To the Graduate Council:

I am submitting a thesis herewith written by Stuart O. Reese entitled "Effect of Paleotopography and Organic Matter on the Mineralogy and Chemistry of Sediments Exposed During a Pennsylvanian Diastem, Hazard Coal Zone, Leslie County, Kentucky." 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

Otto C. Kopp, Major Professor

We have read this thesis
and recommend its acceptance:

Richard W. Counts

Don A. Byerly

Steven A. Driese

Accepted for the Council:

Lewis Winkel

Vice Provost
and Dean of the Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at The University of Tennessee, Knoxville, I agree that the Library shall make it available to borrowers under the rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgement of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major thesis professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature Stuart O. Reese

Date December 3, 1985

EFFECT OF PALEOTOPOGRAPHY AND ORGANIC MATTER ON THE MINERALOGY AND CHEMISTRY OF SEDIMENTS EXPOSED DURING A PENNSYLVANIAN DIASTEM, HAZARD COAL ZONE, LESLIE COUNTY, KENTUCKY

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Stuart O. Reese

March 1986

ACKNOWLEDGEMENTS

The author wishes to thank his advisor Dr. O. C. Kopp for his invaluable input of time, helpful criticisms, and encouragement. Contributions by committee members Dr. R. Arnseth, Dr. D. Byerly, and Dr. S. Driese in their areas of specialty were also helpful and appreciated. The author also wishes to acknowledge sources of financial support which include Graduate Assistant stipends, the Discretionary Fund of the Department of Geological Sciences, the Appalachian Basin Industrial Association, and the Tennessee Division of Geology. Special thanks are expressed to his parents for added financial support and encouragement.

ABSTRACT

Seat rocks below the Middle Pennsylvanian Hazard coal of the Breathitt Formation were investigated in the field and laboratory. Field observations of the study site, which is located on the Daniel Boone Parkway in eastern Kentucky, suggest that the thin coal is part of a channel-fill sequence and that a diastem exists at the coal-underclay contact. Evidence for the diastem includes underlying truncated beds, root traces, a clay horizon on the banks, and the preferential accumulation of peat. In the channel, the coal is up to 48 cm thick, whereas it is only as a few centimeters thick on the northwestern bank. The diastem, in effect, defines a paleotopographic surface. Measurement of the paleotopography indicates that the northwest bank stood 6 m above the base of the channel, whereas the northeast bank was 3-4 m above the base of the channel.

The paleotopography undoubtably influenced groundwater circulation and the presence of standing water, and thus peat deposition. Organic matter in turn affected Eh/pH conditions. Two separate and distinct environments were produced by the irregular paleotopography and subsequent accumulation of organic matter. Because the study site has a limited lateral (200 m) and vertical extent (25 m), variation due to macroenvironmental influences on the rocks at the time of deposition such as climate, sediment source,

chemistry of depositional basin waters, etc., was minimized. Chemical and mineralogical changes in the seat rocks below the diastem may be related to micro-environmental factors such as Eh and pH conditions, groundwater circulation, presence of standing water, etc., which were primarily controlled by the paleotopgraphy.

Fifty-eight seat rock samples were collected from 14 vertical profiles and analyzed by XRD and XRF methods. Bulk mineralogy determined by XRD includes quartz, kaolinite, illite-mixed layer material, chlorite, microcline feldspar, 2_m muscovite, and pyrite. Several mineralogical trends indicate that the banks and the channel were separate environments. Seat rock samples were analyzed for Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, S, K_2O, CaO, TiO_2, Cr, Mn, Fe, Rb, Sr, Zr, and Ba. The analyses reveal distinct chemical trends for the banks and channel.

On the banks, Fe, MgO, and MnO show marked decreases upward towards the coal. Minor reductions upward in P_2O_5, CaO, and Ba are noted. S values in the bank seat rocks are uniformly low. Zr increases upward, especially on the northwest bank. Chlorite is absent in the upper portions of some vertical profiles, most notably on the northwest bank. Kaolinite/Illite ratios were somewhat higher at the paleotopographically highest sample profiles, whereas 3.24A/4.26A (microcline feldspar:quartz) ratios and sharpness ratios of 10A material are typically lower at

these sites. Such trends are consistent with leaching of the paleotopographically higher areas.

The channel area, where the seat rocks directly below the coal consist of dark, carbonaceous shales, was a zone of concentration for several elements. High values of S (12%), Fe (9%), MgO (2.6%), Na_2O (2.2%), Ba (0.25%), and P_2O_5 (1.4%) exist in the 0-3 cm zone of the channel seat rocks. Pyrite is present in substantial amounts in the channel samples, indicating reducing conditions existed. The clays and organic matter of the 0-3 cm zone in the channel apparently collected ions which may have been mobilized from the paleotopographically higher, leached areas as circulating groundwater moved downward. An additional source of ions may have been the initial presence of standing brackish water that remained after the channel-incising event. High values of Na_2O, S, and Mg may have originated in this manner. Chlorite, which probably holds the Mg, may be detrital in origin, having withstood acidic conditions on the channel bottom, or may be chlorite regenerated by the later addition of Mg to degraded chloritic structures or mixed-layer clays.

Chemical and maceral analyses of selected coal samples reveal similar patterns. Coals from the paleotopographically higher northwest bank have greater percentages of detrital material, which may have originated because of drying conditions. Inertinite macerals are also

abundant, which confirms that oxidizing conditions existed during peat deposition. Coals in the channel are banded, and exhibit high percentages of vitrinite macerals, which indicates constant wet conditions existed in the channel during peat deposition.

TABLE OF CONTENTS

LIST OF FIGURES

FIGURE PAGE

CHAPTER 1

INTRODUCTION

Purpose and Background

The purpose of this investigation is to determine the mineralogical and chemical changes that took place during a period of emergence of an area in the Pocahontas Basin, that contained both paleotopographic "highs" and "lows." The rocks that were exposed during this emergent period of an unknown duration are overlain by a thin coal bed, and are all part of the Breathitt Formation of Middle Pennsylvanian age. Based on field observations, a diastem is interpreted to exist between the coal and the underlying rocks; the diastem in effect defines a paleotopographic surface. The effects of organic matter, surface water, and groundwater are thought to have exerted a strong influence on the mineralogical and chemical alterations of the rocks exposed during such a diastem. For these reasons, an abandoned fluvial channel, which subsequently became filled with organic debris, was chosen as the site for this study. It is anticipated that the results of this study will aid in: 1) recognizing an event of subaerial exposure, 2) detecting paleotopographic highs and lows, even in cases where good outcrops are not available, and 3) delineating mineralogical and chemical changes that may indicate the existence of a paleosol.

The initial goal of this study was to test at least one hypothesis concerning underclay genesis. Underclays are nonlaminated, argillaceous rocks that occur beneath coal beds. They are commonly rooted, contain slickensides that are randomly oriented, have a gray color, and range in thickness from a few centimeters to several meters. The upper few centimeters of the underclay is typically a darker horizon created by the addition of organic material. The coal-underclay contact is sharp and the boundary between the underlying sediments and the underclay is commonly gradational (Parham, 1964).

Of the several hypotheses that have been proposed to account for the origin of underclays (Fig. 1), two central ideas are common: 1) underclays are essentially as they were deposited, and 2) underclays are the result of post-depositional alteration. In the former, the provenance and/or sedimentologic processes are the dominant controls on the formation and mineralogy of the underclay. The provenance composition and conditions in the source region, such as weathering rates, control the mineralogy of the clays deposited. Schultz (1958) employed this hypothesis to correlate lateral and vertical variations in the mineralogy of underclays with position in a depositional basin (meaning "shelf" or "geosyncline"), source material for the clays, and with the nature of weathering in the source region. He correlated the slow deposition on a "shelf" environment with

Underclay Genesis

1. No Post-Depositional Alteration

   A. Mineralogy Determined Prior to Sedimentation (inherited material)
      Factors:
      - Weather duration
      - Original rock type
      - Climatic conditions in source area

   B. Mineralogy Determined During Sedimentation
      1. Chemical Factors
         - Cation type, concentration in basin waters (salinity)
         - pH
         - Parent material entering the basin
      2. Physical Factors
         - Differential settling
         - Differential flocculation

2. Post-Depositionally Altered

   A. As a Soil (subaerial formation)
      Factors:
      - Climate
      - Vegetation
      - Parent material
      - Paleotopography
      - Weathering duration

   B. Leaching
      Factors:
      - Duration of leaching
      - Parent material
      - pH
      - Vegetation (roots)
      - Water movement

   C. Diagenesis
      Factors:
      - Increased temperature and pressure
      - Pore water chemistry

Figure 1. Hypotheses concerning the origin of underclays. Revised from Williams, E. G. (1984), Personal Communication. Additional references: Schultz, 1958; Parham, 1964; Huddle and Patterson, 1961; Roeschmann, 1971; Holbrook, 1973; Oldam, 1979; Rimmer and Eberl, 1982.

more deeply weathered material characterized by more kaolinite, mixed-layer clays, and less chlorite. On the other hand, in areas of less weathering which he correlated with rapid deposition in the adjacent "geosyncline," the resulting underclays contained more chlorite and less kaolinite. Mineralogical variations could be accounted for by different sediment sources or climatic variations.

Possible sedimentologic processes acting upon the clays entering the basin include differential settling and flocculation. The chemical effect of the depositional basin waters upon the clays could be in turn a factor on flocculation of clays. Parham (1964) explained lateral variations in the clay mineralogy of underclays by the laterally changing chemistry of the basin waters and its effect upon the clays. He proposed that mixed-layer material was affected by increasing salinity as it was deposited farther out in the basin. Adsorbed magnesium and potassium cations allowed the mixed-layer material to be aggraded. Williams et al. (1968) emphasized that the chemistry of the depositional environment played a "substantial role" in underclay mineralogical variations on a geographic scale. The basic mechanism would be "selective precipitation of clays" because of differences in pH and concentrations of electrolytes in the depositional basin waters. Minor roles in mineralogical variations were attributed to leaching and variable source conditions (Williams et al., 1968).

The second basic concept is that underclays are essentially the products of in situ, post-depositional alteration of sediments. This includes the hypotheses that underclays represent ancient soil horizons and/or products of the leaching of sediments. One of the first opinions concerning underclays, based on the observation of root traces below the coal, was that the underclay was the soil upon which the peat-forming plants grew (Logan 1842, cited in Huddle and Patterson, 1961). Huddle and Patterson (1961) concluded that seat rocks originated in the acidic peat swamp by leaching, and variations were caused by the amount of leaching. Intense acidic leaching would favor kaolinite formation. The study cited present-day Hawaiian swamps as an analogous environment of kaolinite formation. Rimmer and Eberl (1982) also argued for in situ leaching as a mechanism for the alteration of original sediments, citing some mineralogical criteria. Their criteria included an increase of mixed-layer illte/smectite expandability toward the underclay-coal contact and a decrease in calcite and chlorite in the same direction. They also added that the original mineralogy may have been the result of clay source condition and/or the chemistry of the depositional environment. Holbrook (1973), in a study of the Lower Kittanning underclay, hypothesized that the original topography was a prime factor in the local variability of underclays. He also stressed the importance of time in the

weathering of some underclays, and surmissed as much as 20,000-30,000 years of weathering. The lack of chlorite in the upper part of an underclay profile, and the increase in vermiculite and kaolinite/mica ratio upward would indicate a weathered profile (Holbrook, 1973). Oldam (1979) also delineated mineralogical and chemical criteria for underclays as evidence for weathering and thus alteration of the seat rock sediments. Reduction in quartz content and the layer thickness of kaolinite would be indicative of "extreme weathering." Concomitant reductions in concentrations of Fe_2O_3, MgO, CaO, K_2O, and MnO were also attributed to leaching effects (Oldam,1979).

Thus, various opinions exist concerning the origin of underclays and their paleoenvironmental significance. This investigation will examine the influence of an original topography upon the mineralogy and chemistry of seat rocks at a site believed to exhibit a certain paleotopographic control. The area is small enough so that macroenvironmental variables such as climate, water chemistry, sediment source, etc., would not have differed greatly over the area in which these sediments were deposited. The study area selected will show the importance of the former topography and its effect on the strata beneath the coal. At the same time, the study has application to the problems of underclay genesis and paleoenvironmental significance.

Local Stratigraphy

The rocks are part of the Middle Pennsylvanian Breathitt Formation of eastern Kentucky (Figs. 2 and 3). Pennsylvanian rocks are very well exposed on the Daniel Boone Parkway, and are accessible because of the terraced road cuts. Despite the exposure, the geology is still complex because most rock units are not laterally extensive. Horne and Ferm (1978) demonstrated the lateral variability (Fig. 4) in these rocks. The coal at the study site is a Hazard coal, and is stratigraphically beneath the Hazard No. 6 coal (Fig. 4). Both coals (the Hazard and the Hazard No. 6) are part of the Hazard coal zone (Fig. 3). The Hazard zone is stratigraphically above the Magoffin Member by 30-40 m. The Magoffin Member is a persistant marine unit in eastern Kentucky (Chestnut, 1981; and Ketani, 1981).

