are shown in Figure 3. Representative horizons of the sediments and coals were reserved for thin section or polished section mounts and X-ray fluorescence analysis. Selected samples were analyzed using X-ray diffraction and low-temperature ashing techniques.

It should be noted that in some cases the sediment overlying the coal was so friable and shaly it was impossible to extract layers larger than a few millimeters in thickness. Here it was necessary to combine samples and make a bulk sample which represents a layer several centimeters thick.

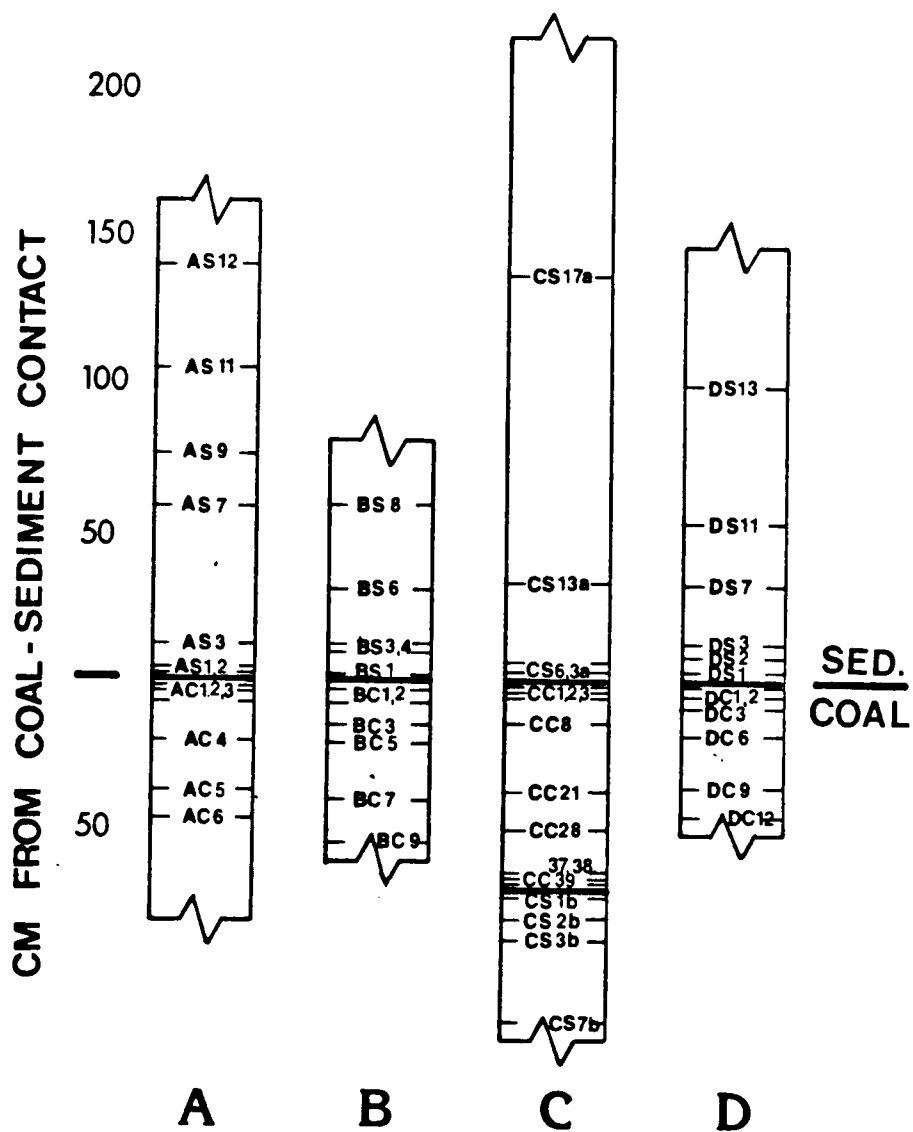


Figure 3. Sampling intervals.

Petrographic Analysis

To supplement the hand sample descriptions of the lithotypes present at the four sample sites, twenty thin sections were examined. Detailed descriptions were made for each noting such characteristics as grain size and, if applicable, size range, mineralogy, opaque constituents and the presence of organic material. Textural features such as pressure solution, secondary overgrowths and bedding plane structures, such as continuity of layers, cross beds, dewatering channels and differential compaction were noted. The detailed petrographic descriptions are given in Appendix B.

Estimates were made for the percent of major lithologic components. Point counts of these fine-grained sediments were not conducted in this study. The predominant clasts sizes ranging primarily from clay to silt, makes the point count procedure relatively ineffective. Petrographic analyses of the thin sections and X-ray diffraction analyses of several samples provided adequate information for lithologic descriptions.

Point count data were obtained for polished sections of coal to test a basic premise of the study, the selection of a relatively homogeneous coal horizon. The detailed study of the coal sections also provided a more accurate description of the morphology, distribution and abundance of sulfide minerals. Details of the petrographic study of the coal are in Appendix A.

X-Ray Fluorescence

X-ray fluorescence was used in this study to determine elemental concentrations in the coal and the associated sediments. The TEFA

(tube-excited fluorescence analyzer) analysis of whole coal specimens provides a linear least-squares fit of X-ray intensity versus elemental concentration using standards of known concentration. The program corrects the observed X-ray intensities for absorption and/or enhancement effects caused by the presence of other elements in the sample. Using this procedure it is possible to obtain quantitative data for major and minor elements of coal.

The EG&G ORTEC 6110 TEFA, was used to determine concentrations for major and minor elements concentrations for selected samples. The coal and sediment samples were analyzed for Si, Al, Fe, Ca, K, Mg, Ti, Mn, and S. Concentrations for some minor elements (Cl, P, V, Cr, Co, Ni, Ba, Sr, Pb, As, Br, U, Rb) were obtained on the coal samples, but were not used in this study since there could be no comparison with the sediments. The spectrometer run conditions for elemental analyses are summarized in Appendix A, Tables 9 and 10.

The sedimentary rocks were analyzed semi-quantitatively, as there was no appropriate computer program nor a sufficient number of well documented sedimentary rock analyses in order to correlate X-ray intensity measurements with elemental concentrations. An attempt to quantify the sedimentary data was made using a USGS standard shale sample (SCo-1) and generating X-ray intensity versus elemental concentration curves. Even though the standard chosen is very similar chemically to the average Paleozoic shale (Clarke, 1924), it is realized that errors from enhancement and/or absorption may be introduced by this procedure. Still, the relationships that may exist between the coal and the sediment are more clearly shown when

X-ray intensities are converted to elemental concentrations, albeit with semi-quantitative determinations of those concentrations.

X-Ray Diffraction

X-ray diffraction was used to determine the minerals present in selected shales and coal ashes. Samples closest to the coal contact and all sediment samples from site B, the most clay- and silt-rich section, were analyzed. Coal samples with the highest percent ash residue (i.e., the highest clastic mineral content) were prepared in an identical manner (Appendix A). The data were recorded from a 2θ arc of 2° through 72° .

Low-Temperature Ashing

Low-temperature ashing (Gluskoter, 1965) was performed on twelve of the coal specimens with the highest percent ash determined by X-ray fluorescence (See Appendix A). Low-temperature ashing was employed to preserve the mineral composition and structure which are often damaged at higher temperatures. The ash from this procedure was analyzed by X-ray diffraction to determine the mineral composition of the coal and coal rash (a very carbonaceous shale unit directly above the coal).

CHAPTER III

RESULTS

Sedimentary Petrology

Detailed petrographic descriptions of the lithologic types are presented in Appendix B. General descriptions of the sediments adjacent to the coal are summarized in the following discussion (See Figure 4).

The sediments overlying the coal at site A comprise alternating layers of claystone and siltstone, suggesting initial deposition within a low-energy environment. Fluctuating current activity within channels is inferred by field evidence including undulating bedding surfaces and lensoid-shaped beds. Grain sizes generally increase vertically away from the coal-sediment contact. The carbonized foliage of the seed fern, sphenopterid, is preserved along the surface of bedding planes. Siderite-rich solutions migrated along bedding planes of sediment and solidified to form concretionary masses at site A.

At site B, the sediment overlying the coal is fine grained (clay to fine silt). There is no general increase in the grain size as at site A. Siderite-rich solutions did not play a significant role in the chemical diagenesis of the sediments at site B. A coal rash separates the shale from the coal. The predominance of clay- and silt-size particles in the upper clastic sequence is consistent with accumulation in a low-energy environment. The bedding surfaces are nonplanar and discontinuous. During deposition, the

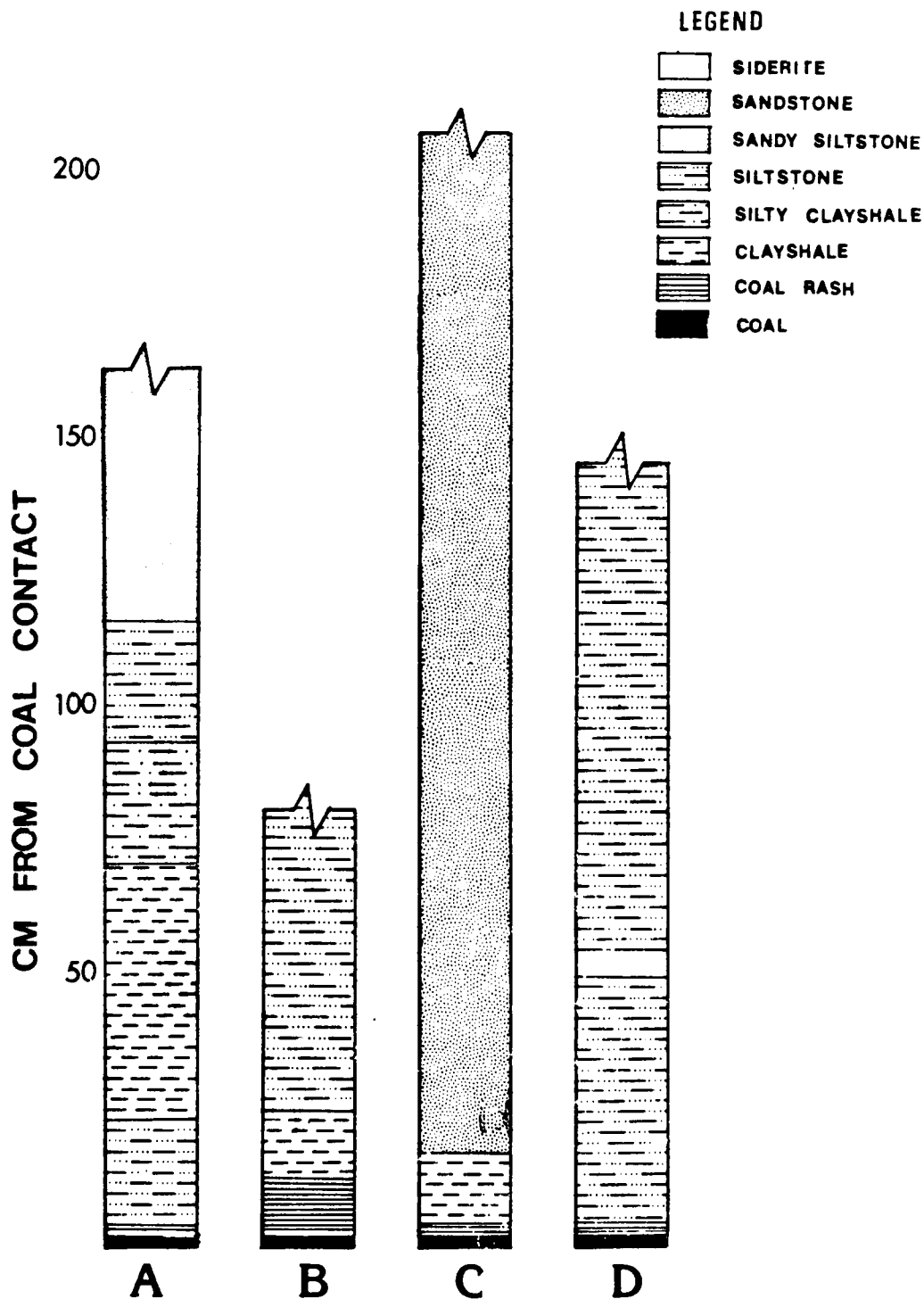


Figure 4. Lithologic character of sediments above the coal at the sampling sites.

unconsolidated sediment varied in initial water content; this resulted in progressive water removal with differential sediment compaction and generation of dewatering channels. Secondary calcite precipitated in fractures that penetrated the partially consolidated sediment. This provides evidence of a redistribution of primary carbonate after the initial stages of lithification or of secondary introduction of carbonate.