Local Geology

The investigation is confined to a channel-fill sequence exposed on the Daniel Boone Parkway, southwest of Hazard, Kentucky. The location (Fig. 5) is 750 m west of the Leslie County-Perry County border, which was denoted as stop "D" in a field trip guidebook by Ferm and Horne (1978), and 4.7 miles (7.6 km) west of Stop 5 in a guidebook published by the Kentucky Geological Survey (Donald C. Haney, Director, 1981). In the latter guide, the road log lists the study site simply as, "Coals in a channel fill."

PERIOD		EASTERN KENTUCKY
UPPER CARBONIFEROUS	PENNSYLVANIAN	Conemaugh
		Breathitt
		Lee
LOWER CARBONIFEROUS	MISSISSIPPIAN	Pennington
		Newman

Figure 2. Generalized Mississippian and Pennsylvanian stratigraphy in eastern Kentucky. After Horne and Ferm (1978).

Formation	EASTERN KENTUCKY
CONEMAUGH	Ames Limestone Member Brush Creek Limestone Member
BREATHITT	Princess #10 Coal Bed Princess # 9 Coal Bed Princess # 8 Coal Bed Princess # 7 Coal Bed Princess # 6 Coal Bed Hitchins Clay Bed Vanport Limestone Princess #5A and 5B Coal Beds Kilgare Flint and Flint Ridge Flint Richardson, Skyline Coal Zone Hazard #10 Coal Bed Stoney Fork Member Hindman Coal Bed (Hazard # 9) — Broas Coal Zone Hazard # 8, Francis Coal Hazard # 7 Coal Bed — Peach Orchard Coal Zone Hazard Coal Zone Haddix Coal Zone Magoffin Member Copland or Taylor Coal Zone Hamlin Coal Zone Fire Clay Rider Coal Bed Fire Clay Coal Bed Whitesburg Coal Zone Kendrick Shale Member Amburgy Coal Zone Elkins Fork Shale Upper Elkhorn # 3 Coal Zone Upper Elkhorn # 2 Coal Upper Elkhorn # 1 Coal — Jellico Coal Zone Campbell Creek Limestone Blue Gem Coal Bed Little Blue Gem Coal Bed Cannelton Limestone Lily, Manchester Coal Bed Van Cleve Coal Bed

Figure 3. Detailed Middle Pennsylvanian stratigraphy in eastern Kentucky. Modified from the field trip guidebook published by the Kentucky Geological Survey for the G. S. A. Coal Division Field Trip, 1981.

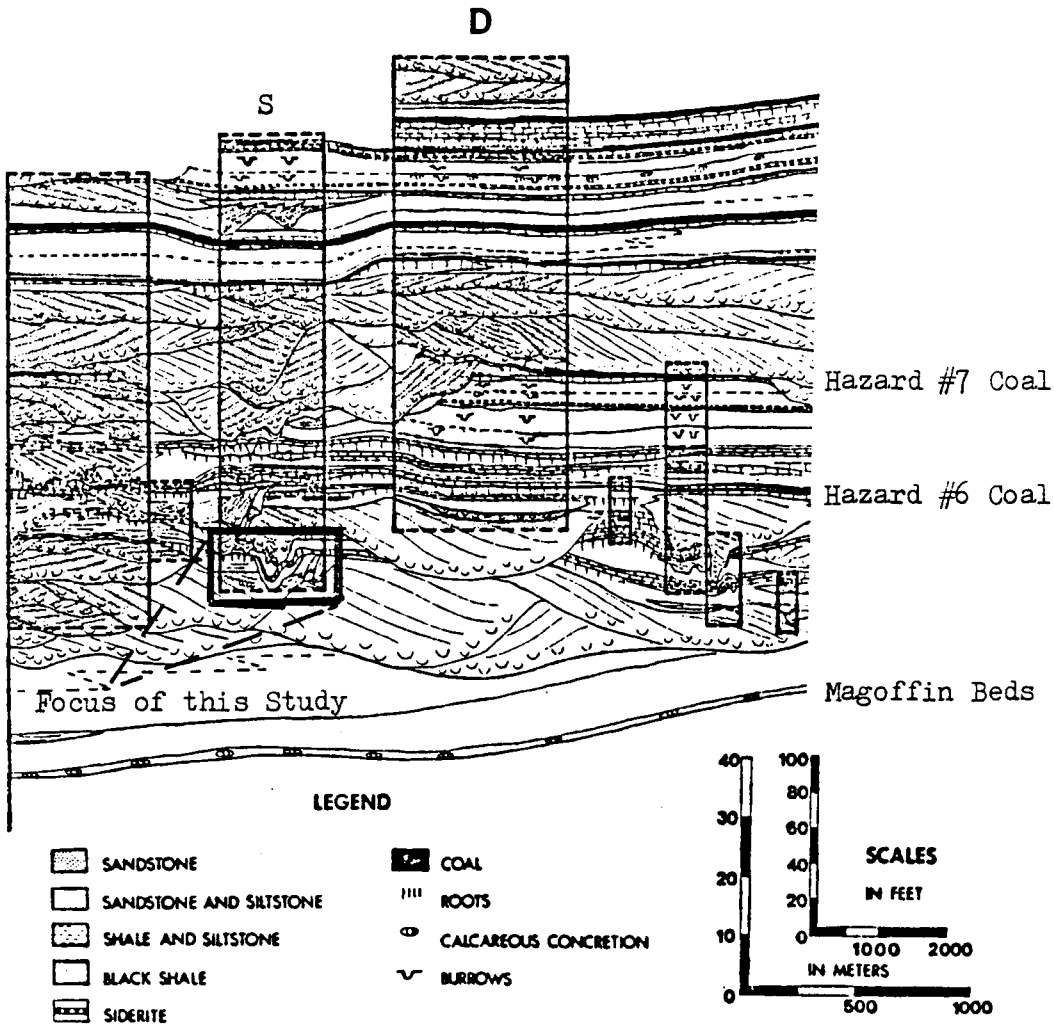


Figure 4. Geologic cross-section along the Daniel Boone Parkway in eastern Kentucky. "S" indicates a stratigraphic column at the study site. "D" represents the outcrop described by Horne and Ferm (1978) at the Leslie County-Perry County border. After Horne and Ferm (1978)

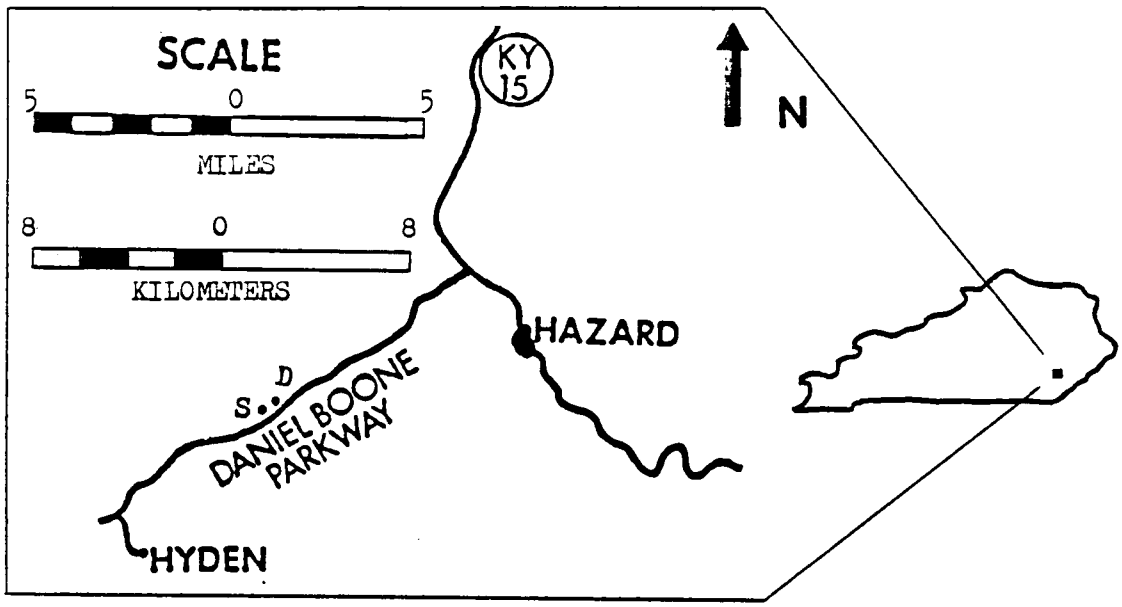


Figure 5. Location of study site (S) in eastern Kentucky. "D" is an outcrop described by Horne and Ferm (1978). After Horne and Ferm (1978).

lists the study site simply as, "Coals in a channel fill." The site is in the Hyden East (7-1/2 minute) Quadrangle.

Stop "D," which is located 750 m east of the study site, has been described as representing "aspects of the transitional lower delta plain and upper delta plain depositional setting" (Horne and Ferm, 1978). The lowest coals exposed at that site are the Hazard No. 6 coals (Fig. 4, page 10). These coals are overlain by a burrowed marine to brackish bayfill deposit. Thus, there was a nearby marine influence on the sediments, because marine deposits occur above and below the thin coal at the study site. Furthermore, Horne et al. (1978) have contended that both lower delta plain and transitional lower delta plain environments are under marine to brackish water influence.

Horne and Ferm (1978) tabulated criteria for the recognition of depositional environments and based on their criteria, the paleoenvironment of the study area most probably represents a transitional lower delta plain. The channel deposits present were both active and abandoned fill deposits, and both abrupt and gradational contacts between various rock units exist. The rock units generally occur as 1.5 to 7.6 m (5 to 25 feet) thick sequences. The sandstone strata exhibit planar-tabular cross-bed sets, which typically grade upwards into ripple cross-laminations. Criteria such as these are most characteristic of the transitional lower delta plain environment.

The study site (Fig. 6) was described as part of a channel complex, which co-existed with the levee floodplain sediments to the east (Horne and Ferm, 1978). The successive channel-like forms which are "stacked" upon one another would support this hypothesis. The present-day topography is probably controlled by the resistant sandstone deposits, which appear to pinch out to the east and west. The site is bounded by two valleys which were eroded more easily than the now topographically higher sandstone strata, which may have been part of a channel complex.

Description of Study Area

Field investigations indicate that the site was a channel or depressed area, with a maximum relief between the central portion of the channel and the northwest bank of 6.2 m (Fig. 7). Details of the relief were accurately measured using a transit. The west side of the study site is noticeably higher than the east side (Fig. 7). Also, a slight depression (Zone I) was indicated on the northeast bank.

The coal is much thicker (up to 48 cm) in the central portion of the channel (A) than on the west banks (C), where it thins to a few cm (Fig. 7). On the east side, the coal is 15-25 cm thick. A possible slump feature, which resembles a rotational block, is apparent at the southwestern section of the outcrop on the channel slope