The sediments at site C are the most coarse grained of any represented by the study sections. The sandstones and silty sandstones (below the coal) reflect deposition within higher energy environments such as major river channels. The sediments both stratigraphically above and below the coal were accessible at site C and thus provide a relatively complete depositional content for interpreting the original coal environment. A coal rash stratigraphically overlying the coal seam records the transitional period between coal swamp and then primarily clastic deposition. The shales above the coal rash are, in turn, overlain by massive sands deposited in a higher energy environment. The energy level was relatively constant although shifting through time. Within these sands are angular, granule-sized fragments of coal which had been introduced to this depositional sequence after formation in adjacent environments. Locally, the development of silt and clay laminations along irregular depositional surfaces indicate periods of quiescence. Variable interstitial material indicates changing chemical environments. Initially, silica-rich fluids were dominant, but with further deposition, the solutions moving through the sediment became more carbonate-rich.

A sandy siltstone stratigraphically underlies the coal seam at site C. The nature of the coal swamp development is apparent as the (lower) sediment coal contact is approached. Coal stringers increase in frequency and thickness as the sediment grain size decreases. Coal fragments, possibly reworked from adjacent peaty environments, are found in the siltstone below the coal at site C.

A laterally continuous band of siderite subdivides a massive sequence of siltstone at site D. The sediment coarsens upward from a very fine siltstone (below the siderite) to a siltstone (above the siderite band). As the coal swamp was buried under layers of silty siliceous sediment, a notable decrease occurred in the amount of organic material transported into this area and preserved in situ as coal. This may reflect a decrease in organic productivity or an apparent dilution effect resulting from increased influx of clastic material. The siltstone above the concretionary siderite band is very homogenous, texturally, with only slight variations in composition. Partings have developed, possibly from the alternating wet-dry nature of the depositional regime. The siderite band (50 cm above the coal-sediment contact) is 5 cm thick and is laterally continuous on the outcrop for at least 20 m (65 feet).

Sideritic concretions provide evidence of the original constituents of the clastic sediment and the subsequent redistribution of elements and minerals (Hemingway, 1968). Hydrosols of iron and other oxides were initially dispersed throughout the interstitial spaces, protected from chemical interaction by stable organic colloids.

The colloids undergo a dehydrating stage and then a gelatinous stage before the final formation of the siderite concretion. Carbon dioxide originates in abundance through the process of devolatilization of the underlying coal and diffuse carbonate debris. Devolatilization occurs by the further decomposition of organic matter and from the reduction in volume caused by an increased sediment overburden. Minor amounts of carbonate are supplied by indigenous fauna, bicarbonate in solution in the interstitial water and primary detrital carbonate. The iron and carbonate combine to form siderite in a late diagenetic process.

Coal Petrography

The Pewee coal was chosen for this study because of its apparent homogeneity in texture and chemical composition. Point count data (see Table 1) was taken to evaluate the variability of the maceral composition. The chart developed by Van der Plas and Tobi (1965) allows for the determination of the reliability of modal analysis in terms of standard deviation. Using approximately 250 points, the point count analyses are subjected to an error of $\pm 5\%$ with a 95% confidence. Slight variations occur, but typical abundance (i.e., expressed as percent by volume) of the coal constituents are vitrinite (80%), exinite (15%) and inertinite (5%). See Appendix C for definition of terms. Slight variations, particularly in the amount of pyrite and other mineral matter, are found within the seam at different stratigraphic positions.

The four sites were subjected to varying degrees of intensity and duration of surficial weathering. Site A was considered to have

TABLE 1
POINT COUNT DATA FOR PEWEE COAL

SAMPLE	VITRINITE	INERTINITE	EXINITE	FRAMBOIDAL PYRITE	OTHER MINERAL MATTER	TOTAL COUNTS
AC-1	49.4	14.9	34.9	0.8	0.0	255
AC-2	89.0	1.5	9.1	0.0	0.4	263
AC-3	81.7	7.0	10.6	0.0	0.7	302
AC-4	92.5	1.1	6.4	0.0	0.0	266
AC-5	79.9	2.0	18.1	0.0	0.0	293
AC-6	82.7	4.3	11.8	0.0	1.2	255
MEAN	79.2	5.1	15.2	0.1	0.4	272
ST.DEV.	15.4	5.3	10.4	0.3	0.5	
BC-1	92.1	1.1	6.4	0.0	0.4	265
BC-2	80.2	4.0	15.8	0.0	0.0	278
BC-3	71.8	10.4	16.6	0.0	1.2	259
BC-5	89.4	1.1	9.1	0.0	0.4	265
BC-7	79.9	4.3	15.0	0.0	0.8	254
BC-9	78.1	3.7	17.6	0.0	0.7	301
MEAN	81.9	4.1	13.4	0.0	0.6	270
ST.DEV.	7.5	3.4	4.6	0.0	0.4	
CC-1	77.1	4.6	18.3	0.0	0.0	306
CC-2	84.4	6.8	8.8	0.0	0.0	250
CC-3	85.3	5.3	8.7	0.0	0.8	265
CC-8	81.8	0.7	15.4	0.0	2.1	280
CC-21	64.9	11.6	22.5	0.0	1.1	276
CC-28	76.6	6.6	16.8	0.0	0.0	256
CC-37	71.8	10.0	17.0	0.8	0.4	259
CC-38	65.9	7.1	23.5	0.8	2.7	255
CC-39	77.9	10.0	7.7	0.7	3.7	271
MEAN	76.2	7.0	15.4	0.3	1.2	269
ST.DEV.	7.4	3.3	5.9	0.4	1.3	
DC-2	81.9	1.7	16.3	0.0	0.0	288
DC-3	90.7	0.8	8.5	0.0	0.0	259
DC-6	91.7	0.4	7.1	0.0	0.8	253
DC-9	86.0	4.5	9.4	0.0	0.0	286
DC-12	80.6	1.9	15.6	0.0	1.9	263
MEAN	86.2	1.9	11.4	0.0	0.5	270
ST.DEV.	5.0	1.6	4.3	0.0	0.8	
PEWEE SEAM MEAN	80.1	4.9	14.1	0.1	0.7	270

TABLE 1 (continued)

SAMPLE	VITRINITE	INERTINITE	EXINITE	FRAMBOIDAL PYRITE	OTHER MINERAL MATTER	TOTAL COUNTS
SITES A THROUGH D AST. DEV.	9.7	3.9	6.5	0.3	0.9	
SITE E BARRETT'S DATA UPPER 65 CM MEAN ST.DEV.	78.0 12.9	7.7 6.1	13.2 9.0	0.2 0.8	0.9 1.9	

been the most weathered, having been exposed for several years. Sites B and D are less weathered and site C (the core) is considered unweathered. The point count data showed no obvious relationship between the major coal constituents preserved and the degree of weathering.

The abundance and stratigraphic distribution of the mineral matter at site D is distinctive. Near the coal-sediment contact the mineral matter reaches 33%, by volume. DC-1 is a coal rash and not a pure coal. This sample is an example of a transitional lithology between relatively pure coal and terrigenous clastics. Below the rash, the coal at site D is relatively pure, containing only small amounts of pyrite and other mineral matter. If sample DC-1 is excluded from the calculations, the coal at site D has the highest average concentration of vitrinite (86%), higher than the overall Pewee seam average (78%), but within two standard deviations of the average.

X-Ray Fluorescence

The X-ray fluorescence data provides information concerning the elemental distributions in the coal and sediments. The data are shown in Figures 5 to 13. Statistical parameters for the data are given in Tables 2, 3, 4 and 5, pages 40, 41, 42, and 43, respectively. A summary of major elemental trends, as well as apparent anomalies, is presented here.

1. As expected, most of the elements analyzed in both the clastic sediments and the coal (Si, Al, Fe, Mg, K and Ti) are present

Figure 5. Silica distribution in the Pewee coal and associated sediments.

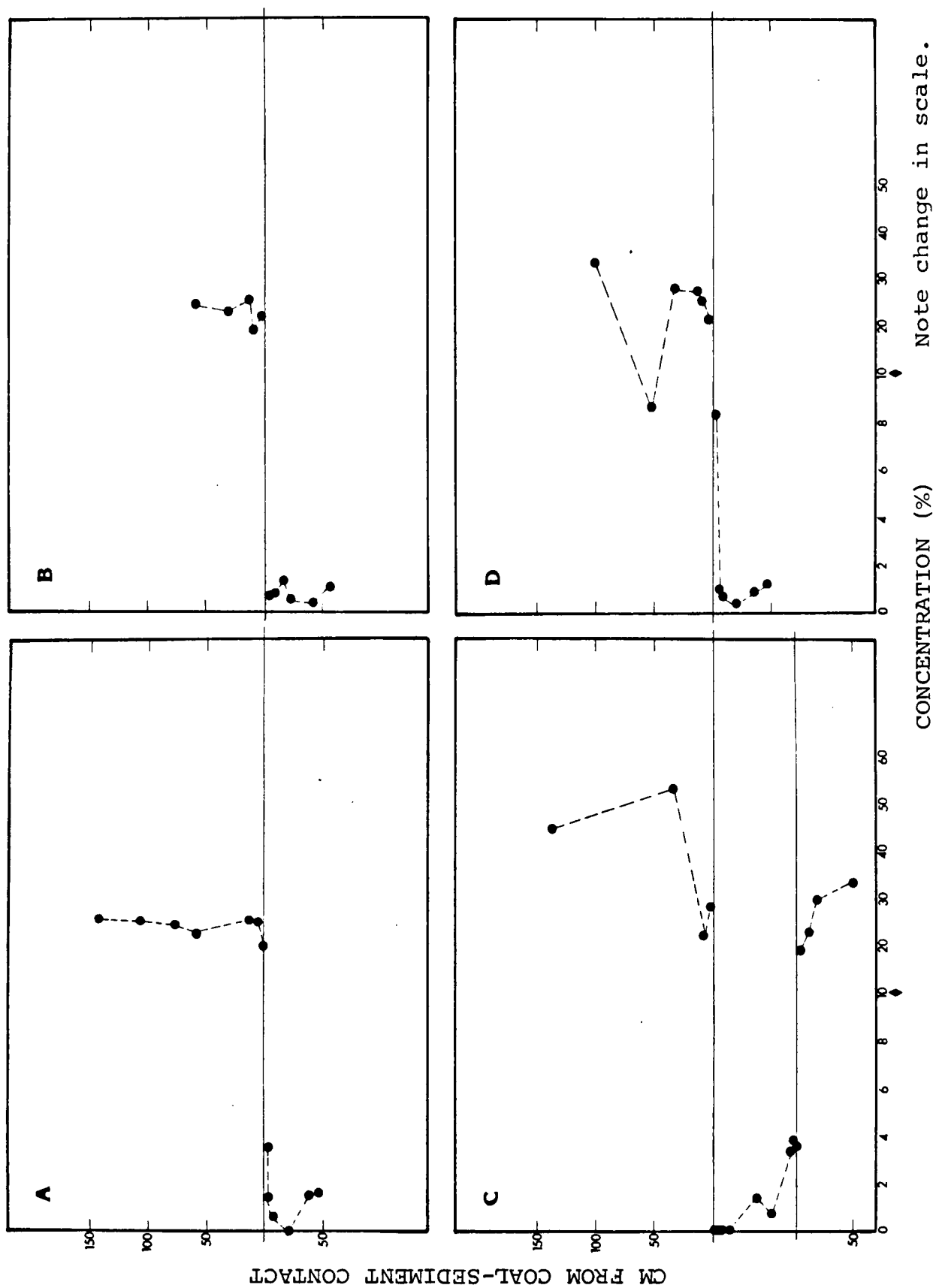


Figure 6. Aluminum distribution in the Pewee coal and associated sediments.

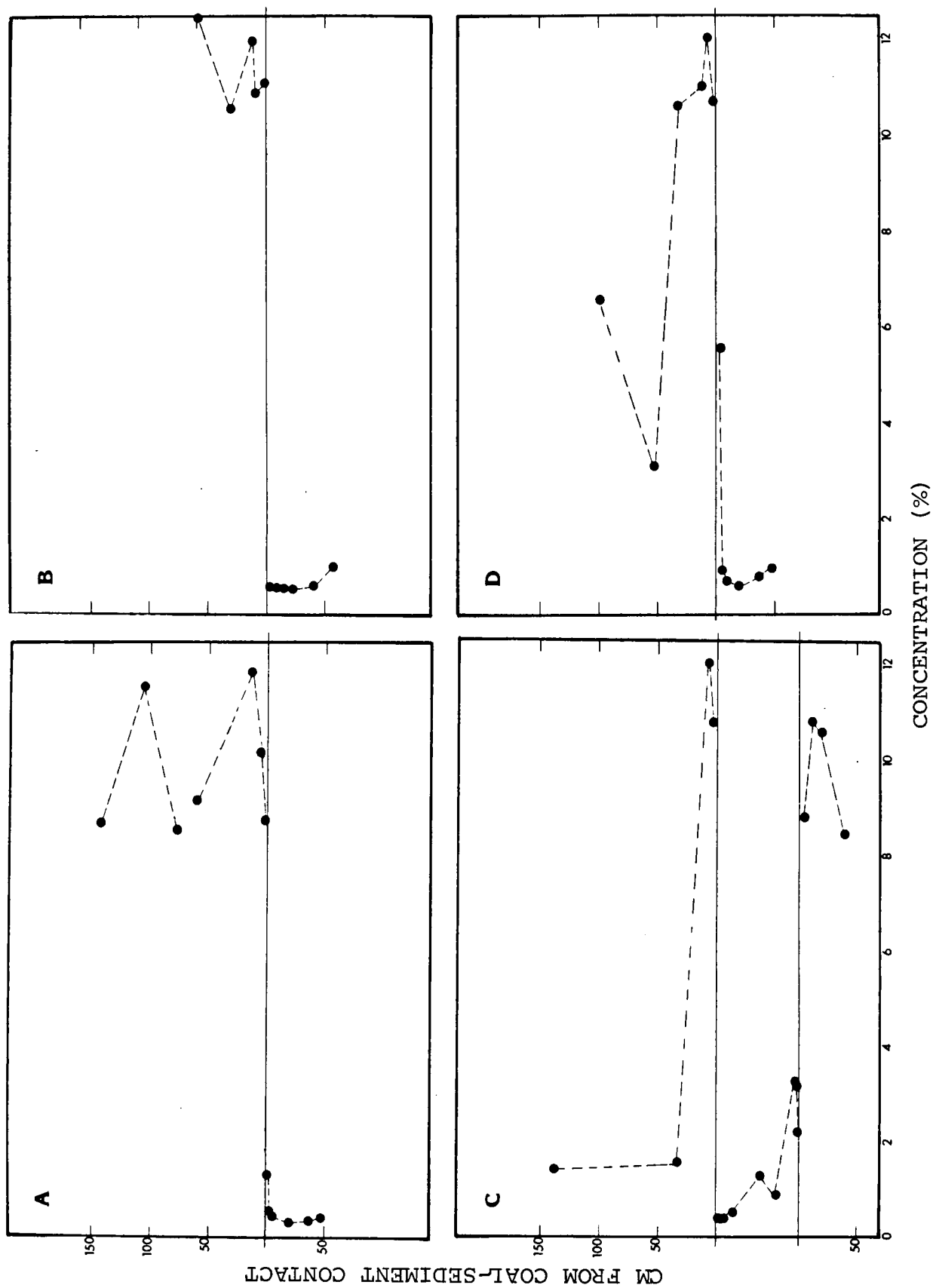


Figure 7. Iron distribution in the Pewee coal and associated sediments.

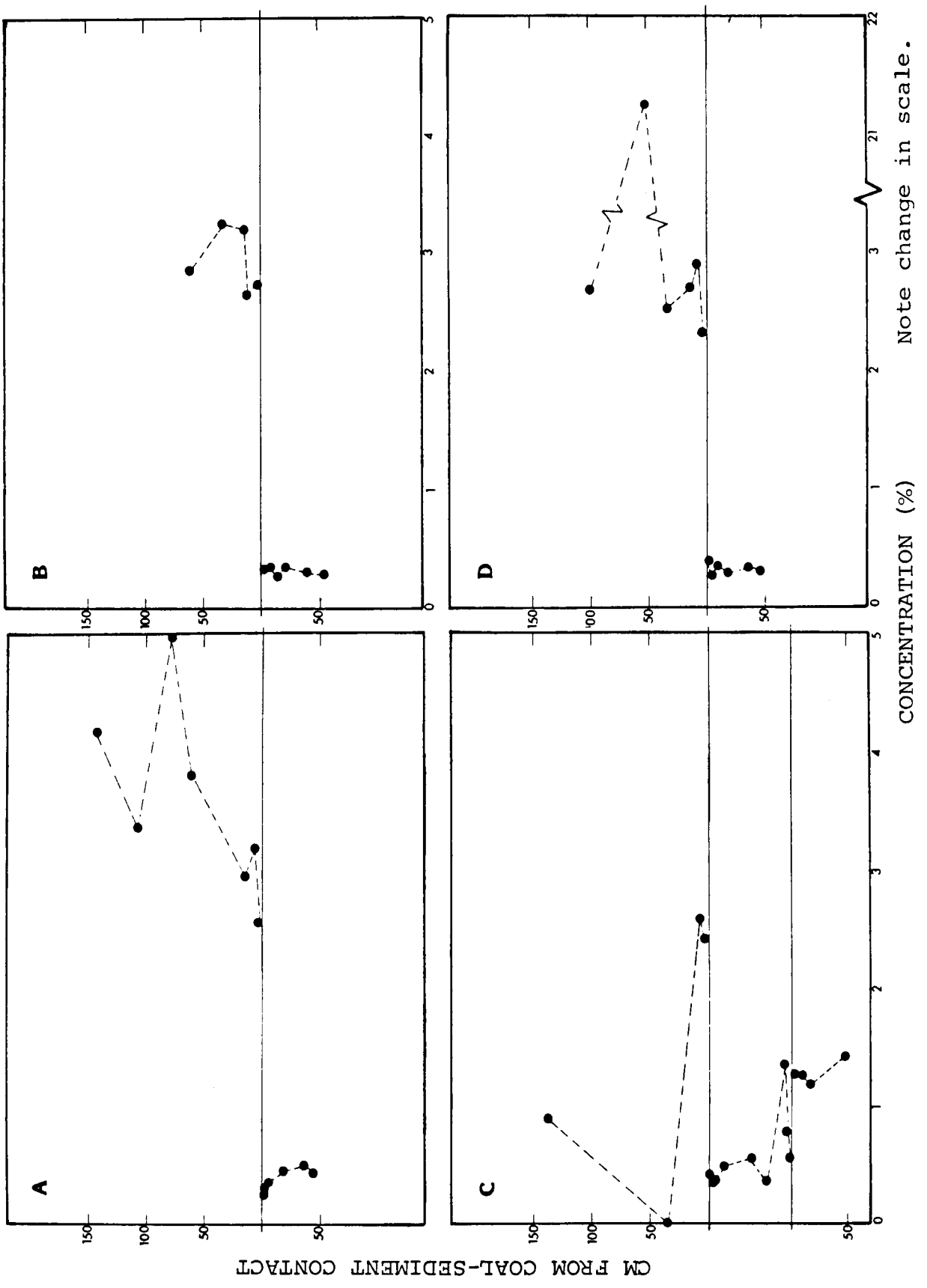


Figure 8. Calcium distribution in the Pewee coal and associated sediments.

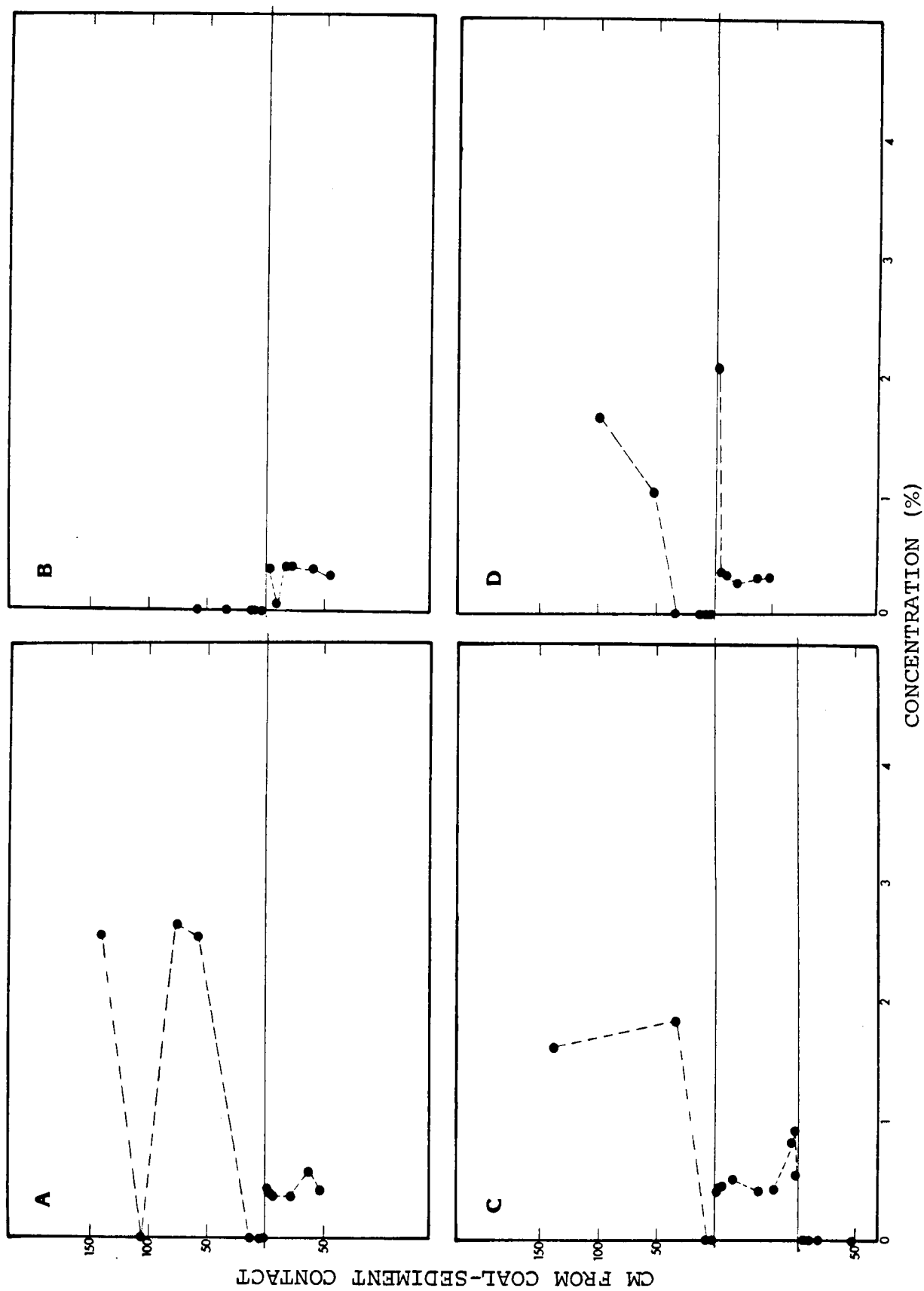


Figure 9. Potassium distribution in the Pewee coal and associated sediments.