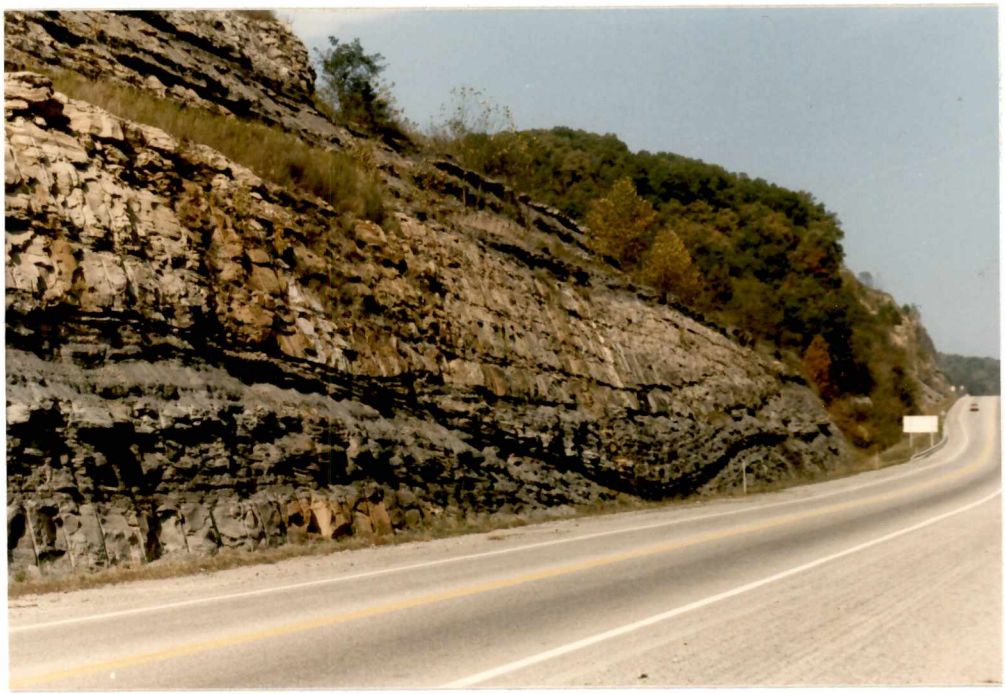
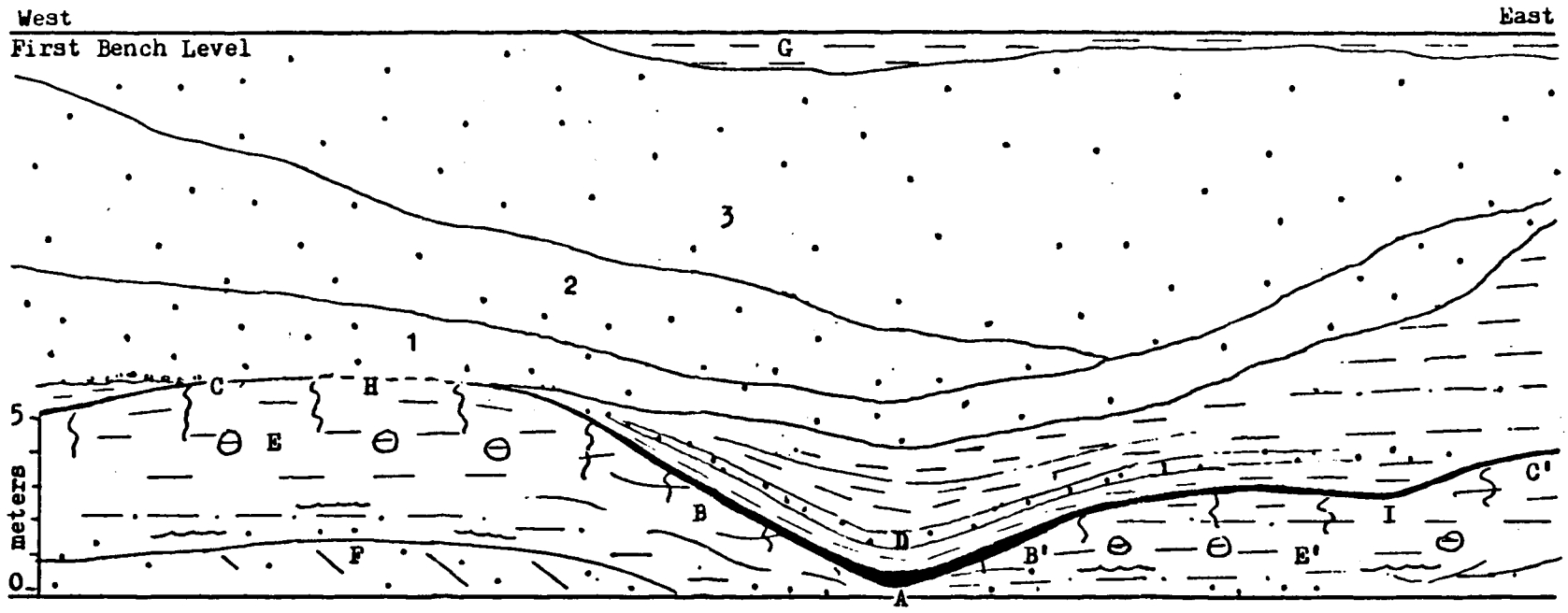


Figure 6. Photograph of the study site. Area shown is the northern side of the Daniel Boone Parkway.



LEGEND

- shale
- siltstone
- sandstone
- underclay
- coal
- root traces
- planar tabular cross-bedding
- ripple cross-laminations
- siderite pebbles
- siderite nodules
- 1-3 sandstone packages

SCALE (meters)

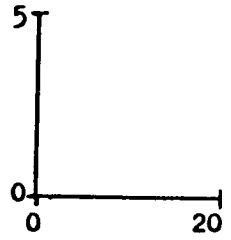


Figure 7. Sketch of the study site. Letters A-I represent sites described in text.

(Fig. 8). A rather large cast of a Stigmaria root (approximately 5 cm in diameter and over 90 cm long) was found on the northwest bank just beneath the coal. The penetration of roots, as evidenced by root traces in the rocks below the coal, was greatest (as much as 2 m) on the banks (C and C'), whereas the roots were sparse or absent near and in the channel. On the banks, a zone of siderite concretions (E and E') is present. In some cases the concretions appear in rootlet form. Furthermore, there is a distinct, lighter colored clay horizon on the banks (Zones C and C'), but no such feature was observed in the channel. To the contrary, the rocks beneath the coal in the channel are dark, laminated, carbonaceous shales which contain pyritized Calamites fossils. Below the shale in the center of the channel is a fine-grained sandstone dominated by plant debris (Calamites). Near the channel, truncated beds (Fig. 7) are found in Zones B and B' (see also Fig. 9). The rocks above the channel-fill coal (area D) are shale with some sandstone beds. These rocks are for the most part confined to the channel, but do not show a substantial thickening in the middle of the channel as the coal bed does. At the center, the sandstone bed is 80 cm thick. Twenty m to the west, the sandstone is nonexistent. A large-scale, cross-bedded sandstone (F in Fig. 7), which grades upward into a fine-grained sandstone with ripple cross-lamination, underlies the seat rocks. The last

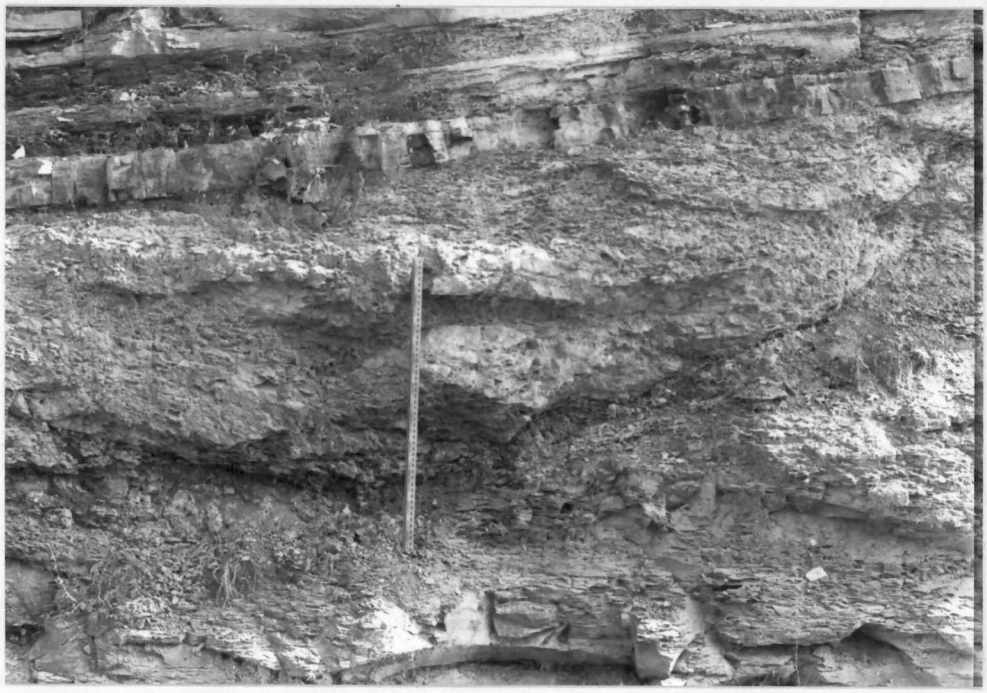


Figure 8. Possible slump feature. Located on the western slope of the channel on the southern side of the Daniel Boone Parkway.

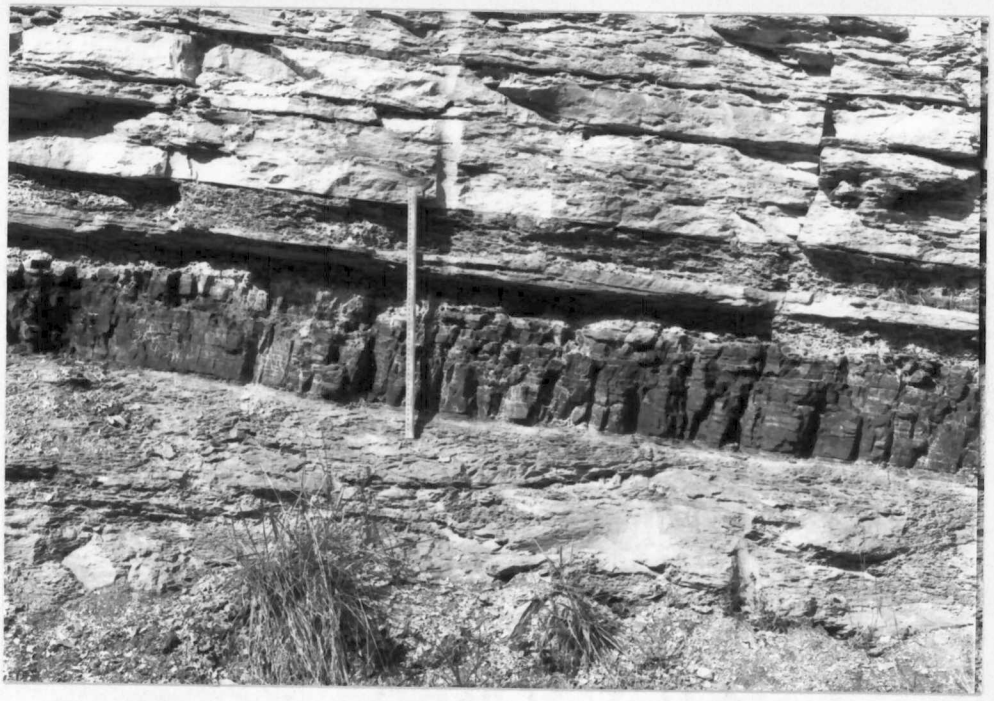


Figure 9. Truncated sandstone and siltstone beds beneath coal. Located on the northern side of the Daniel Boone Parkway.

accretionary bounding surface (beneath area B in Fig. 7) of the coarse sandstone exhibits a dip similar to the northwestern slope of the channel directly above.

The massive, coarse sandstone above the coal also retains a similar channel form at the top of the unit (area G), although the geometry is much less pronounced. The sandstone contains coal spar and siderite pebble lag at the base, which is a scour surface that has at some places (Zone H) removed the coal bed. This same sandstone unit can be subdivided into three genetic packages of strata (Fig. 7; Nos. 1, 2 and 3), which are bounded by erosional surfaces.

Interpretation of Study Site

The irregular thickness of the coal is most likely in response to the paleotopography. The thickness of the coal closely correlates with the measured relief. The coal bed on the paleotopographically high areas such as the west bank is much thinner than the coal of the lower areas, such as in the channel. The lack of root traces in the channel suggests that some of the peat may have had an allochthonous origin. However, root traces on the banks indicates *in situ* peat accumulation. Large *Stigamaria* indicate arborescent lycopods existed at the site (Stewart, 1983). A pool in the channel may have collected vegetation from the surrounding trees. Also, some peat may have drifted into the channel as it was incised and subsequently abandoned.

Differential compaction processes by themselves are not judged capable of producing the thickness variations of the coal. However, after peat accumulation, there would have been compaction effects on the peat. Different compaction ratios (peat:coal) have been calculated (Stutzer, 1940). A 12:1 ratio of peat to coal was calculated by Muller (1964, in Murchison and Westoll, 1968). Using this ratio, 48 cm of coal would have resulted from the compaction of approximately 5.8 m (19 feet) of peat that accumulated in the channel. With a lower ratio such as 7:1 (Stutzer, 1940), 48 cm of coal would have been the result of the compaction of 3.4 m (11 feet) of peat. Therefore, sediments deposited above the peat might be expected not to retain a drastic thickening in the center. Five m of peat would have been sufficient to have filled the paleochannel to the banks. The irregular thickness of the coal may indicate differential subsidence on a local scale that permitted the peat to preferentially accumulate in an area that was subsiding more rapidly than the area surrounding this depression. The similarity in geometry between the cross-bedded sandstone unit and the coal bed above may have originated because of a differential subsidence phenomenon, creating the similar forms.

However, several characteristics of the site attest that the original topography was the major factor involved in the establishment of the geometry of the rock unit

contacts, specifically, the coal-underclay contact. The presence of truncated beds (Fig. 9) is strong evidence for an origin as a channel of a distributary that eroded underlying sediments. There must have been some physical cause of the truncation; differential subsidence or compaction could not have been responsible. The appearance of the light-colored clay horizon on the banks, but not in the channel also suggests that the banks at one time stood topographically above the channel. The clay horizon may thus represent a leached zone. The siderite concretions that occur in zones below the banks, may have been a function of the leaching/diagenetic environment, which chemically differed from the banks to the channel. Decaying roots could have created a suitable diagenetic environment for the precipitation of iron (in the form of iron carbonate) that may have been mobilized by leaching. The presence of pyritized plants primarily in the channel is also evidence for greatly differing oxidizing/reducing environments within a small area. Pyrite is also found below the coal on the northeast bank where measurement of the relief revealed a depression. A small but persistent pool on the banks could have maintained conditions similar to those in the channel. The differing penetration depths for the root traces also suggests an area which had topographic highs and lows. The plants seemed to have reached farther down on the banks, i.e., the topographic

highs. The scarcity of root traces in the channel seat rocks and the presence of the pyritized fossils provides evidence that the central portion of the channel was submerged all or most of the time the channel feature was exposed at the surface of the earth. The presence of a slump feature on the slope of the channel would be evidence for the failure of sediments toward the channel, perhaps the result of undercutting of the bank.