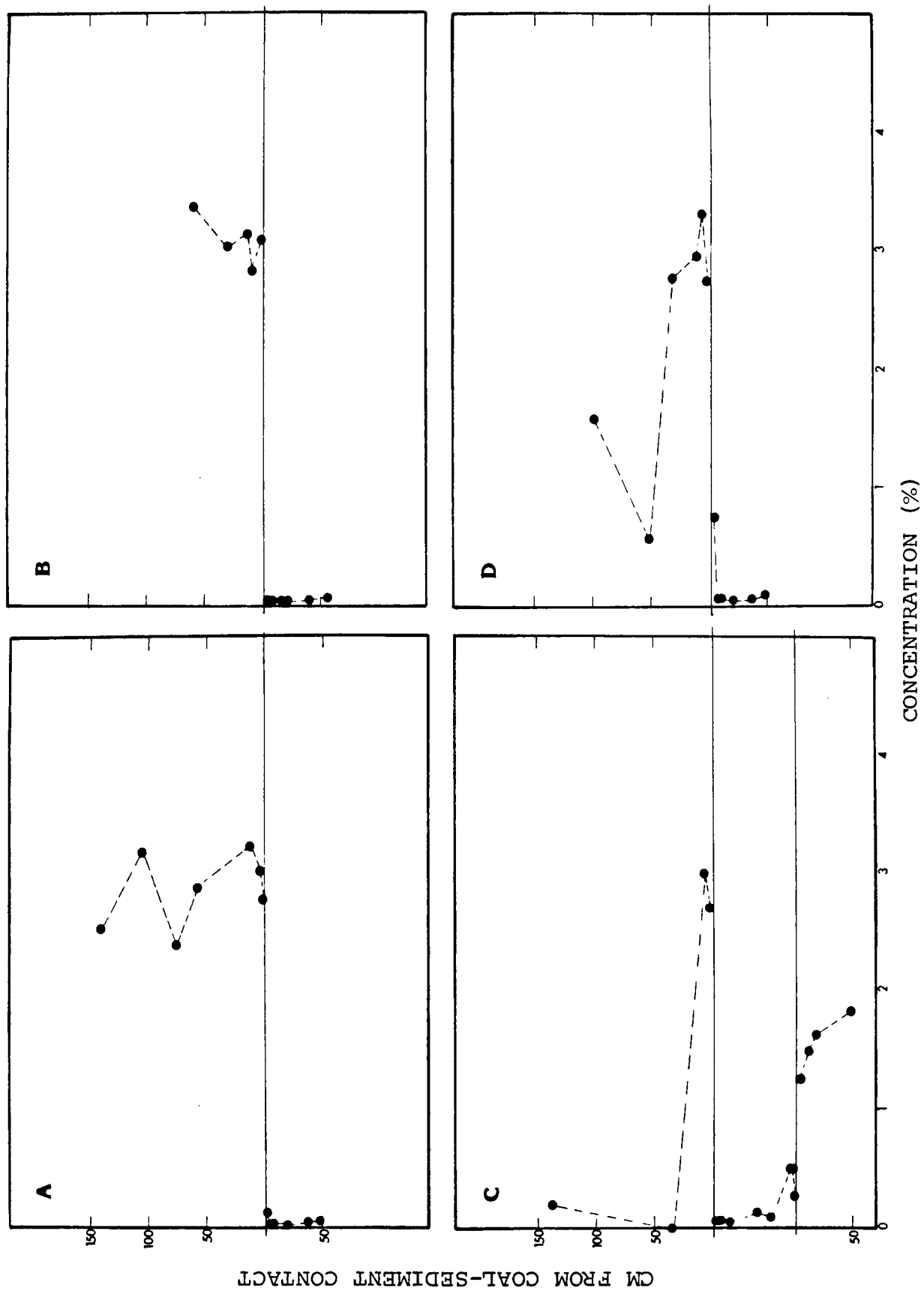


Figure 10. Magnesium distribution in the Pewee coal and associated sediments.

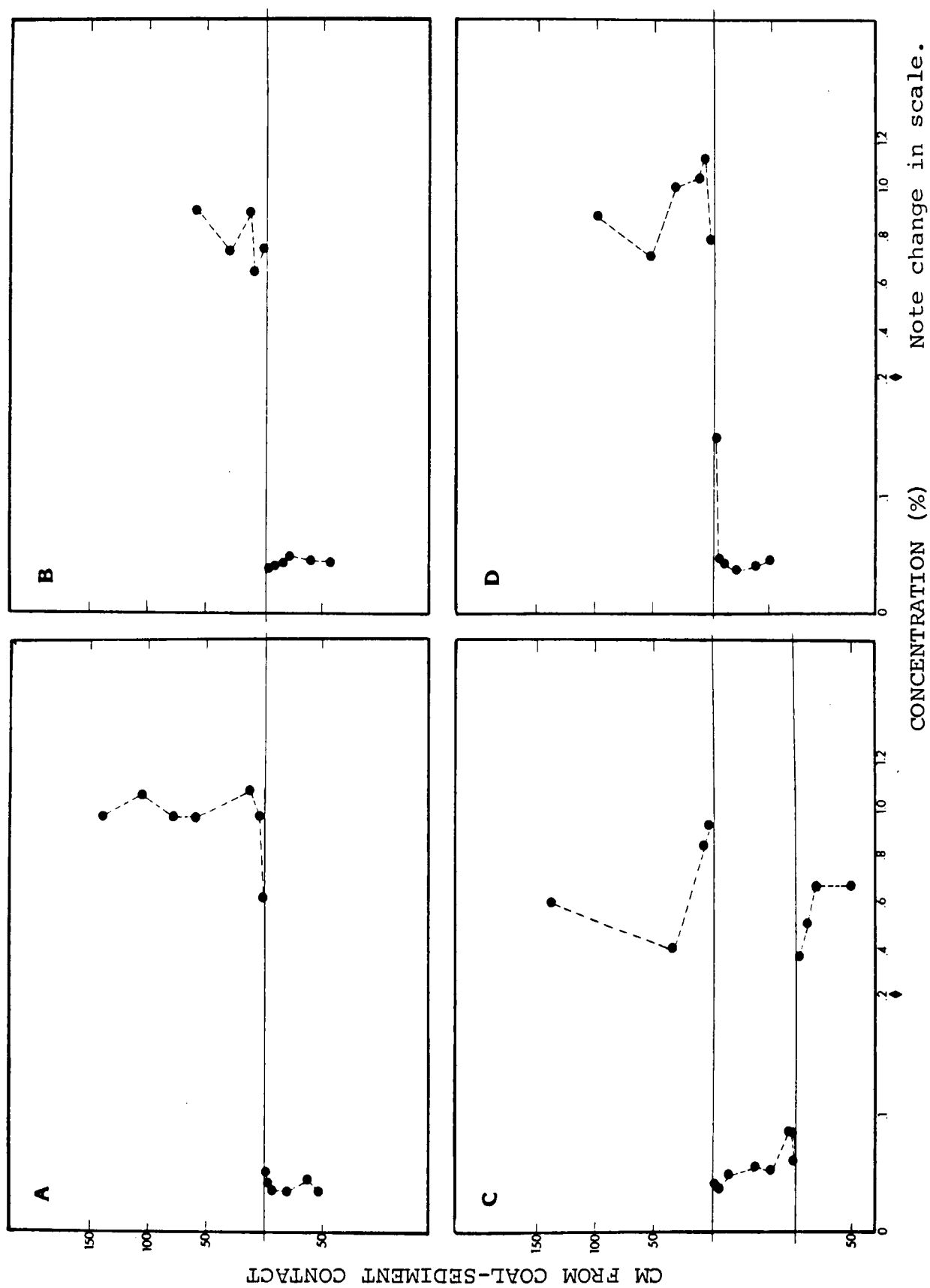


Figure 11. Titanium distribution in the Pewee coal and associated sediments.

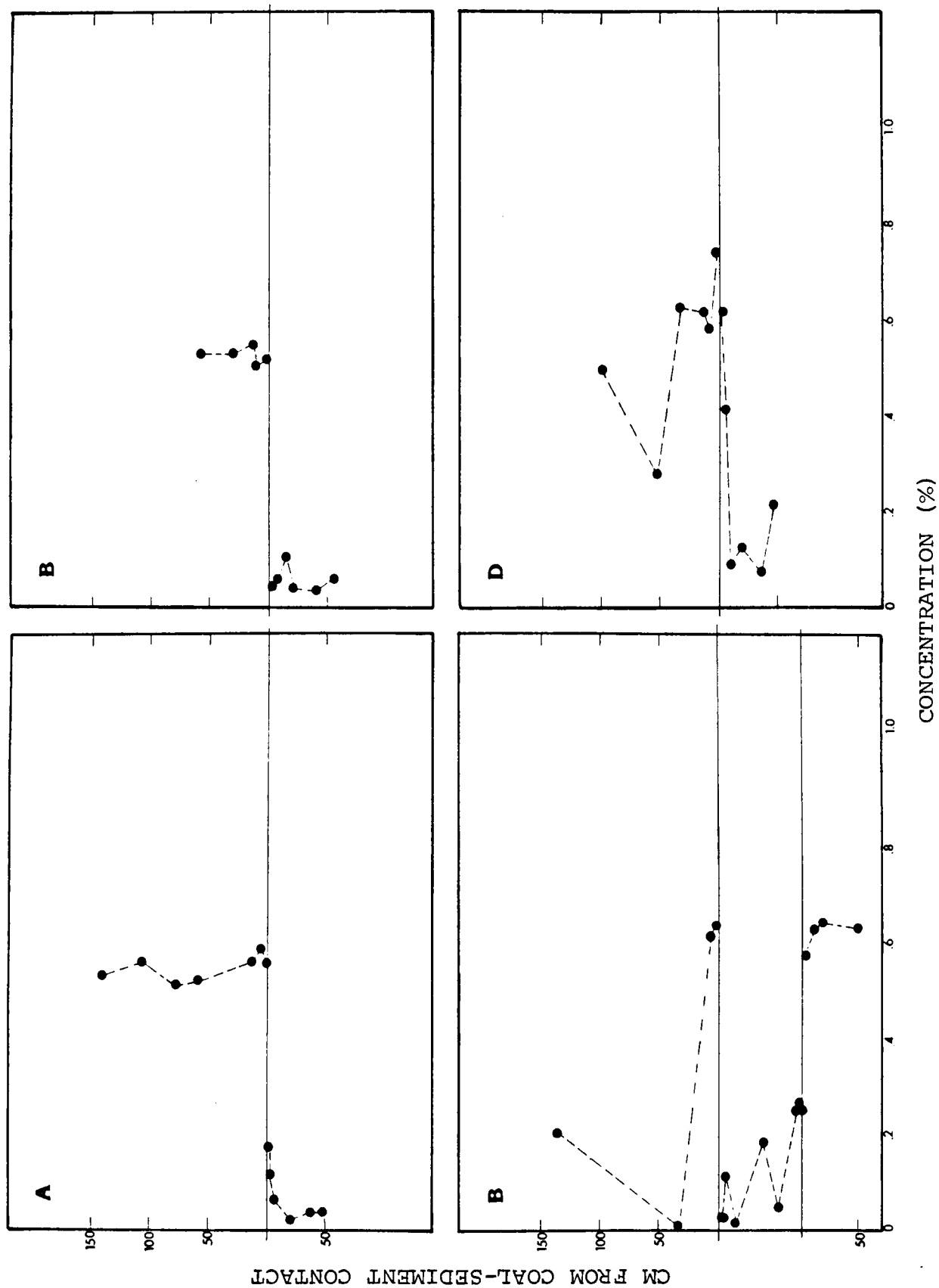


Figure 12. Manganese distribution in the Pewee coal and associated sediments.

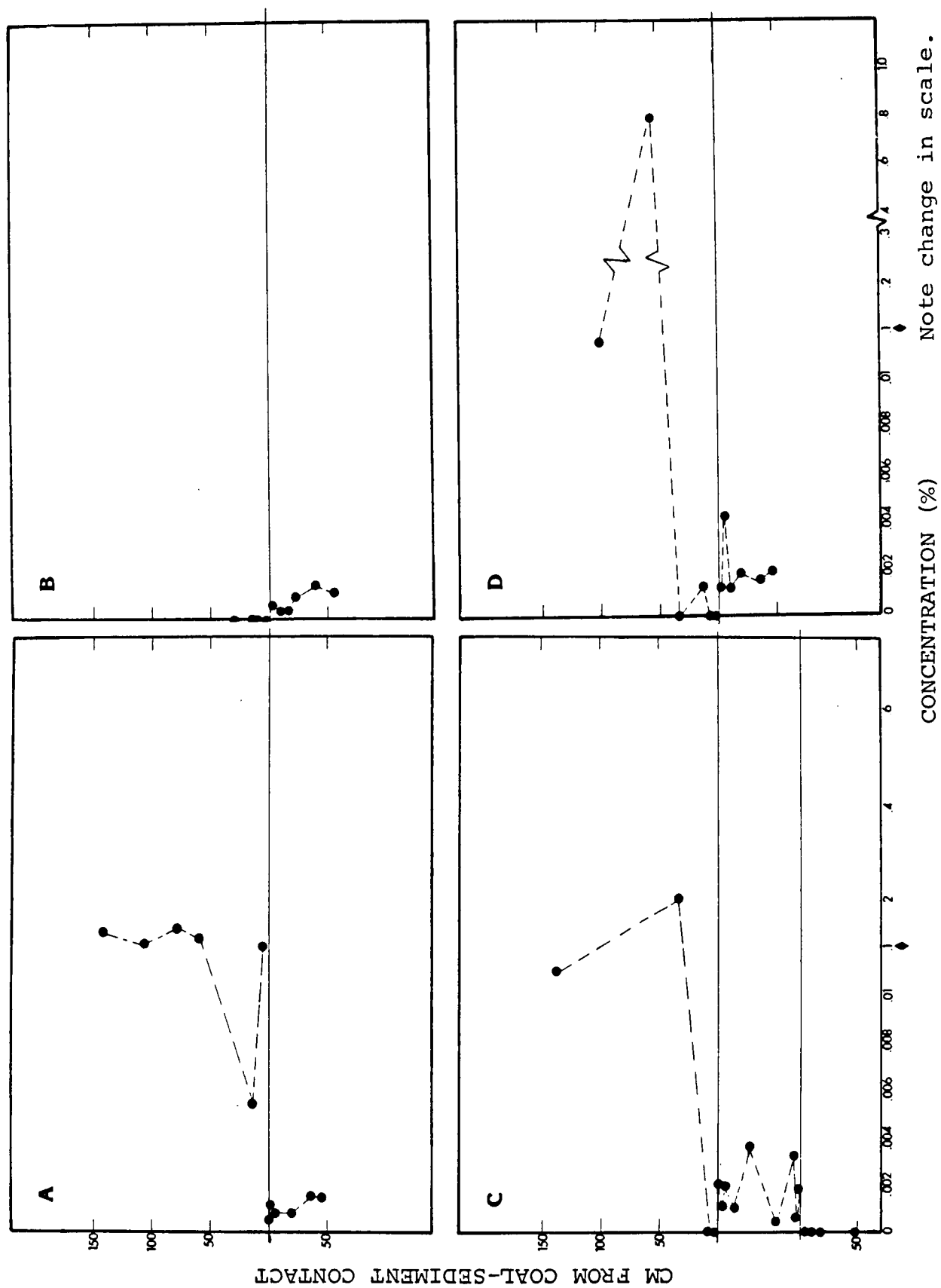


Figure 13. Sulfur distribution in the Pewee coal and associated sediments.

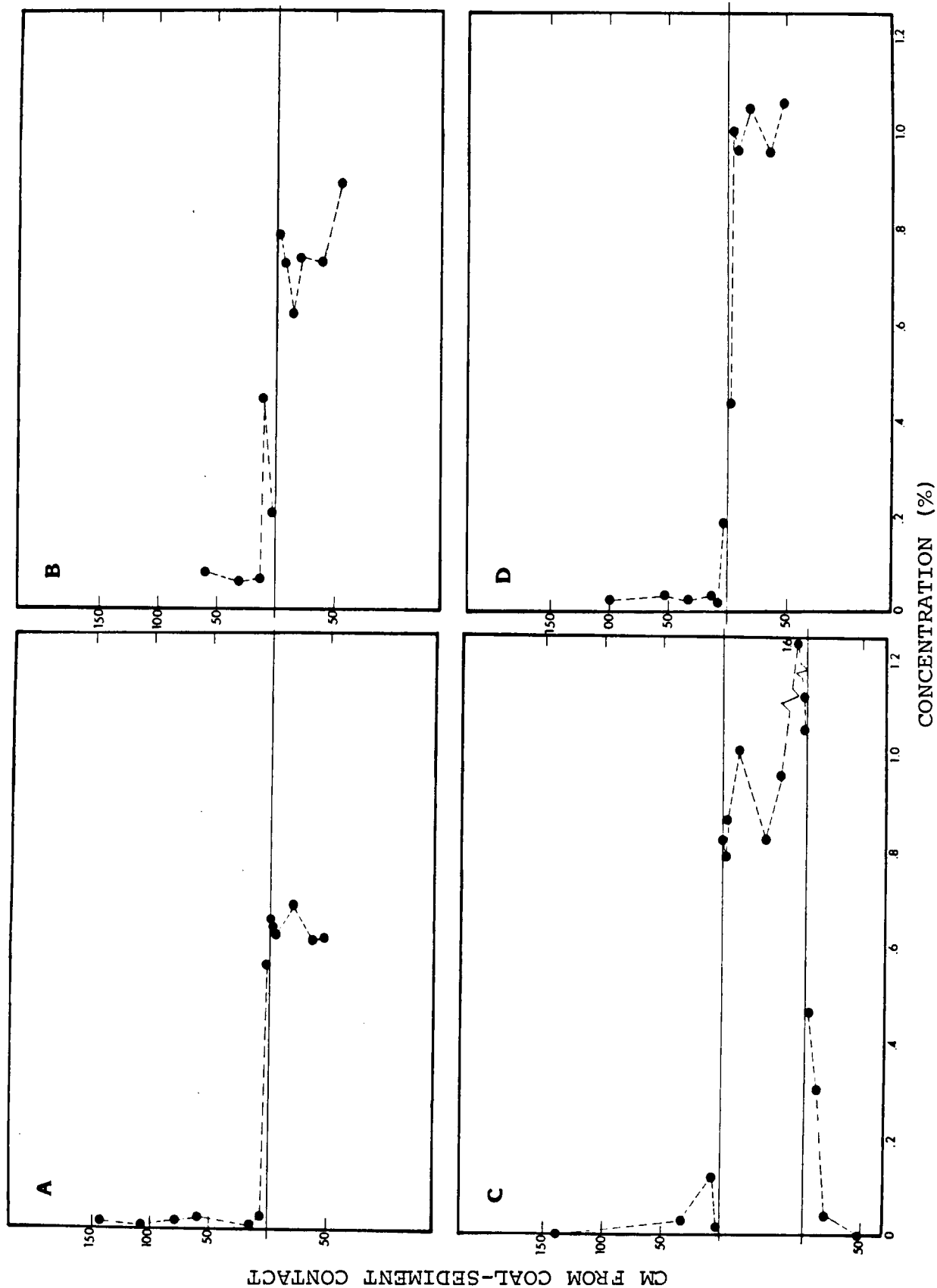


TABLE 2
MEANS AND STANDARD DEVIATIONS OF ELEMENTAL CONCENTRATIONS
FOR THE PEWEE COAL

	SITE D	SITE B	SITE C	SITE E	SITE A
Si	0.82(0.28)	0.84(0.38)	1.52(1.63)	1.93(1.12)	0.97(1.35)
Al	0.80(0.16)	0.64(0.07)	1.39(1.19)	1.02(0.75)	0.56(0.38)
Fe	0.31(0.03)	0.32(0.03)	0.57(0.32)	0.53(0.10))	0.38(0.09)
Ca	0.33(0.03)	0.30(0.12)	0.55(0.19)	0.44(0.70)	0.41(0.08)
K	0.07(0.02)	0.05(0.01)	0.19(0.19)	0.07(0.13)	0.06(0.03)
Mg	0.04(0.00)	0.04(0.00)	0.05(0.02)	0.04(0.06)	0.04(0.01)
Ti	0.18(0.14)	0.06(0.03)	0.13(0.11)	0.13(0.03)	0.08(0.06)
Mn	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)
S	1.00(0.05)	0.74(0.09)	1.01(0.25)	0.84(0.03)	0.63(0.03)

TABLE 3

MEANS AND STANDARD DEVIATIONS OF ELEMENTAL CONCENTRATIONS
FOR SEDIMENTS ASSOCIATED WITH THE PEWEE COAL^a

	SITE D	SITE B	SITE Ca ^b	SITE A	SITE Cb
Si	24.6(8.5)	23.1(2.3)	37.2(14.7)	24.2(2.1)	26.7(7.0)
Al	9.0(3.5)	11.4(0.9)	6.5(5.8)	9.8(1.4)	9.7(1.2)
Fe	5.7(7.6)	3.0(0.3)	1.4(1.3)	3.6(0.8)	1.3(0.1)
Ca	0.5(0.7)	0.0(0.0)	0.9(1.0)	1.1(1.4)	0.0(0.0)
K	2.3(1.0)	3.1(0.2)	1.5(1.6)	2.9(0.3)	1.5(0.2)
Mg	0.9(0.2)	1.0(0.1)	0.7(0.2)	0.9(0.2)	0.6(0.2)
Ti	0.6(0.2)	0.5(0.0)	0.4(0.3)	0.6(0.0)	0.6(0.0)
Mn	0.1(0.3)	0.0(0.0)	0.1(0.1)	0.1(0.1)	0.0(0.0)
S	0.1(0.1)	0.2(0.2)	0.0(0.1)	0.1(0.2)	0.2(0.2)

^a The sediments at site E (Barrett, 1979) were not available.

^b Ca designates sediment samples at site C which overlies the coal. Cb designates the sediment below the coal.

TABLE 4

RANGE OF ELEMENTAL CONCENTRATIONS IN THE PEWEE COAL IN %

	SITE D	SITE B	SITE C	SITE E	SITE A
Si	0.42-1.16	0.47-1.41	0.12-3.90	0.87-6.88	0.00-3.52
Al	0.60-3.31	0.54-0.99	0.39-3.31	0.26-4.20	0.29-1.33
Fe	0.28-1.34	0.27-0.36	0.35-1.34	0.41-0.78	0.25-0.50
Ca	0.29-0.91	0.06-0.38	0.41-0.91	0.21-0.57	0.35-0.57
K	0.06-0.50	0.03-0.08	0.05-0.50	0.00-0.70	0.04-0.12
Mg	0.04-0.09	0.04-0.05	0.04-0.09	0.00-0.26	0.03-0.05
Ti	0.08-0.41	0.03-0.11	0.02-0.27	0.09-0.25	0.03-0.18
Mn (ppm)	0.00-41.0	0.00-0.00	0.00-36.0	0.00-49.0	0.00-0.00
S	0.61-1.60	0.62-0.89	0.79-1.60	0.78-0.91	0.61-0.68

TABLE 5
RANGE OF ELEMENTAL CONCENTRATIONS FOR SEDIMENTS
ASSOCIATED WITH THE PEWEE COAL^a IN %

	SITE D	SITE B	SITE C _a ^b	SITE A	SITE C _b
Si	8.6-33.4	19.7-25.4	21.8-53.6	20.0-25.9	19.0-34.7
Al	3.0-12.1	10.5-12.6	1.4-12.1	8.6-11.9	8.4-10.8
Fe	2.3-21.3	2.7- 3.3	0.0- 2.6	2.6- 4.9	1.2- 1.4
Ca	0.0- 1.7	0.0- 0.0	0.0- 1.8	0.0- 2.6	0.0- 1.8
K	0.6- 3.3	2.8- 3.3	0.0- 3.1	2.5- 3.2	1.3- 1.8
Mg	0.7- 1.1	0.8- 1.1	0.4- 0.9	0.6- 1.1	0.4- 0.7
Ti	0.3- 0.7	0.5- 0.6	0.0- 0.6	0.5- 0.6	0.6- 0.7
Mn	0.0- 0.8	0.0- 0.0	0.0- 0.2	0.0- 0.1	0.0- 0.0
S	0.0- 0.2	0.1- 0.4	0.0- 0.1	0.0- 0.6	0.0- 0.5

^a The sediments at site E (Barrett, 1979) were not available.

^b C_a designates sediment samples at site C which overlie the coal. C_b designates the sediment below the coal.

in significantly greater amounts in the clastic sediments. Exceptions to this are sulfur, calcium and manganese.

2. The abundances of Si, Al, K and Mg in the sediments reflect the lithologies present (sandstones, siltstones and shales). Key minerals include quartz and clay minerals such as kaolinite and illite.

3. In general, most elemental concentrations decrease upwards, from the base to the top of the coal. This trend is best shown for samples from site C where the entire seam was available.

4. The sulfur content of the coals varies slightly. Site A has the least (average 0.6%), while B, C and D have successively higher amounts (up to average 1.0%).

5. At the very top of the coal, several elemental concentrations show a significant increase.

6. Ca and Mn were not detected in the sediments immediately adjacent to the coal, both above and below. Within approximately 35 cm (13.8 in.) above the coal contact (for all sections except B and the sediments below at C) the concentration increases to approximately 2.5% for Ca and to variable amounts (all below 0.8%) for Mn. Ca and Mn were not detected in the sediments above the coal at site B and below the coal at site C.

7. The highest Fe concentrations are found in the sediments which are siderite-rich (up to four times the next highest value). The sandstones at site C are very low in iron. The concentrations of Al, K and Ti are low in the sandstones at C and in the siderite band at site D. The Mn concentration is highest at and above the siderite band at site D.