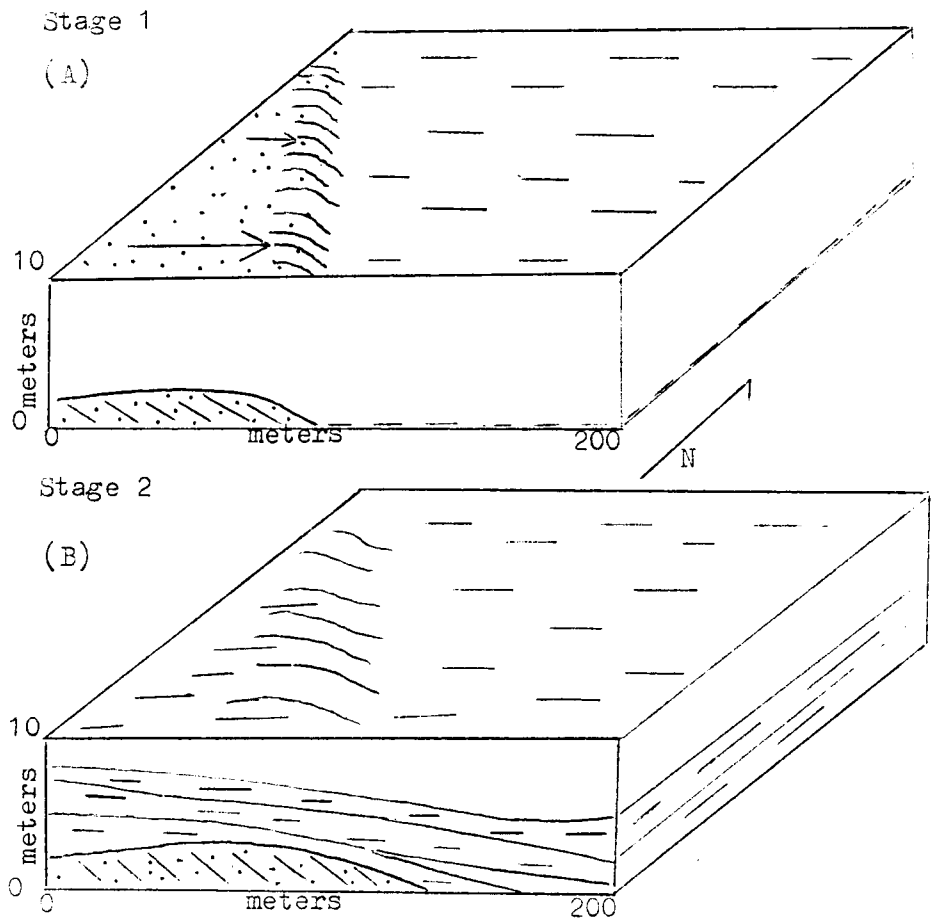
The bedforms of the oldest sandstone unit exposed suggests an origin as a primary depositional feature, such as an episodically migrating sand bar. The sand bar eventually ceased migrating, as evidenced by finer-grained deposits draping a final, accretionary bounding surface (Fig. 10). It is possible that this feature controlled the geometry of the channel-fill coal directly above the sandstone unit. The channel would then reflect the underlying coarse sandstone body, which exerted some control over the sediments deposited above.

The case for the site possessing an original topographic depression is strong, and significant differential compaction below the coal is unlikely, based on field observations. Although differential subsidence cannot be totally ruled out (because it may have occurred concurrently with sedimentation), the presence of such features as clay horizons, root traces, and truncated beds indicates that the geometry of the coal/seat rock contact

Figure 10. Planar tabular, cross-bedded sandstone showing a final accretionary surface.

represents an ancient topographic surface now exposed along the Daniel Boone Parkway in eastern Kentucky.

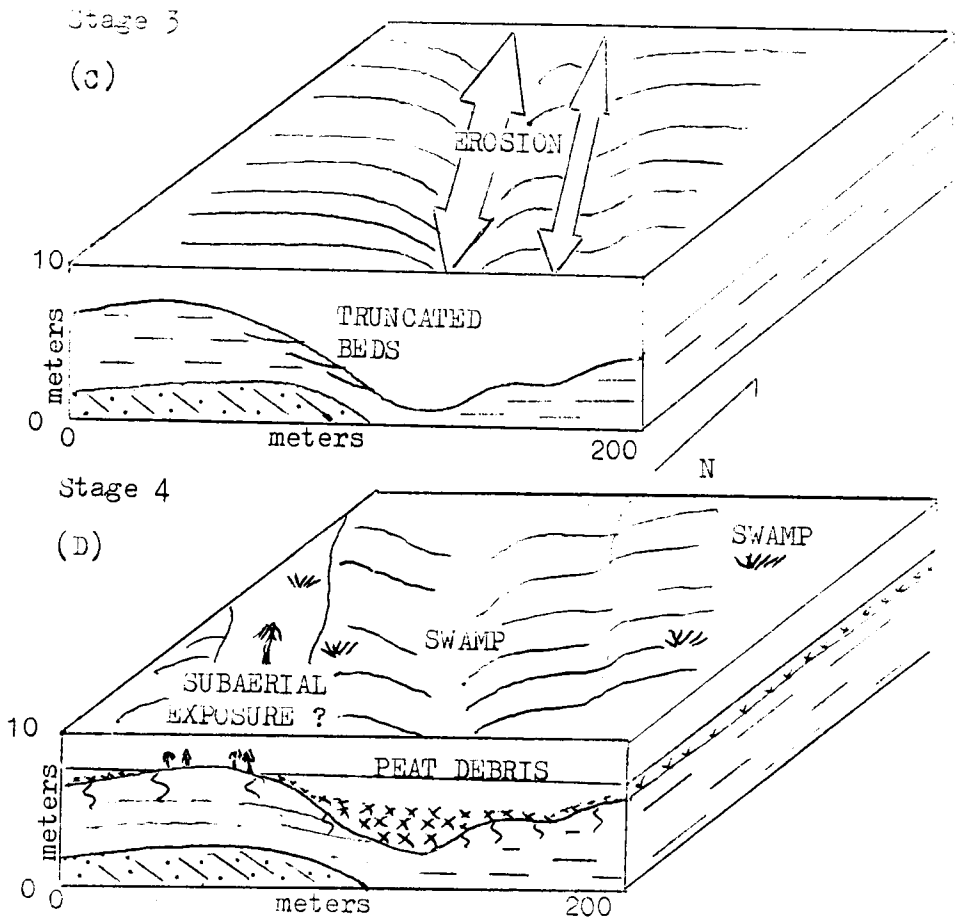
A possible depositional history is summarized in Figure 11 (A-D). Stage 1 (A) represents the building of a coarse-grained sand bar or sand wave from the southwest, as determined from the paleocurrent orientations of the cross-sets examined. Seven measurements were taken using a Brunton compass. The values ranged from N55W to N28W, with a mean dip of 11 degrees to the northeast. This indicates an average flow direction of N52E. The apparent final accretionary surface is shown (A, Fig. 11). Stage 2 (B) exhibits the addition of a fining-upward sequence of fine-grained sandstone (which shows small-scale, ripple cross-laminations), siltstone, and shale. Stage 3 (C) is a period of erosion, cross-cutting the sediments deposited in Stages 1 and 2. The erosive agent most likely represents a flood event of a distributary from the southeast or northwest. Stage 4 (D) is the establishment of the peat swamp and possible subaerial exposure and/or leaching of sediments, especially on the topographic highs. Peat is shown preferentially accumulating in the abandoned channel, which was possibly a cut-off distributary meander. Oxbow lake accumulations of organic material are not uncommon (Wanless, Baroffio, and Trescott, 1969, cited in Ross and Ross, 1984). After peat accumulation and the possible weathering/leaching of the sediments, the swamp was overlain



(A) Prograding sand wave, producing planar tabular cross-bedding from the southwest.

(B) Deposition of finer-grained sediments. This followed erosion of leading edge of sand wave and cessation of sand wave migration.

Figure 11. Four stages of development of strata at the study site.



(C) Erosional stage. Most likely caused by a flood event which carved a channel as water flowed from the southeast or northwest.

(D) Establishment of a swamp and a period of leaching/subaerial exposure (?) of the topographically higher areas of the abandoned channel.

Figure 11 (continued)

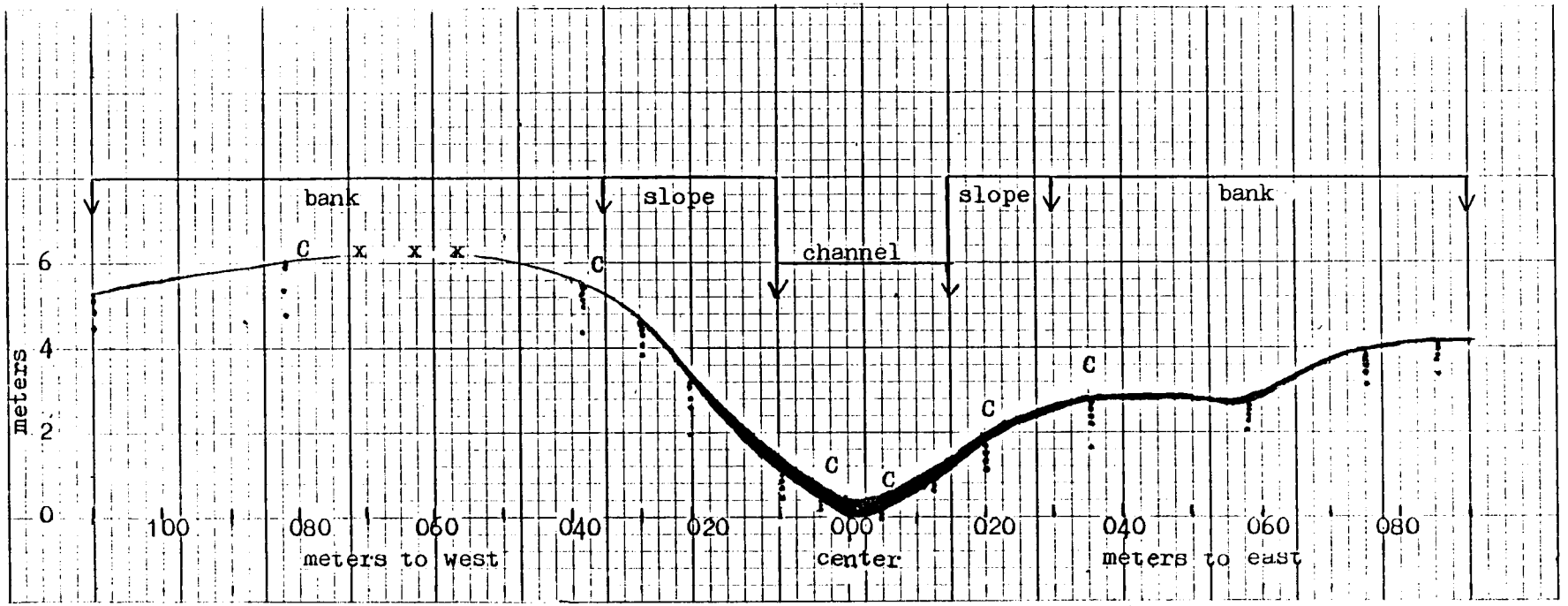
by muds and fine-grained sands that filled the channel as the peat compacted. Then a coarse-grained sand with siderite pebble lag and plant debris (now coal spar) was deposited. This sandstone, which also seems to be derived from the southwest, caps the channel-fill sequence.

Selection of Samples

Samples were collected at the study site both north and south of the Daniel Boone Parkway; however, only samples from the north side were analyzed because of better exposure and accessibility. Samples from the north side were thus gathered in a more consistent manner.

Samples were numbered according to their distance from the center of the channel, where the base of the coal was essentially level. Thus, a sample located 35 m east of the center of the channel on the north side is designated NE035. Vertical samples beneath the coal at this point would be numbered 1, 2, etc., for example, NE035-1.

Fifty-eight seat rock samples were gathered on the north side at 14 locations, and the entire coal was obtained for each location. These samples can be described as being in the "channel," on the "slopes," or on the "banks." The vertical profiles are at locations NW110, NW082, NW037, NW029, NW020, NW009, NW003, NE005, NE012, NE020, NE035, NE058, NE075, NE087. The boundaries between the zones have been arbitrarily chosen (Fig. 12). The northwest bank



LEGEND

C coal sample location
. seat rock sample location
x no coal present

Figure 12. Location of seat rock and coal samples. Vertical exaggeration is 6.25X.

constitutes NW110 - NW035, and the northwest slope is designated NW035 - NW010. The channel is a zone from NW010 to NE015. The northeast slope comprises the area from NE015 to NE030, and the northeast bank is the zone NE030 to NE090.

All of the seat rock samples were collected less than 1.5 m beneath the coal. Figure 12 shows the distribution of the samples studied from the north side. The base of the channel is not well exposed and no samples more than 20 cm beneath the coal could be obtained in a zone within 10 m east or west of the center of the channel. These rocks appear to be altered little; root traces are rare and bedding is intact.

Samples were selected on the basis of visual change in the strata. The typical vertical profile on the banks shows a gradual change upward from a thinly bedded, fine-grained sandstone through an apparent leached zone to an unlaminated underclay. Samples were gathered to the base of the leached zone and into the bedded and apparently unaltered sandstone. Samples in the channel do not exibit this type of change. These rocks are bedded and grade from a coarse-grained sandstone (which is the dominant lithology) into a carbonaceous shale at the base of the coal. Typically, 4-5 samples were taken at each of the 14 sites (except for the 20 m zone at the center of the channel), and each site included a sample from the 0-3 cm interval below the coal (Fig. 12).

CHAPTER II

ANALYTICAL METHODS

Introduction

The primary analytical methods employed during this study included X-ray fluorescence (XRF) and X-ray diffraction (XRD). XRF and XRD analyses were performed on all 58 seat rock samples. Coals from 6 representative sites were analyzed by XRF and petrographic analysis (point-counting technique) using reflected light.

XRF

Elemental analyses were accomplished using an energy dispersive, EG&G ORTEC TEFA III (Tube Excited Fluorescence Analyzer) System. ORTEC's ATAC program and a Clays protocol prepared in the Department of Geological Sciences were used for quantitative elemental analysis. Six g sample splits were made into pressed pellets (briquets) utilizing a Shatterbox, pellet die, and press (Appendix 1). Each sample was ground in the Shatterbox with a tungsten carbide mill for 6 minutes. Fifty-eight seat rock pellets were prepared and analyzed including duplicate standard samples. Concentrations were recorded as weight percent (hereafter referred to as percent). Values of precision and standard errors of calibration are reported in Appendix 2. XRF results are reported in Appendix 3.

XRD

XRD analysis on 58 seat rock samples, including both bulk and <2-μm fractions, were performed using a Phillips Norelco diffractometer with Cu K (λ = 1.5418 A) radiation at one degree 2Θ per minute. A 10 g split, obtained from the approximately 200 g of sample gathered for each sample, was ground with a mortar and pestle and passed through a 200 mesh (63 μm) sieve. Bulk mineralogy was determined for each using a pack mount, and scanning from 2 to 60° 2Θ. The <2-μm fraction was obtained by differential settling of the ground, 10 g splits for 3 hours and 50 minutes (Brown, 1961). The <2-μm material was syphoned off and flocculated with 50 ml of 1N $MgCl_2$. Several comparisons of saturated (Mg++) and unsaturated (no $MgCl_2$ added) clays were made. Little or no observable change was recorded in the subsequent X-ray patterns. Mg^{++} saturation served the purpose of allowing for the quick settling and easy collection of the <2-μm fraction.

Smear mounts of uniform thickness were run from 2-30° 2Θ. Twenty slides of the <2-μm fraction were exposed to ethylene glycol vapor in a glycolating device for 24 hours at 65° C, and then scanned from 2-14° 2Θ. These samples were then heated at 300° C for one hour and X-rayed, and then heated to 550° C for one hour and X-rayed again from 2-14° 2Θ. Two samples were saturated with K+ to verify the presence of expandable layers in the mixed-layer clays, and

the presence of expandable layers in the mixed-layer clays, and analyzed from 2-30° 2θ.

Semi-quantitative analysis of clay minerals was accomplished based on peak height ratios. Relative amounts of chlorite, kaolinite, and illite were determined based on a procedure by Griffin (1970). The procedure serves as a rough estimate for clay mineral percentages. A sample calculation is shown in Appendix 4. Four assumptions are made in this procedure: 1) for equal peak heights, illite at 10A is 2.5X greater in abundance than kaolinite and/or chlorite at 7A (Weaver, 1961), 2) the (001)/(002) peak ratio for chlorite is approximately 1.7 (Holbrook, 1973), which was the average value computed by Lithgow (1972) and Holbrook (1973) in their analyses of chlorite in Pennsylvanian shales and underclays, 3) clay minerals equal 100% of the sample, and 4) the diffraction of X-rays by the clay minerals is consistent, i.e., the factors affecting the diffraction of X-rays by clays are constant (Griffin, 1970). These assumptions allow for internal comparison only of relative clay mineral percentages (Appendix 5). The values obtained warrant some degree of caution to their signficance, and numbers should serve as generalizations only.

The X-ray diffractometer was periodically checked using a silica standard to guard against unknown instrumental drift.

Coal Analyses

XRF analyses were made for 6 representative coal samples; 5 of these samples were analyzed for maceral composition, which included NW037, NW003, NE005, NE020, and NE035. XRF analyses were performed on these samples and also NW082. The samples were chosen because they represent different paleotopographic elevations. Coal XRF pellets were made in the same manner as the seat rock pellets. Coal samples were splits from the entire coal bed at that sample location. The coal was prepared for splitting by crushing it with a porcelain hammer and plate, and passing the coal through a 2 mm sieve.

Epoxy mounts for petrographic analysis were prepared with 1-2 g splits from the crushed coal, and were then polished with a Merimet polisher. Macerals were identified using a Zeiss microscope with reflected light. Volume percentages of macerals were estimated by the Cheyes point counting method (Cheyes, 1956). Relative error for maceral percentage estimation was assessed by the Van Der Plas and Tobi method (Van Der Plas and Tobi, 1965). One thousand counts were made for each sample. The macerals were categorized as either vitrinite, exinite or inertinite macerals. Pyrite and terrigenous clastic material were also counted.

CHAPTER III

RESULTS AND DISCUSSION

XRF

Samples of the sedimentary rock underlying the coal were analyzed by XRF for Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, S, K_2O, CaO, TiO_2, Cr, Mn, Fe_2O_3, Rb, Sr, Zr and Ba. All 58 samples included in the 14 vertical profiles were analyzed for these 16 elements (Appendix 2). Values are reported in weight percent (wt. %), except for the concentrations of Cr, Mn, Rb, Sr, and Zr (<0.1%), which are reported in ppm. Percent Fe_2O_3 was stoichiometrically converted to % Fe in order to compare directly with amounts of Fe allotted to pyrite (FeS_2).

Fe, MgO, and MnO (Figs. 13, 14, and 15 respectively) show similar vertical and horizontal trends. Concentrations typically decrease upward on the banks and slopes, whereas they increase upward in the channel. Values of Fe typically decrease upward from 4-5% to 2-3% on the banks. Upward increases from 2-3% to as much as 12% Fe occur in the channel (Fig. 13). MgO typically decreases upward from 2% to 1% on the banks (Fig. 14), whereas the highest values occur in the 0-3 cm zone at the channel (NE005 - 2.6%). Concentrations of MnO are greatest in the lower portions of the vertical profiles. MnO decreases upward at all sites except those in the channel (Fig. 15). At site NE058, which

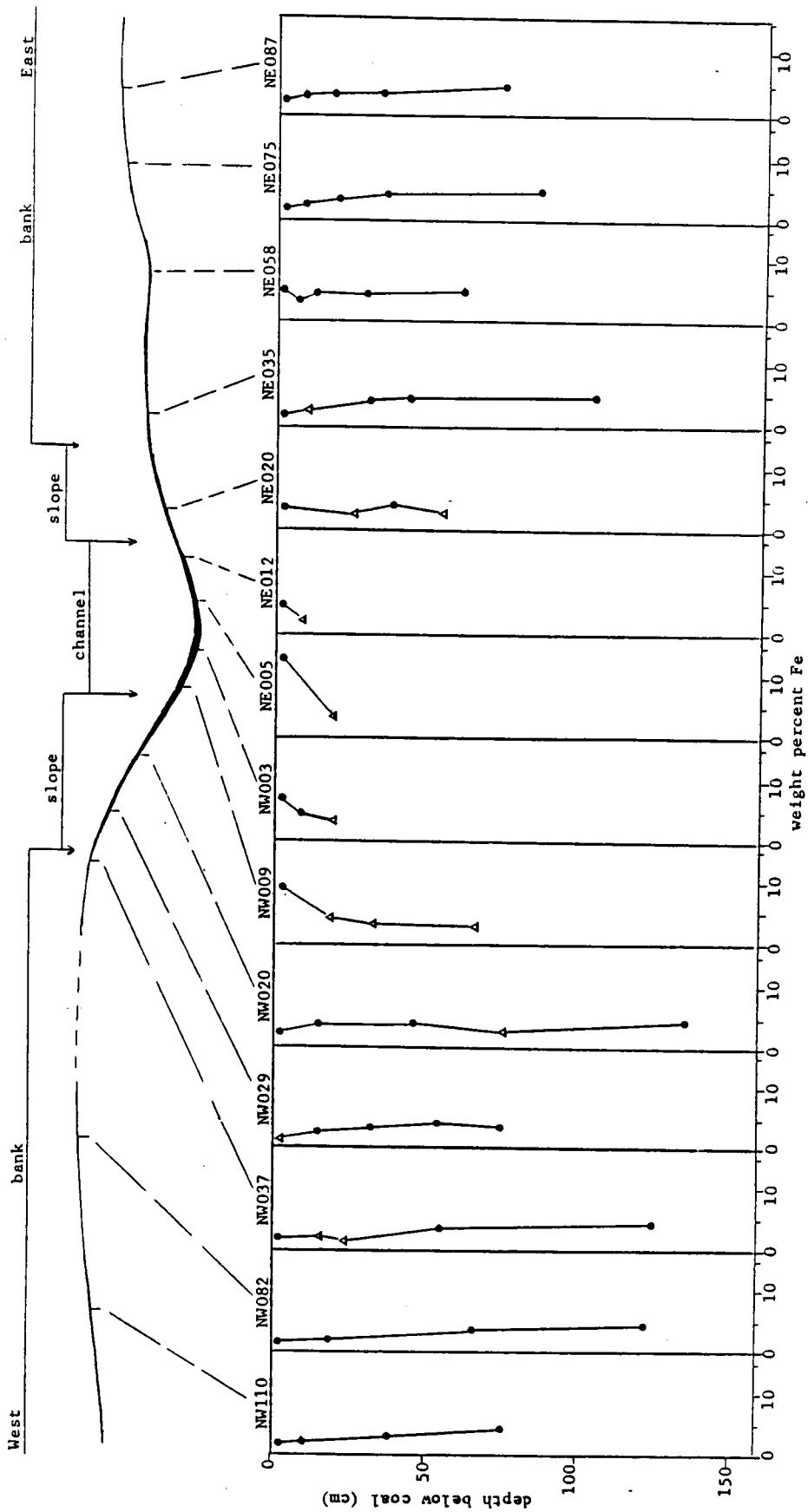


Figure 13. Trends in Fe with depth below the coal. Triangles represent sandstone samples.

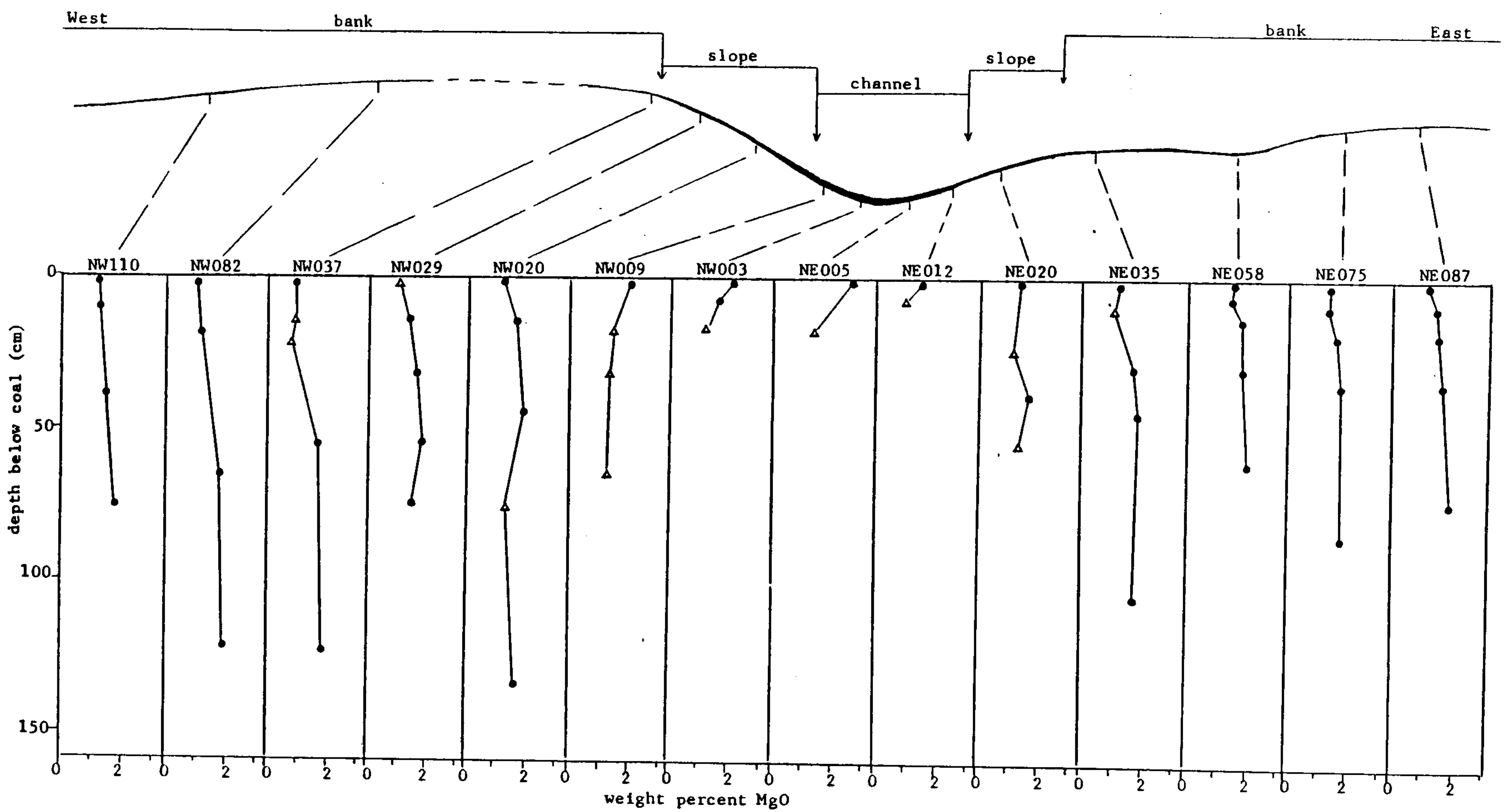


Figure 14. Trends in MgO with depth below the coal. Triangles represent sandstone samples.