8. All of the coal, except at site C, has very low concentrations (<0.1%) of potassium. The potassium is derived from the inorganic detritus, although the content of alkalis in plant material is well known (Bouska, 1981).

Correlation Coefficients

The correlation coefficients for element pairs in the sediment are shown in Table 6. Element pairs showing high correlations (>.70) reflect the typical associations in phyllosilicate minerals. Al has correlation coefficients of 0.86 with both K and Ti. Ti may substitute for Si and Al in clay minerals, or may occur in trace amounts of minerals such as rutile or ilmanite. The correlation between Si and Al, K, Ca, Mg appears rather low if phyllosilicates are the predominant mineral phases; however, the inclusion of data from several samples of very pure quartz sandstone may result in lower values of the correlation coefficients between Si and these elements. Mn and Fe have a coefficient of 0.90. This is thought to result from the large amount of siderite in some of the sediment samples and the solid solution series between MnCO_3 (rhodocrosite) and FeCO_3 (siderite).

Correlation coefficients for elemental pairs were also determined for the Pewee coal. The correlation coefficients are shown in Table 7. Many of the element pairs in the Pewee coal have correlation coefficients greater than 0.70. Most are thought to reflect the compositions of the clay minerals present (with little contribution from quartz sand). In addition, the organic components of coal are known to contain minor amounts of elements such as Al, Ti.

TABLE 6
CORRELATION COEFFICIENTS FOR SEDIMENTS
ASSOCIATED WITH THE PEWEE COAL

	Si	Al	Fe	Ca	K	Mg	Ti	Mn	S
Si	1.00								
Al	.33	1.00							
Fe	.53	.24	1.00						
Ca	.08	.61	.05	1.00					
K	.40	<u>.86</u>	.16	.30	1.00				
Mg	.29	.24	.06	.38	.58	1.00			
Ti	.35	<u>.86</u>	.19	.58	.66	.03	1.00		
Mn	.22	.55	<u>.90</u>	.21	.49	.14	.49	1.00	
S	.40	.28	.10	<u>.70</u>	.11	.21	.27	.08	1.00

TABLE 7
CORRELATION COEFFICIENTS FOR THE PEWEE COAL

	Si	Al	Fe	Ca	K	Mg	Ti	Mn	S
Si	1.00								
Al	<u>.95</u>	1.00							
Fe	.31	.50	1.00						
Ca	<u>.86</u>	<u>.90</u>	.33	1.00					
K	<u>.91</u>	<u>.98</u>	.58	<u>.90</u>	1.00				
Mg	<u>.92</u>	<u>.97</u>	.42	<u>.94</u>	<u>.95</u>	1.00			
Ti	<u>.84</u>	<u>.84</u>	.21	<u>.75</u>	<u>.78</u>	<u>.82</u>	1.00		
Mn	.02	.13	.33	.04	.12	.11	.41	1.00	
S	.01	.18	.65	.09	.22	.06	.10	.44	1.00

Ca, etc. (Stach, 1975). Some correlation coefficients are lower than expected. For example, Fe and S have a correlation coefficient of only 0.65. This results because Fe occurs not only in sulfides such as pyrite, but also in clay minerals such as illite. In a similar manner, not all the sulfur is present in sulfides. Some fraction is present in the macerals as well.

X-Ray Diffraction

X-ray diffraction was done on the sediments closest to the coal and on low-temperature ash residues that were calculated to have high ash percents based on XRF analyses. The clays were identified using the procedures described by Carroll (1970). A comparison of the clays found in the sediments and those found in the coals might provide evidence for the infiltration of detrital material or diagenetic changes within the sediments and adjacent coals during coalification and lithification. The X-ray diffraction results are summarized in Table 8.

Clay minerals account for up to 70% of all mineral matter in coal. The most frequent clays in coal are kaolinite and illite (Mackowsky, 1968). Kaolinite was found in every sample, both clastic sediment and coal ash, in this study. Illite ($\pm$ detrital muscovite) was also found to be ubiquitous except in the ash from coal at site B (although illite was found in the sediment at site B). Quartz was a common mineral in the sediments and most of the ashes.

The intensities of the peaks on the diffraction patterns for clay minerals in the ash were lower than those in the clastic sediment. In some samples, this made positive identification of the mineral

TABLE 8
SUMMARY OF XRD DATA

	Kaolinite	Illite	Chlorite	Siderite	Quartz
AS-2	X	X	X	X	X
AS-2 ash	X	X	X	X	X
AC-1 ash	X	X ^a		X	X
AC-2 ash	X			X	X
BS-6	X	X	X		X
BS-4	X	X	X		X
BS-3	X	X			X
BS-1	X	X			X
BC-3 ash	X				X
BC-9 ash	X				
CS-3a	X	X	X		X
CS-1a ash	X	X			
CC-21 ash	X			X	
CC-37 ash	X	X			
CC-38 ash	X	X			X
CC-39 ash	X	X			X
CS-1b	X	X			X
DS-11				X	X
DS-1	X	X	X	X	X
DC-1 ash	X	X			X
DC-2 ash	X				
DC-12 ash	X	X			X

^a10 Å peak is poorly developed; identification of illite is questionable.

phases difficult. Selected samples were glycolated and heat-treated at 550° C for one hour to aid in clay mineral identification.

To ascertain that the low-temperature ashing technique (Gluskoter, 1965) was not damaging to the clay minerals present, a sediment sample which was known to contain chlorite (sample AS-2) was oxidized under the same conditions as the coal. The resulting X-ray pattern contained only a very minor peak at 14 Å; however, this peak was enhanced after the sample was heated to 550° C for one hour. Such enhancement often occurs when chlorites are heated. This is considered evidence that the chlorite lattice is not destroyed by low-temperature ashing. Chlorite is present in most of the sediment samples, but in none of the coals.

Siderite was identified in both sediments and coal using XRD. Siderite is present in the concretionary band and in the sediment immediately adjacent to the coal at site D. The sediments and coal from site A also contain siderite. Sites B and C did not show any siderite in the sediments, nor did the coal at site B. One horizon (sample CC-21 ash) in the middle of the coal at C appears to contain minor siderite.

Mackowsky (1968) states that siderite is syngenetic in coal. It is formed in the coal swamp from either aqueous or colloidal solutions. It is intergrown with coal in diffuse mixtures. The biochemical stage of coalification lasts for such a long period of time that several generations of syngenetic minerals may form successively. Diagenetic siderite may occur in the overlying sediments.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

Several conclusions have been reached based on the data presented in this study. Some of the conclusions could have been anticipated or verify what was anticipated. Others add new details to our understanding of the relationship between a coal and the associated sediments.

1. The Pewee coal is a fairly homogeneous coal within the study area, as demonstrated by the XRF and point-count analyses. Small variations, both laterally and vertically, in chemistry can be attributed to interbedded microenvironments within the coal seam (Caruccio, et al., 1977). In the Pewee coal these variations are not of sufficient magnitude to alter the general elemental distribution. The nature and extent of the observed variations are discussed below.

2. Coal sections exposed to varying degrees of weathering were sampled in this study. Samples from an unaltered core were examined as were samples from outcrops subject to as much as several years of exposure. In the latter case, as much of the outer, obviously weathered rind was removed as possible. The chemical data obtained show no distinctive trend related to degree of sample weathering. The Pewee coal was not seriously altered by exposure to physical and chemical conditions on the earth's surface.

3. The chemical data for the elemental concentrations in the sediments corresponds well with the petrographic and XRD determined

mineralogy. The finer-grained fraction of the sediments are richer in Al, K, Mg, and Ti than the coarser grained sediments. The elemental distribution clearly reflects an increase in abundance of the clay minerals in the smaller sediment sizes. Silica is concentrated in the quartz sandstone while iron is concentrated in the sedimentary layers cemented by siderite concretions.

4. The clastic sediments have much higher concentrations of elements which comprise the typical rock-forming minerals (Si, Al, Fe, K, Mg and Ti). These concentrations are often an order of magnitude higher in the sediments than in the adjacent coal. This was expected, but the fact that the concentrations of sulfur, calcium and manganese are exceptions to this generalization is significant. Sulfur concentrations are higher in the coals than in the sediments. The sulfur concentration in the coal is approximately ten times greater than in the sediments. Ca and Mn are also found in higher concentrations in the coal than in the sediment immediately adjacent to the contact, although their concentrations increase away from the contact in some sections. Ca and Mn appear to have been depleted in concentration, i.e., they may have reacted with low pH fluids driven out of the peat during early diagenesis and have been transported some distance from the coal-sediment contact.

5. XRD analyses of the low-temperature ashing residue of the coals show a rather uniform clay mineralogy. Every sample contained kaolinite and two-thirds of the samples contained illite. The predominant clay mineral in other (English) bituminous coals is kaolinite with some illite present (Hicks and Nagelschmidt, 1943).

Kaolinite and illite appear to be stable with respect to the physico-chemical environment that exists in a coal swamp.

6. Chlorite is present in the overlying sediments but not in the coal. Chlorite's absence in coal may result from its removal by acids produced by the decomposition of plant material. In present-day peat bogs a low pH (<6), acidic environment is developed (Baas Beeking, et al., 1960). Chlorite is very soluble in acid (Grim, 1968). Any chlorite initially present in the peat bog may have readily gone into solution during the early stages of coalification. The impermeable mat of peat of overlying clays would prevent the infiltration of any chlorite added later into the developing peat. Alternatively, the coals may be chlorite free simply because chlorite was not present as a detrital mineral due to the mineralogic character of the source area.

7. When the analytical data from all four sites were compared there were no obvious trends between the elemental concentrations in the coal and the overlying sediments. The concentrations of elements in the sediments vary independently of the variation in concentration of elements in the coal, and vice versa. Any chemical interaction between the coal and the sediment in the form of solutions must have had only negligible effects for the Pewee coal. No significant variation could be attributed directly to sediment type.

8. The chemical data in this study were obtained for samples from both sides of the coal-sediment contact. The thicknesses of the varying lithotypes are known and can be used in conjunction with the chemical data. It is possible to examine the extent of the

transitional layer where changing elemental concentrations show the interactive influence of the clastic environment and the coal swamp. A transitional coal rash is developed above the coal at all of the sites studied. It is thickest (11 cm) at site B and only 2, 3 and 3 cm thick at sites C, A and D, respectively. The chemical distribution graphs (Figures 5 to 13, pages 22 to 38 respectively) display an abrupt increase in the characteristic concentration for that sediment type immediately above the coal-sediment contact. In the most noticeable cases of gradual change, the elemental concentration has reached the characteristic proportions within 10 cm. It may be significant that for any element for which the concentration changes gradually at the contact, the gradual change occurs only in the sediments of the coal, never both. At site B, the 10 cm thickness of the chemically transitional zone corresponds to the maximum thickness of the coal rash.

9. There are trends of decreasing upwards elemental concentrations from the base of the coal to the top. This is most clearly illustrated in the graphs for site C (Figures 5 to 13, pages 22 to 38 respectively), where the entire seam was available, although the other sections show this to some extent also.

The amount of detritus being brought into the Pewee swamp may have gradually decreased through time. The sudden increase in clastic content is cited as evidence for a sudden change in conditions. For example, the depositional sequence at site C is consistent with the establishment of a new distributary channel, flooding the area with clastic sediment and ending the stage of plant growth in the Pewee swamp.

At the very top of the coal (within 8 cm) there is often a rapid increase in many of the elemental concentrations. This sudden change suggests that the mat of decomposed vegetation was already well developed and dense enough so that clastic detritus could not penetrate it. If an increase in element concentration reflects an increase in the amount of detritus, the initiation of the Pewee coal swamp was more gradual than its demise.

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APPENDICES

APPENDIX A

APPENDIX A

Sample Numbering Scheme

All of the samples are identified using the following procedure. The first alphabetic letter designates the site. The second letter, S or C, designates whether the sample is sediment or coal. Arabic numerals were assigned in increasing order away from the upper coal-sediment contact to indicate the relative positions between samples. Samples AS-1 and AC-1, for example, are adjacent samples from site A, just above (AS-1) and below (AC-1) the upper coal-sediment contact. See Figure 3, page 10.

At site C, where both the upper and lower contacts of the coal were accessible, the sediments above the coal have the subscript 'a'. The sediments below the coal seam are numbered from the base of the coal, using the subscript 'b'.