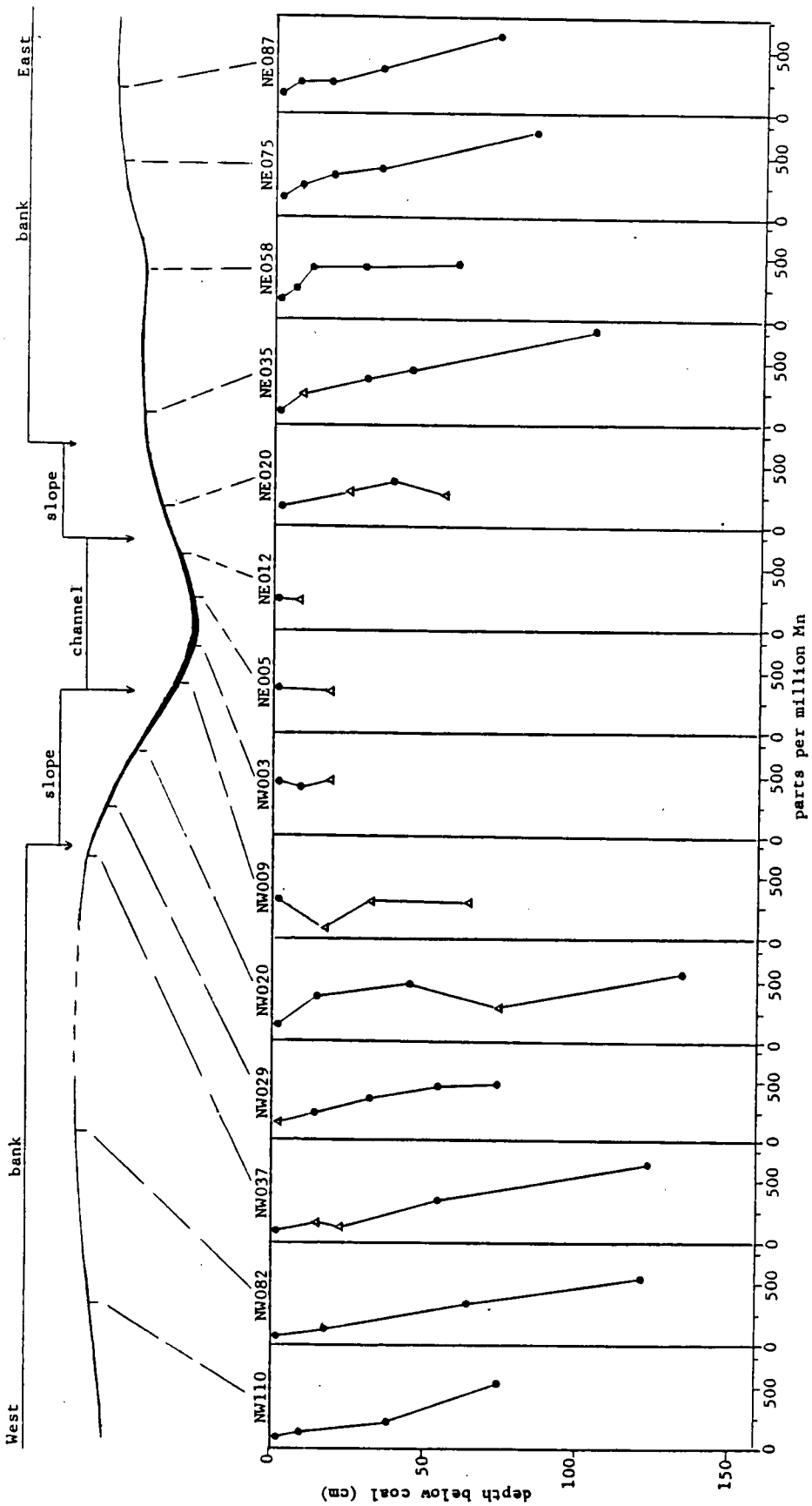


Figure 15. Trends in MnO with depth below the coal. Triangles represent sandstone samples.

is a depression on the northeast bank, concentrations of MgO and Fe increase at the 0-3 cm zone in a manner similar to the channel sites. MnO does not increase at this location.

Fe, MgO, and MnO have apparently migrated downward on the banks. The mobilized Fe was probably the source for the siderite concretions formed on the banks and slopes. Siderite nodules may have been precipitated when different Eh conditions, which may have been controlled by an ancient water table, were encountered. Although siderite concretions are not found in the channel, Fe has been concentrated in the form of pyrite. The Fe could have originated from below the coal, or been flushed from the banks and slopes by a reflux mechanism. On the other hand, the elevated Fe concentration in the channel may have resulted from the lack of leaching of material. Fe may have been "locked" into place in the form of pyrite by reducing conditions which existed in the paleotopographic lows. Moreover, an additional source of Fe might have been complex ions held in acidic standing water at the paleotopographic lows (Garrels and Christ, 1965).

The average value of MgO for the channel samples in the 0-3 cm zone is 2.04%. Since no other high magnesium minerals were determined by XRD analysis, the Mg would appear to be in the structure of chlorite. The identification of chlorite at NW003-1 was confirmed by the near doubling of the (001) peak intensity by heating the

sample to 550° C and also its destruction by heating in 1N HCl at 60° C for 10 hours. Chlorite may have persisted in these channel seat rocks despite acidic conditions that are associated with bog waters. Weathering processes tend to destroy chlorite (Weaver, 1979). However, groundwater flow through the sediments immediately following accumulation of organic matter in the paleotopographic lows may have been insignificant. Processes involved in weathering such as water movement, aeration, etc., possibly were ineffective in destroying chlorite in this environment.

Although Mg ions are likely to be removed by acidic waters (Parham, 1964), the relict chloritic structures may have undergone "chloritization" by the later addition of hydroxy-Mg, a process not uncommon in soils (Weaver, 1979). Standing water may have contributed ions. More likely, Mg ions may have been introduced from the paleotopographically higher areas that were leached. The initial flow of acidic, chlorite-destroying bog waters was probably downward, but as peat accumulated, groundwater flow may have reversed and flowed upward. Deevey (1958, cited in Parham, 1964) contends that groundwater flow in bogs is upward. If such a flow was established after chlorite had been partially destroyed, Mg ions might have been added to this zone as they percolated through the ground toward the channel. Chlorite then might have been regenerated.

Alternatively, sharpness ratios (discussed later) seem to indicate a lower degree of crystallinity (and possibly a higher amount of mixed-layering) in 10A material of the 0-3 cm zone. Consequently, sites for Mg ions may have existed in non-chloritic, degraded clays. Parham (1964) hypothesized that chlorite may form from mixed-layer clays coming in contact with waters of increased Mg content.

Therefore, the presence in the channel of chlorite, which holds the concentrations of Mg, may have originated in three ways: 1) detrital chlorite which persisted despite acidic conditions, 2) regenerated chlorite from relict chloritic structures (created by the acidic waters of the bog) by the later addition of hydroxy-Mg, and 3) the positive transformation from detrital mixed-layer clays to chlorite.

Sulfur is concentrated in the 0-3 cm zone (Fig. 16), most notably in the channel and site NE058. Below this zone, S does not exceed 0.1%, with the exception of sample 2 of NW003 (0.6%). Assuming that S is present as pyrite (FeS_2), proportional amounts of Fe may be allotted to pyrite. High pyritic Fe values are recorded only for samples NW009-1 (6.0%), NW003-1 (3.0%), NE005-1 (10.5%), NE012-1 (1.6%), and NE058-1 (3.0%). However, significant amounts of non-pyritic Fe (Fig. 17) remain for these samples. This confirms the abundance of Fe at these sites and also suggests that Fe was added to this zone (0-3 cm)

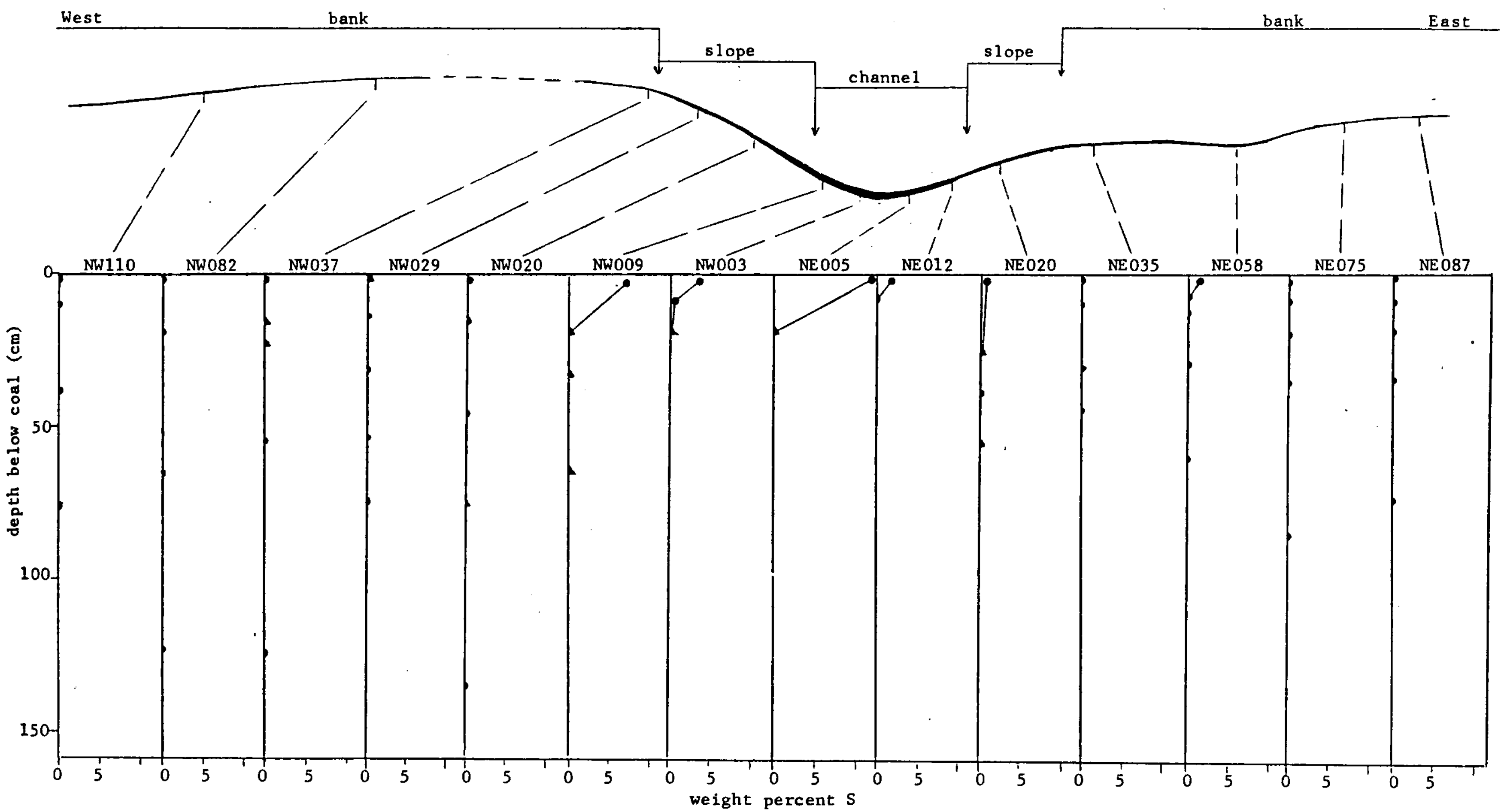


Figure 16. Trends in S with depth below the coal. Triangles represent sandstone samples.