Coal Petrography

Twenty-seven polished coal sections were made (six each from sites A, B, D and nine from site C). The sections were made from cuts perpendicular to bedding to preserve structural relationships. Point counting was done using a minimum of 250 counts per section (Swift point counting stage, 20X oil immersion objective, 10X ocular, reflected light). The point to point distance along a line was 0.34 mm. The lines were spaced 0.40 mm apart. The reliability of the modal analysis has been determined using the method of Van der Plas and Tobi (1965) to be subject to an error of $\pm 5\%$ with a 95% confidence interval. The constituents identified were vitrinite,

inertinite, exinite, framboidal pyrite, and other mineral matter. Traverses across the surface were taken at a 39° angle to the bedding of the coal (Chayes, 1956). The percentage of error versus inclination at this angle is zero.

XRF

Sample preparation for X-ray fluorescence was done in the Application Laboratory at EG&G ORTEC, Oak Ridge, Tennessee. The coals were dried for twenty-four hours prior to sample preparation. All other steps were the same for the coal and the clastic sediment. 4.0000 ($\pm$.0001) grams of sample were combined with 0.1000 ($\pm$.0001) grams sodium stearate (a grinding aid) and 1.0000 ($\pm$.0001) gram of boric acid (a binding agent) before grinding in a tungsten carbide mill (Spex Industries Shatterbox) for six minutes. Differential absorption may be caused by varying particle size (Zerny, et al., 1954; Burstien, 1962). Six minutes of grinding is sufficient to obtain a sample uniformly 30 microns in size and eliminate particle size variation (Wheeler, 1979). The pellets were formed using boric acid as a backing with a pelletizing pressure of 15 tons. Samples were stored in a vacuum dessicator until X-ray fluorescence analyses were run.

The EG&G ORTEC 6110 TEFA, tube-excited fluorescence analyzer, was used to analyze the major and minor elements of the coals and the major elements in the clastic sediments. An exponential, software program (ATAC) was used to quantitatively analyze the data. This program provides a linear least-squares fit to the interelement corrected intensities. The corrected intensities are the observed

X-ray intensities with absorption and/or enhancement effects removed. This compensates for the presence of other elements in the sample. In order to correct for overlapping lines, an interelement correction equation and a spectral deconvolution equation were utilized in this analysis (Wheeler and Jacobus, 1980). The spectrometer run conditions for the coal analyses are summarized in Table 9.

Because of the widely varying nature of sedimentary rocks, no accepted correlation line has been developed to relate X-ray intensities to concentrations. A few standards are available, but the great variability in chemistry between shales and sandstones, even among different shales, makes correlation procedures difficult and time consuming. In an attempt to obtain semi-quantitative values from the XRF data, the USGS standard, Cody Shale (SCo-1) was analyzed with each batch of sediments. The run conditions are summarized in Table 10. The USGS standard, the Cody shale (SCo-1), is similar to the average of 51 Paleozoic shales provided by Clarke (1924). See Table 11.

No attempt was made to correct the data for enhancement of absorption effects; however, those effects usually results in errors less than $\pm 15\%$ of the values calculated by linear correlation (Zussman, 1967).

The raw data from the XRF analyses are summarized in Tables 12 and 13.

The assayed concentrations of the Cody Shale standard were expressed as oxides. In order to compare the coal and clastic

TABLE 9

TEFA INSTRUMENTAL PARAMETERS FOR ANALYSIS OF
MAJOR AND MINOR ELEMENTS OF COAL

PARAMETERS	Mg, Al	Si, S, K, Ca, Ti, Fe	Mn
Anode	W	Rh	W
Filter	none	none	Cu
Anode Voltage (keV)	6	10	25
Energy Scale (keV)	0-10	0-10	0-10
Atmosphere	vac	vac	vac
Counting Time (seconds)	100	100	100

TABLE 10
TEFA INSTRUMENTAL PARAMETERS FOR ANALYSIS OF
MAJOR ELEMENTS OF SEDIMENTS

PARAMETERS	Mg, Al, Si, S, K, Ca, Ti, Mn, Fe
Anode	Rh
Filter	none
Anode Voltage (keV)	10
Energy Scale (keV)	0-10
Atmosphere	vac
Counting Time (seconds)	100

TABLE 11
COMPARISON OF SHALE ANALYSES

Oxides	Cody Shale ^a	51 Paleozoic Shales ^b
SiO ₂	62.808	63.7
TiO ₂	0.607	0.75
Al ₂ O ₃	13.807	17.0
Fe ₂ O ₃	5.237	4.3
FeO		3.1
MnO	0.060	trace
MgO	2.325	2.5
CaO	2.567	1.5
Na ₂ O	0.782	1.1
K ₂ O	2.655	3.8
P ₂ O ₅	0.198	0.2

^a Fabbi, B. P. and Espos, L. F., 1976, X-ray fluorescence analysis of 21 selected major, minor and trace elements in eight new USGS standard rocks, pp. 89-93, In: Flanagan, F. J., 1976, Ed., Descriptions and analyses of eight new USGS rock standards, USGS Prof. Pap. 840.

^b Clarke, F. W., 1924, The data of geochemistry, Geol. Surv. Bull. 778, 841 pp.

TABLE 12
ELEMENTAL CONCENTRATIONS IN % FROM X-RAY FLUORESCENCE
DATA ON PEWEE COAL

SAMPLE NUMBER	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe
AC-1	0.05	1.33	3.52	0.65	0.12	0.43	0.18	0.00	0.25
AC-2	0.04	0.54	1.43	0.64	0.04	0.37	0.12	0.00	0.31
AC-3	0.04	0.46	0.55	0.62	0.04	0.36	0.06	0.00	0.37
AC-4	0.03	0.29	0.00	0.68	0.05	0.35	0.03	0.00	0.45
AC-5	0.04	0.37	0.16	0.61	0.05	0.57	0.04	0.00	0.50
AC-6	0.03	0.39	0.17	0.61	0.06	0.40	0.04	0.00	0.43
BC-1	0.04	0.60	0.72	0.78	0.06	0.36	0.04	0.00	0.33
BC-2	0.04	0.54	0.80	0.72	0.05	0.06	0.06	0.00	0.36
BC-3	0.04	0.55	1.41	0.62	0.03	0.37	0.11	0.00	0.27
BC-5	0.05	0.57	0.48	0.74	0.04	0.38	0.04	0.00	0.35
BC-7	0.04	0.60	0.47	0.72	0.05	0.36	0.03	0.00	0.31
BC-9	0.04	0.99	1.16	0.89	0.08	0.29	0.06	0.00	0.29
CS-2a	0.05	0.69	0.84	0.95	0.12	0.46	0.06	0.00	0.43
CS-1a	0.05	1.25	1.70	0.82	0.24	0.64	0.11	0.00	0.40
CC-1	0.04	0.39	0.12	0.83	0.06	0.41	0.03	0.00	0.40
CC-2	0.04	0.39	0.15	0.79	0.06	0.43	0.03	0.00	0.35
CC-3	0.04	0.41	0.17	0.86	0.06	0.45	0.12	0.00	0.36
CC-8	0.05	0.54	0.16	1.01	0.05	0.51	0.02	0.00	0.48
CC-21	0.05	1.29	1.51	0.83	0.13	0.42	0.18	0.00	0.54
CC-28	0.05	0.88	0.73	0.97	0.09	0.43	0.05	0.00	0.36
CC-37	0.09	3.31	3.39	1.60	0.50	0.83	0.25	0.00	1.34
CC-38	0.08	3.16	3.90	1.12	0.50	0.91	0.27	0.00	0.77
CC-39	0.06	2.18	3.51	1.05	0.26	0.55	0.26	0.00	0.57
DC-2	0.05	0.89	0.96	1.00	0.07	0.36	0.41	0.00	0.28
DC-3	0.04	0.70	0.68	0.96	0.07	0.34	0.09	0.00	0.35
DC-6	0.04	0.60	0.42	1.05	0.06	0.29	0.13	0.00	0.29
DC-9	0.04	0.81	0.88	0.95	0.06	0.32	0.08	0.00	0.34
DC-12	0.04	1.00	1.16	1.06	0.10	0.32	0.21	0.00	0.31

TABLE 13
ELEMENTAL CONCENTRATIONS IN % X-RAY FLUORESCENCE
DATA FOR SEDIMENTS

SAMPLE NUMBER	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe
AS-12	1.0	8.7	25.9	0.0	2.5	2.5	0.5	0.1	4.2
AS-11	1.0	11.6	25.6	0.0	3.2	0.0	0.6	0.1	3.4
AS-9	0.9	8.6	24.6	0.0	2.5	2.6	0.5	0.1	4.9
AS-7	1.0	9.2	23.0	0.0	2.9	2.5	0.5	0.1	3.8
AS-3	1.1	11.9	25.6	0.0	3.2	0.0	0.6	0.0	2.9
AS-2	1.0	10.2	24.9	0.0	3.0	0.0	0.6	0.0	3.2
AS-1	0.6	8.7	20.0	0.6	2.8	0.0	0.6	0.0	2.5
BS-8	1.1	12.6	24.3	0.1	3.3	0.0	0.5	0.0	2.9
BS-6	0.9	10.5	23.4	0.1	3.0	0.0	0.5	0.0	3.3
BS-4	1.1	11.9	25.3	0.1	3.1	0.0	0.5	0.0	3.2
BS-3	0.8	10.9	19.7	0.4	2.8	0.0	0.5	0.0	2.7
BS-1	0.9	11.1	22.7	0.2	3.1	0.0	0.5	0.0	2.8
CS-17a	0.6	1.4	45.0	0.0	0.2	1.6	0.2	0.0	0.8
CS-13a	0.4	1.5	53.6	0.0	0.0	1.8	0.0	0.2	0.0
CS-6a	0.9	12.1	21.8	0.1	3.1	0.0	0.6	0.0	2.6
CS-3a	0.9	10.8	28.4	0.0	2.7	0.0	0.6	0.0	2.4
CS-1b	0.4	8.8	19.0	0.5	1.3	0.0	0.6	0.0	1.2
CS-2b	0.5	10.8	23.2	0.3	1.5	0.0	0.6	0.0	1.2
CS-3b	0.7	10.6	29.8	0.0	1.6	0.0	0.6	0.0	1.2
CS-7b	0.7	8.4	34.7	0.0	1.8	0.0	0.6	0.0	1.4
DS-13	0.9	6.6	33.4	0.0	1.6	1.7	0.5	0.1	2.7
DS-11	0.7	3.0	8.6	0.0	0.6	1.1	0.3	0.8	21.3
DS-7	1.0	10.6	28.3	0.0	2.8	0.0	0.6	0.0	2.5
DS-3	1.0	11.0	27.7	0.0	2.9	0.0	0.6	0.0	2.7
DS-2	1.1	12.1	25.7	0.0	3.3	0.0	0.6	0.0	2.9
DS-1	0.8	10.7	23.8	0.2	2.7	0.0	0.7	0.0	2.3
SCO-1	1.4	7.3	29.4	0.1	2.2	1.8	0.4	0.0	3.5

sediment data directly, the oxide concentrations were multiplied by a molecular weight factor to yield elemental concentrations.

X-Ray Diffraction

X-ray diffraction was performed on sediment samples of the lithology directly above the coal and samples rich in clay. Twelve coal ash samples were obtained through low-temperature ashing.

Sample preparation was identical for the sediment and the ash. Approximately 0.05 g of sample, crushed to pass a 200 mesh sieve, was mixed with deionized water to form a slurry. This slurry was air dried on a frosted glass slide.

Copper radiation ($\text{CuK} = 1.5418 \text{ \AA}$) at 35 keV and 17 μ a was used. The strip chart recorder was set at 100 counts full scale with a time constant of 2 seconds. The sample data was recorded from $2\theta = 2^\circ$ through $2\theta = 72^\circ$. Samples which gave evidence of peaks for smectites, vermiculite and/or chlorite were glycolated and also heat treated (550° C, 1 hour) and rerun from $2\theta = 2^\circ$ through $2\theta = 17^\circ$.

Ashing

Low-temperature ashing was performed on twelve of the coals which had highest ash percentages as determined by the X-ray fluorescence analysis. Low-temperature ashing is preferred because the ash components are not heated to such an extent that their physical properties are altered. The residue from this procedure were analyzed by XRD. The ashing was done at Oak Ridge National Laboratory in a Low Temperature Asher, Model 302 (LFE Corporation). The instrument makes use of a radio frequency field to produce a ring discharge in a

flow of oxygen. The parameters were set for a chamber pressure of 1 mm Hg at 100 RF watts and 200 cc/minute of oxygen flow. Forty-eight hours was determined to be sufficient to oxidize most of the organic matter and concentrate the residue.