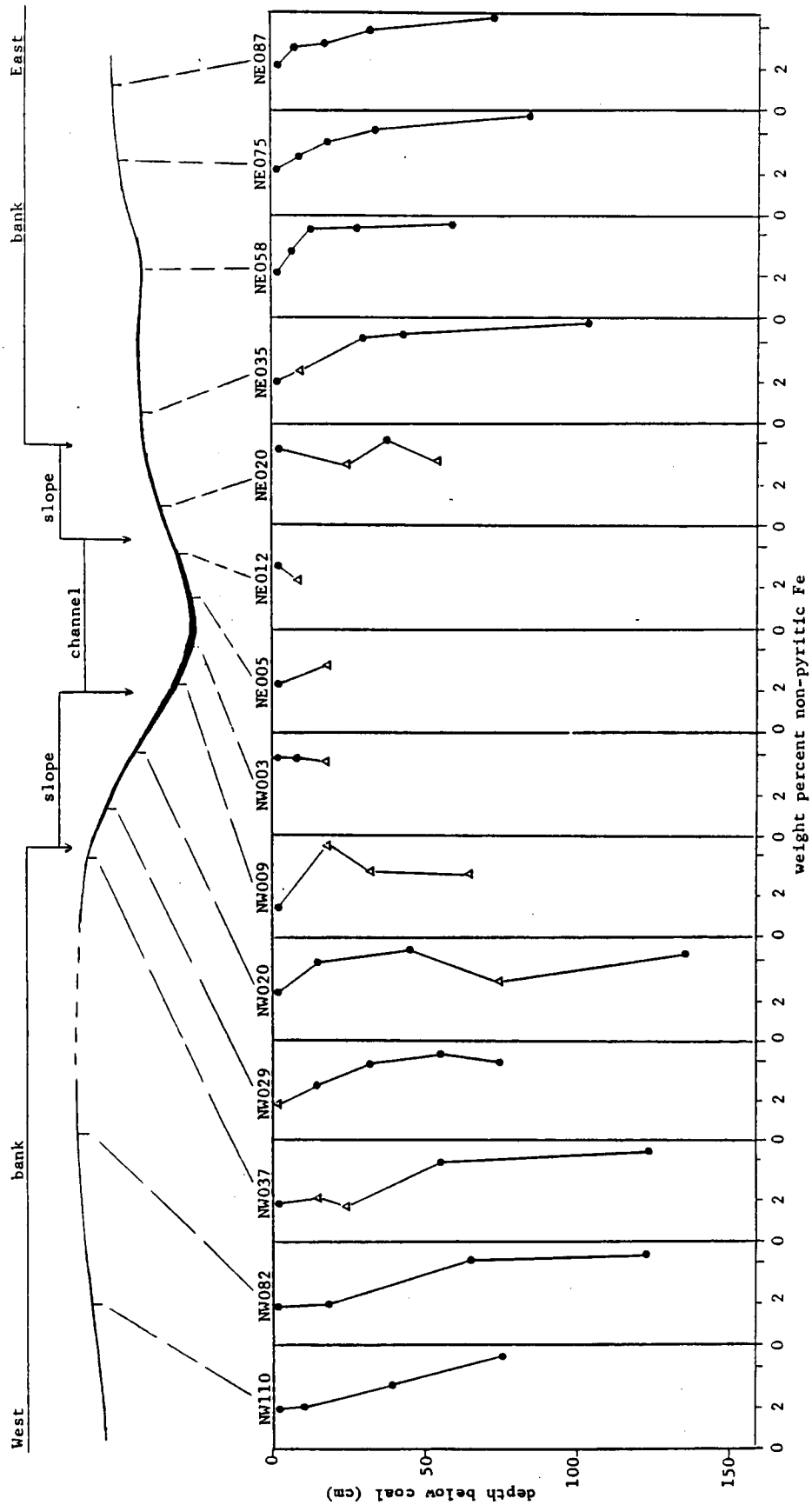


Figure 17 Trends in non-pyritic Fe with depth below the coal. Triangles represent sandstone samples.

from a source outside the channel seat rocks. Two likely sources of Fe include Fe in standing surface water and Fe mobilized by leaching at the slopes and banks. The source of the sulfur (probably in the form of reduced sulfate ions) is not obvious, although several possibilities exist. All sites with high S concentrations have a common factor of having been located in areas which were topographically low, i.e., which may have had standing water. Brackish surface water may have been the source of the sulfur, and leaching may not have been of any consequence at sites with high S concentrations. Subsequently, S persisted in the form of pyrite under reducing conditions. Conversely, S may have been incorporated by plants and/or dispersed by leaching at sites with low S values. It has been stated previously that the channel seat rocks for the most part lacked root traces. However, because of the very high S values in the channel, it is more likely that S was added to the low areas, and then was retained subsequently by reducing conditions which enabled pyrite to form.

For samples below the 0-3 cm zone, % SiO_2 (Fig. 18) does not change significantly. In the channel, values decrease slightly. On the banks and slopes, consistent trends are not apparent below the 0-3 cm zone. Percent SiO_2 is typically much lower in the 0-3 cm zone. Percent Al_2O_3 (Fig. 19) is somewhat inversely proportional to SiO_2. For 30 northwest samples, a correlation coefficient of -.51 (95%

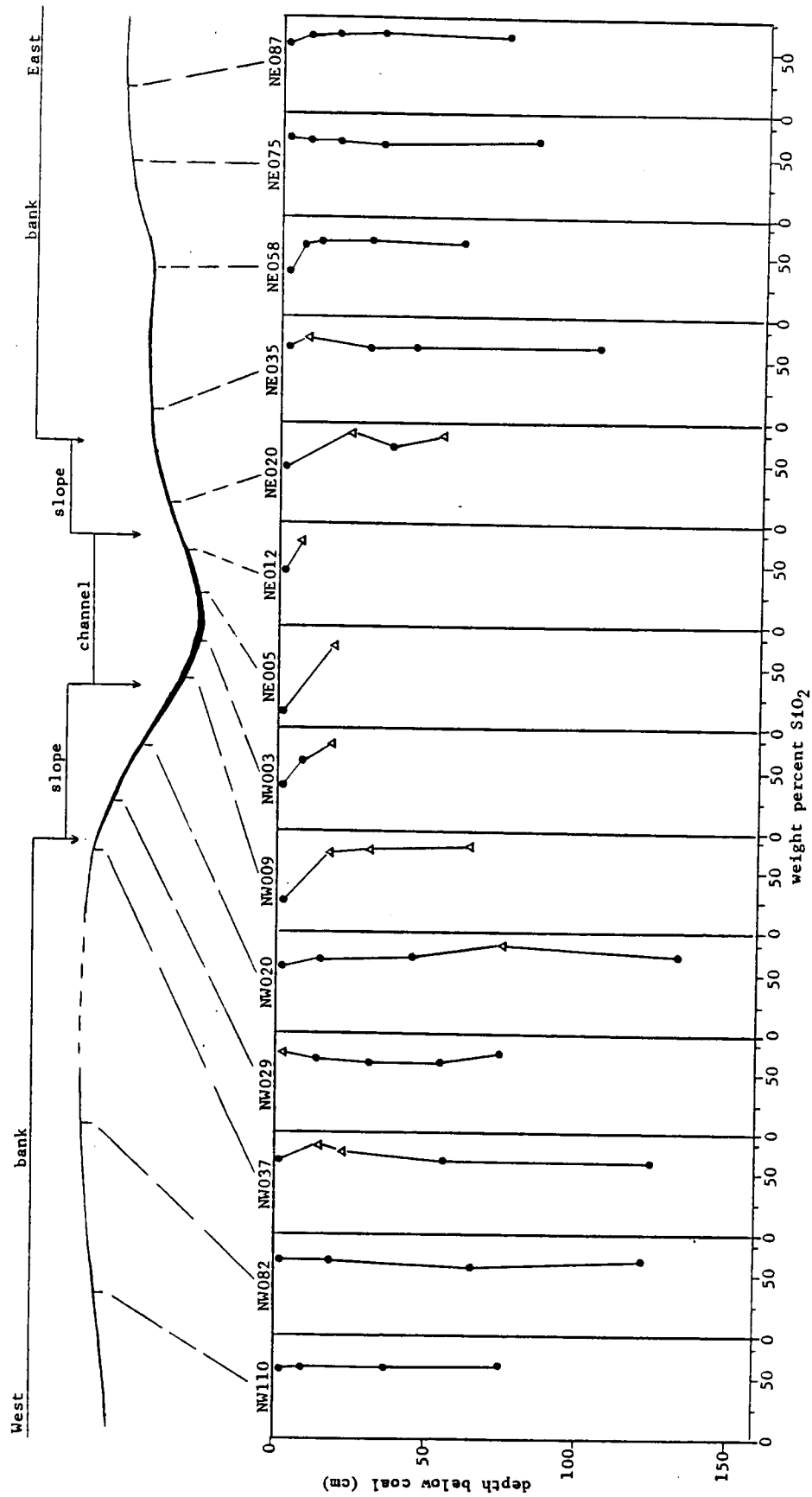


Figure 18. Trends in SiO_2 with depth below the coal. Triangles represent sandstone samples.

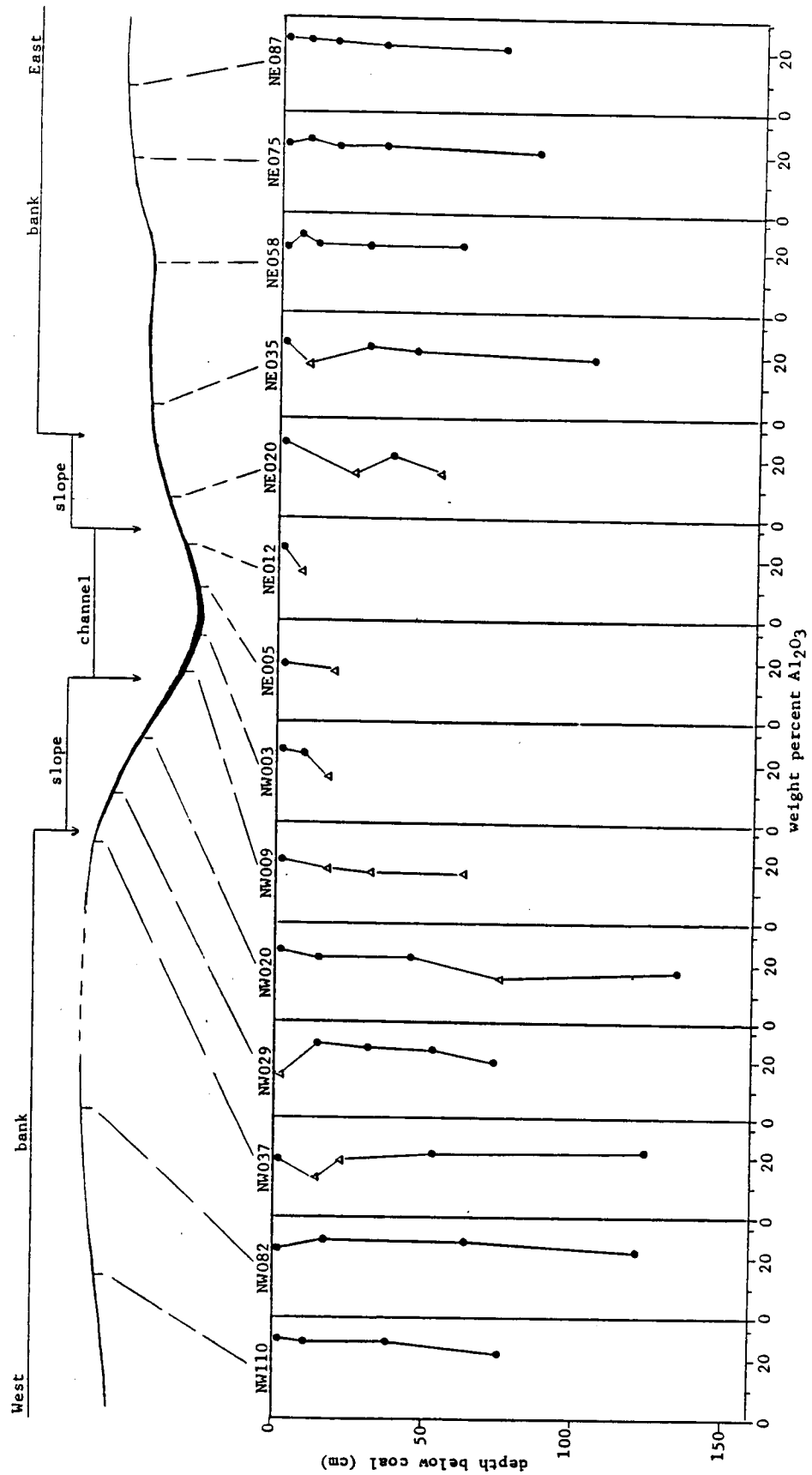


Figure 19. Trends in Al_2O_3 with depth below the coal. Triangles represent sandstone samples.

confidence) was calculated, which indicates 25% of the variation of the data might be explained as having a linear relationship. Percent SiO_2 for NE087 decreases upward from 60.6% to 58.4%, whereas % Al_2O_3 increases from 22.0% to 27.2%. Such patterns can be seen in part at each vertical sample profile. High SiO_2 values probably reflect increases in the amounts of quartz silt, whereas increases in Al_2O_3 probably reflect higher concentrations of clay minerals. The fine-grained nature of the underclay and carbonaceous shale of the 0-3 cm zone (which comprise this zone at each sample site) would account for the decrease in SiO_2 and increase in Al_2O_3. Such chemical changes would reflect variations in the relative percentages of the mineral suite, i.e., more clays and less quartz. Although the overall trend of the rocks beneath the coal is to fine upward, it is not necessarily reflected in SiO_2 and Al_2O_3 trends, because interbedded sandstone exists among the siltstone and shale, which interrupt the gradation from coarse-to fine-grained rocks.