APPENDIX B

APPENDIX B

SEDIMENTARY PETROGRAPHY

The following are descriptions of lithologies found above and below the Pewee coal horizon at the designated sites in this study. The descriptions are based on both hand sample and thin section observations. Mineralogic data obtained through XRD is included where appropriate. The thin sections were also viewed under reflected light to help identify iron sulfides.

The sizes given for individual grains were measured by visually estimating the number of grains in a field of view of known diameter. The grain sizes are averages, most of which had only a small variation, if any. Size range is given only when it is exceptional. Percentage estimates were made visually using the comparison chart of Terry and Chilingar (1955) as a guide. For the very clay-rich samples, such as those at site B, percentages and mineralogy were omitted if their exact determination was questionable. Descriptive terminology for the stratification and splitting characteristics was taken from Jackson (1970). If adjacent samples comprise similar lithologic types, they are described together (e.g., AS-9, 10).

AS-12

A grey, weathering to tan, moderately indurated, well-sorted sandy siltstone. Thin laminations break into shaly sheets, with fossil imprints preserved on the bedding planes. Sub-rounded quartz, averaging 0.1 mm (20%), organic stringers, 0.6 mm in length (15%), silt and clay aggregates, ranging from 0.2 - 0.07 mm (60%) are the

major constituents. Opaque constituents are predominantly rounded and flattened organic debris with a very minor amount of an iron sulfide such as pyrite. Deformed clay aggregates, mica and the organic stringers define the bedding which is deformed around nodules accreted in situ from iron-rich solutions.

AS-11

A grey, weathering to tan, well-indurated, moderately well-sorted siltstone. Laminations break into shaly sections along non-planar bedding. The clay fraction amounts to no more than 25% of the sample by volume.

AS-9, 10

A grey, weathering to tan, well-indurated, well-sorted, silty clayshale. Thin laminations part into sheets ranging from flaggy (2 cm) near the top to shaly (0.5 cm) at the base. In the upper layers, bands of sediment have occasionally been cemented by iron-rich solutions. The bedding is defined both texturally and compositionally, and is highlighted by subparallel alignment of organic stringers and elongate mica flakes along continuous, non-planar contacts. Darker, more clay-rich layers are finer grained than the more siliceous and silty light-colored layers. Identifiable constituents are rounded, 0.1 mm quartz, (15%) rounded opaques, predominantly organic material with some minor iron sulfides, averaging 0.04 mm (25%), mica flakes, also 0.04 mm (10%), clay aggregates and clay (50%).

AS-5, 6, 7 and 8

A grey, weathering to tan, well-indurated, well-sorted claystone. Laminated to thinly bedded, this claystone breaks into shaly to flaggy partings. Aggregates of sediment encased in siderite and weathered spheroidally, are found throughout at irregular intervals. Microscopically, the layers are relatively homogeneous, composed mainly of clay with less than 5% identifiable quartz and mica. The layers vary in intensity and hue of color. Organic stringers are rare and very thin.

AS-2, 3 and 4

A grey, weathering to tan, moderately indurated, well-sorted siltstone. Thinly laminated to laminated, the rock breaks into papery (<0.2 mm) or shaly chips. Laminations are distinguished by compositional variations, some enriched in siderite, with lensoidal and undulating shapes. The constituents are clay (chlorite, kaolinite and illite) and clay aggregates, ranging up to 0.5 cm (80%), 0.06 mm quartz and euhedral mica (10% each), and organic debris with minor iron sulfide, up to 1.0 mm (<1%).

AS-1

A black, well-sorted coal rash. This organic-rich sediment is thinly laminated, breaking along papery partings. Silt and clay-size mineral matter constitute 25% of the rock.

BS-6, 7, 8 and 9

A grey, weathered and friable siltstone. The thin laminations break into shaly partings along non-planar beds. X-ray diffraction

identifies the minerals as kaolinite, illite, chlorite and quartz.

BS-4, 5

A light to dark grey, weathered and soft, well-sorted, fissile clayshale. Laminations and partings range from 1 mm to 5 mm. The laminations are lensoidal and overlapping, exhibiting differential compaction features, although some are remarkably planar surfaces. The laminations are distinguishable by alternating grey, white, tan or brown bands, designating layers of a more siliceous component (kaolinite and illite) versus layers richer in ferrigenous cements and/or chlorite. There is no textural difference between layers. Identifiable constituents are quartz, mica flakes, coal stringers and opaques, some of which are iron sulfides. Secondary calcite cement fills in some of the partings.

BS-1, 2

A soft, black coal rash. This highly organic shale is thinly laminated and exhibits papery parting. Laminations are mostly planar and relatively continuous. Coal layers, up to 5 mm in thickness, occur throughout the rock but are more abundant closer to the coal contact. Kaolinite, illite and clay-sized quartz are present.

CS-13a Through CS-19a

A white, unweathered, massive, moderately sorted, submature, fine quartz sandstone with grey lensoidal shale fragments (up to 5 mm thick), very angular coal pieces (up to 3 cm) and coal seams

(ranging from less than 0.1 mm to 2.0 mm thick). Orientation of shale lenses and coal pieces show that the bedding surface was non-planar. The sand comprises subangular, undulose quartz (85%) and chert (5%), both averaging 0.3 mm, and trace amounts of mica within a clay matrix. In the upper half of this lithology the cement is calcite with more abundant deformed clay aggregates. In the lower half the cement is siliceous with secondary overgrowths on the quartz grains. Pressure solution between grains is evident.

CS-3a Through CS-12a

A grey to black, unweathered, well-sorted, thinly laminated shale. Laminations are non-planar and discontinuous. Microscopic cross beds are developed to a limited degree. The layering is developed by alternating more siliceous (lighter) material and layers rich in organics and/or ferrigenous cement. Coal drapes accentuate the irregular depositional horizon. Identifiable constituents are quartz, mica and the clay minerals kaolinite, illite and chlorite. The amount of coal stringers is greater than in samples CS-13a through CS-19a.

CS-1a, 2a

A black, unweathered, thinly laminated coal rash. Laminations are both lensoidal and planar. Cell structure is preserved to a limited degree. The clay fraction is composed of kaolinite and illite.

CS-1b Through CS-4b

A black, unweathered, moderately sorted, sandy siltstone. Laminations break into shaly partings which are non-planar and

discontinuous, and are developed both compositionally and (to a minor degree) texturally. Some laminations drape over introduced fragments of consolidated coal or sediment. The lithotype is composed of grains 0.1 mm or less in size. These are subangular, undulose quartz (15%) (some grains exhibiting embayments), mica (10%), and feldspar (10%). Subequant opaques (20%), include iron sulfides and coal stringers up to 4 mm in length. The coal stringers account for variable amounts in layers and range up to 70% in some. The iron sulfides are restricted to these layers. The fine sand grains are suspended in a clay matrix (kaolinite and illite) with grain size decreasing upwards toward the coal contact.

CS-5b Through CS-7b

A medium grey, unweathered, well-sorted, sandy siltstone. Thin laminations break along shaly partings. Laminations are marked by a discontinuous green coloration. The constituents are 0.1 mm quartz (20%), feldspar (5%), muscovite (<5%), euhedral to subhedral opaques, predominantly iron sulfides (<1%), and abundant silt-sized particles.

DS-12 Through DS-14

A grey, weathered to tan, well-sorted, thinly laminated to laminated siltstone. Partings range from shaly to flaggy. Compositional laminae correlate with textural laminae in which the dark layers have a higher percent of clay. This lithotype is composed of 0.06 mm particles of sub-rounded quartz (25%), sub-rounded feldspar (25%), clay aggregates (30%), clay (10%), mica (5%) and

organic material. Iron sulfides are found in trace amounts in layers rich in organics, which are identified by their morphology, reflectance and (if very thin) color in transmitted light.

DS-11

An orange-brown, dense aggregate of clay with siderite cement. Layering is developed around a central core and is indicative of accretionary processes in situ. This unit is 3 cm thick with a compositional variation from center to rind, especially noticeable in the outer 5 mm. Minor silt-sized mineral constituents of quartz, feldspar, mica and opaques (a small portion of which are iron sulfides) are present throughout.

DS-1 Through DS-10

A light grey, weathered tan, friable, well-sorted, very fine siltstone. Thinly laminated, the partings range from papery to flaggy. Laminations are compositionally and texturally developed with the black, rounded, organic material concentrated in the finer grained laminations and the more siliceous (lighter) laminae being composed of slightly coarser material. Identifiable constituents are quartz, up to 0.05 mm (30%), mica, 0.03 mm (<3%), organic material, 0.05 mm (5%), and a major clay component. X-ray diffraction identifies these minerals as kaolinite, illite and chlorite. Siderite is also present.

APPENDIX C

APPENDIX C

POINT-COUNT CLASSIFICATIONS

Coal Petrology

Macerals are to coal what minerals are to inorganic rocks. The macerals are the microscopically identifiable constituents of coal. Macerals are not crystalline and, within a group, have a variation in physical properties and chemical composition. The groups are defined on a morphologic basis. The three maceral groups are: vitrinite, exinite and inertinite.

Vitrinite is the most common constituent of coal. It has a reflectance intermediate between exinite and inertinite, and a conchoidal, angular fracture pattern. Vitrinite is derived from cellular structures originating in trunks, branches, stems, leaves and roots. A reprecipitated gel, structureless and filling in cells is included in this group. It is identified by similar reflectance. Larger, massive, homogenous bodies (rounded or squashed) with the same reflectance are also classified as vitrinite.

Exinite is the darkest maceral with the lowest reflectance, and usually exhibits a very characteristic morphology. Exinite is derived from skins of spores and pollen, the cuticle layer of leaves, stems and some seeds, algae and any of the natural resins produced by metabolism. The morphology of the spores and cuticle is that of elongated, deflated balloons; wormy and bulbous forms. The resins and oils form small rounded bodies, usually cell fillings and are often zoned due to oxidation. This maceral group is characterized by

its toughness, as opposed to the brittleness of inertinite. Fractures in the coal are sometimes unable to penetrate this resilient material.

Inertinite derives its name from its non-reactive behavior; that is, it will not soften during the carbonization process. Optically, it is characterized by high reflectance which is related to the fact that much inertinite originates as charcoal and has the highest carbon content of any maceral. Distinguishing morphologies of this group are a honey comb structure of well preserved, un-collapsed cell structures or the bogen or star structure, which results from the fracture of the cell walls into splintery spikes and triangles. The hardness of this maceral group is exemplified by these rigid, pointed fragments.

Framboidal Pyrite

All of the pyrite in the coal samples studied has a framboidal morphology. The occurrence is mainly determined by Eh conditions in the strata, which are largely a function microbial activities and the sulfate-reducing capacities of the bacterial populations present.

Neavel (1966) showed that there is insufficient energy for the purely chemical reduction of sulfates to disulfides. If there is an ample supply of sulfur and iron, sulfur bacteria have the special role of making FeS_2 in peats. Sulfur originates predominantly from bacterial protein and iron is present wherever silicate minerals are weathering or where the ground water carries iron ions. This

explains the concentration of pyrite usually in the lowest and uppermost parts of the seam and within the vicinity of old washouts.

Other Mineral Matter

In the point-count analysis, any mineral other than pyrite is counted under "other mineral matter". Clay minerals account for 60-80% of the total mineral matter in coal. These clays could be secondary, having formed from aqueous solutions or they could be clastic material, derived mainly from weathered feldspar and mica. Other minerals which are commonly associated with coals are the carbonates (siderite, ankerite, calcite, dolomite), quartz, limonite and some salts.

VITA

Anne Elizabeth Dorsey was born in Fresno, California on September 28, 1955. She spent her early years in the San Fernando Valley before moving to Orange County in 1960. The rest of her life has been spent education herself in order to reach a moderate level of autonomy.

Anne graduated from Marywood High School in June, 1973. She worked towards a bachelors degree in geology, receiving her B.S. in August, 1978 from the University of Iowa. Returning to the academic environment at The University of Tennessee, Knoxville (home of the 1982 World's Fair) she was conferred the Master's of Science degree in December, 1982.

She is currently employed as a geologist for Gulf Oil Exploration and Production Company in New Orleans, Louisiana. Anne is a member of the American Association of Petroleum Geologists and Sigma Gamma Epsilon.