Important chemical variations such as Fe are not wholely the result of changes in the mineralogical suite proportions. For example, samples from sandstone beds (with average SiO_2 contents equal to 70.2%) comprise 13 out of 58 seat rock samples: NW037-2,3, NW029-1, NW020-4, NW009-2,3,4, NW003-3, NE005-2, NE012-2, NE020-2,4, and NE035-2. The average non-pyritic Fe value for these rocks

is 2.8%, which is relatively low. Values of non-pyritic Fe range from 3.5-5% in shale and siltstone bank samples that are low in the vertical profiles (numbered 4 and 5). In a typical sedimentary deposit of sand, silt and clays, clay minerals would account for most of the Fe present. All vertical profiles include fine-grained rocks in the 0-3 cm zone. However, on the banks, low Fe values exist (an average of 2.0%). The Fe concentration trends are maintained whether the lithotypes are uniform or grade from medium-to fine-grained rocks in the vertical profiles. This confirms that although changing mineral proportions strongly influenced the chemical trends, the trends cannot be explained wholely on such a basis.

The majority of the samples from the study site are siltstone and shale, including 13 sandstone samples. The Al_2O_3/SiO_2 ratios portray the lithologic consistency both laterally and vertically (Fig. 20), as they do not vary greatly in vertical profile below the 0-3 cm zone. More consistency in the ratios is obtained when samples from sandstone beds with relatively low Al_2O_3/SiO_2 ratios are considered. In general, there is a tendency for Al_2O_3/SiO_2 ratio to increase upward at some vertical profiles. The highest ratios commonly occur in the 0-3 cm zone, of which values from the channel (NE005-1 - 1.4) are the highest recorded.

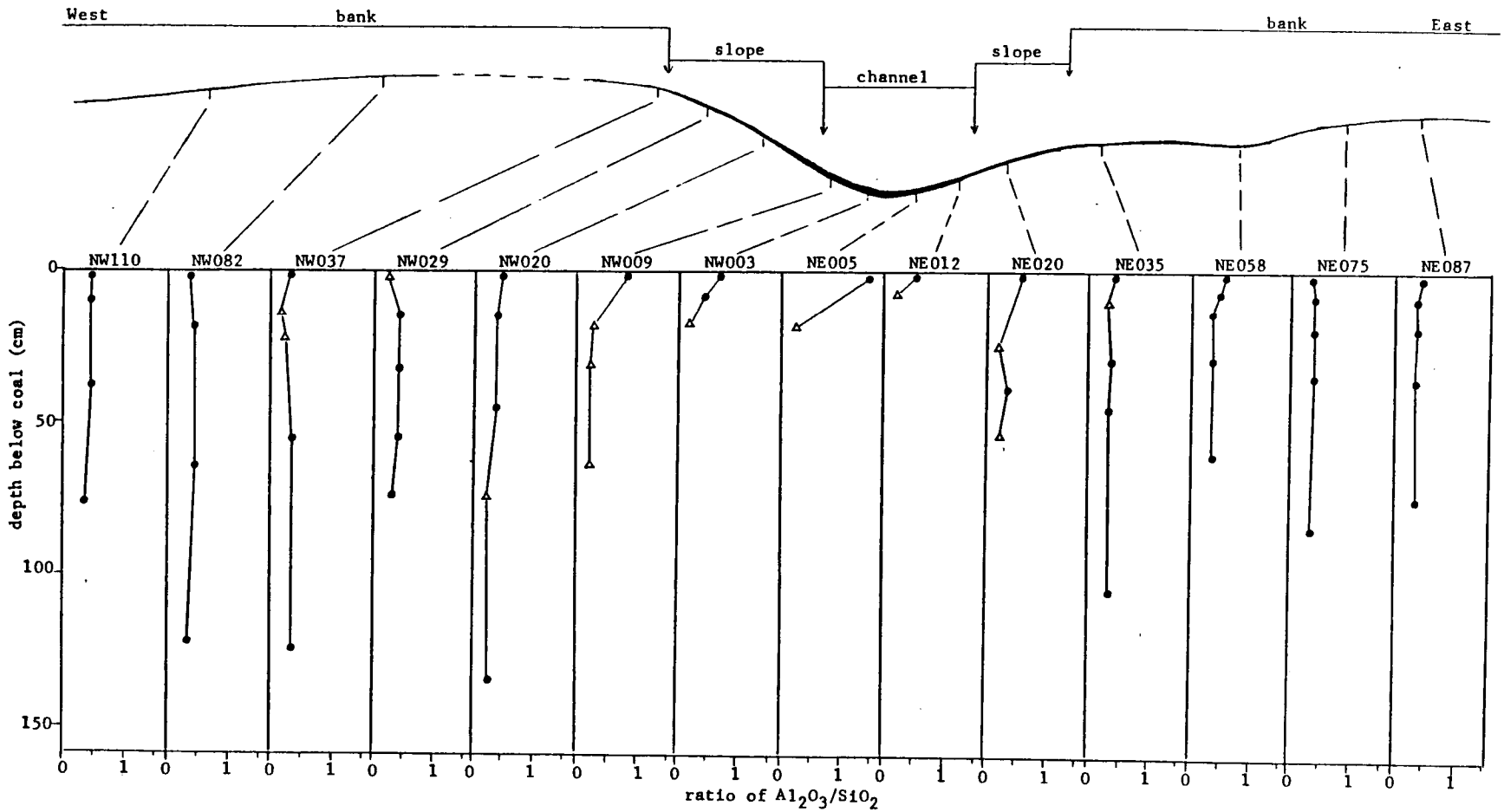


Figure 20. Trends in Al_2O_3/SiO_2 ratios with depth below the coal. Triangles represent sandstone samples.

Samples from sandstone beds (NW037-2,3, NW029-1, NW020-4, NW009-2,3,4, NW003-3, NE005-2, NE012-2, NE020-2,4, and NE035-2) have an average K_2O value of 2.9%, which is relatively low. When these sandstone samples are eliminated, an upward increase in K_2O in the vertical profiles is evident (Fig. 21). Most of the potassium is probably in illite, and the subsequent rises in K_2O might be related to the increase in clays upward, especially illite (and 2_m muscovite). Although potassium feldspar was detected by XRD analysis, it seems probable that the amount of K_2O contributed by feldspar is low. More feldspar would be expected in the sandstone samples than in the other lithotypes. Yet these rocks were low in K_2O. Therefore, it seems likely that the amount of K_2O was primarily controlled by the amount of illite. The fining upward (an increase in clay content) would account for the general increase upward in K_2O, which increases from 3.7% (average value for samples lowest in vertical profiles) to 4.8% (average value for samples numbered 1). There is a lack of significant lateral variability in K_2O. A visual comparison of Al_2O_3/SiO_2 ratios and % K_2O (Figs. 20 and 21) reveals similar trends in the sample profiles. However, calculation of the correlation coefficient between K_2O and Al_2O_3/SiO_2 ratio for 58 samples yields a value of .34 (99% significance), which does not indicate a strong relationship.

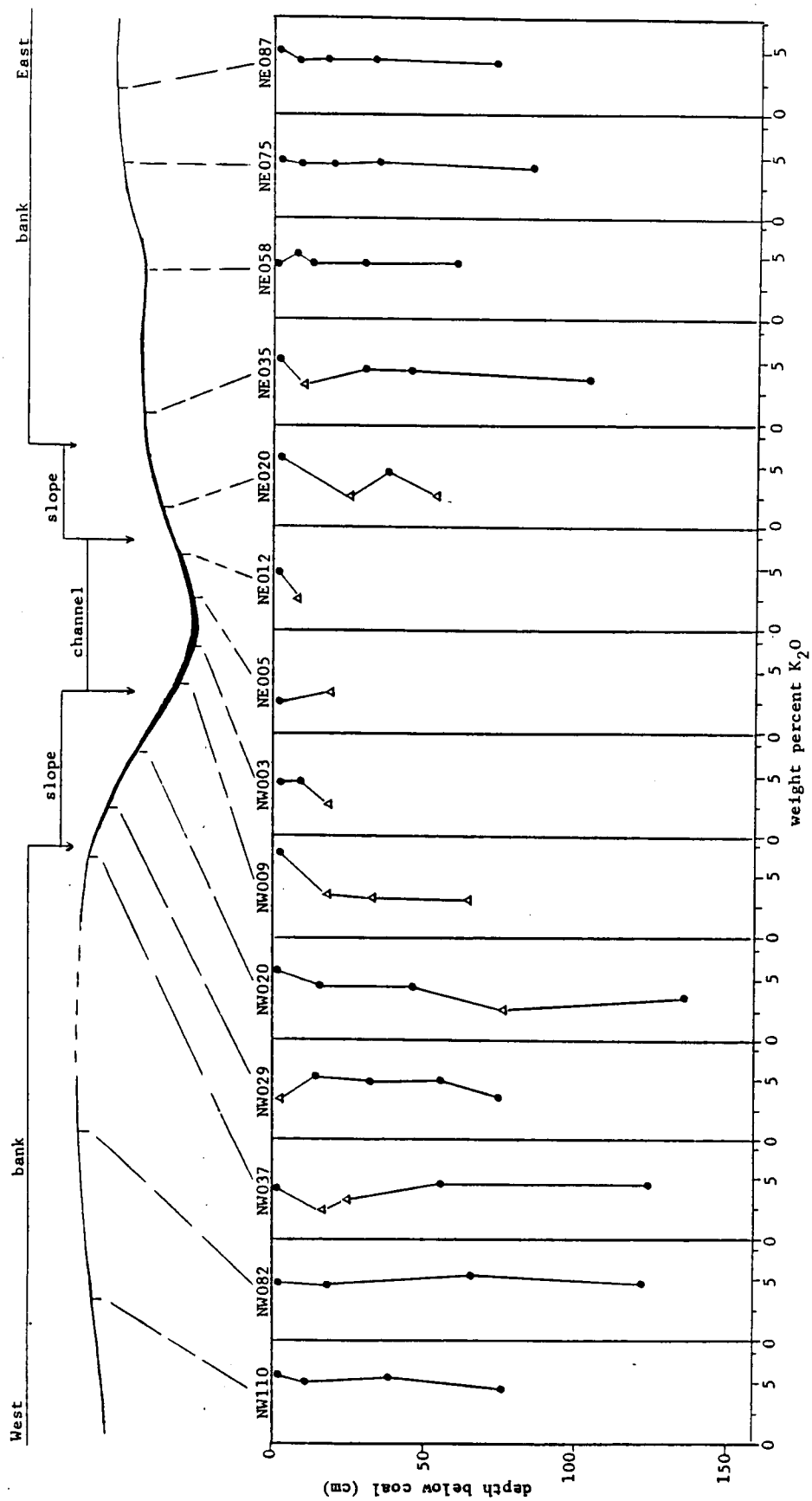


Figure 21. Trends in K_2O with depth below the coal. Triangles represent sandstone samples.

Rb (Fig. 22) is associated with K_2O (Fig. 21). Similar vertical trends are apparent, and Rb may be correlated with illite. The correlation coefficient between K_2O and Rb is .85 (99.9% significance) which indicates a fairly strong correlation. Rb is most likely incorporated in the structure of 2_m muscovite, a high temperature polymorph. The presence of 2_m muscovite was confirmed by XRD analysis, which will be discussed in a later section.

CaO is not abundant (Fig. 23), and concentrations values range from only 0.1% to 0.4%, with a standard error of calibration equal to $\pm$0.06%. The high error indicates that trends cannot be supported statistically. Several trends may exist. Below the 0-3 cm zone, % CaO (Fig. 23) exhibits minor decreases upward on the banks and slopes, whereas values rise slightly in the 0-3 cm zone, except for sites NE075, NE058, and NW029. In the channel, % CaO decreases upward (with the exception of site NE012). The highest values of CaO typically occur low in the vertical profiles. Sandstone samples show low concentrations of CaO (with an average of 0.20%), except for samples in the channel (NW003-3, NW009-2,3,4, and NW005-2) which have a higher average (0.27%). The low amounts of CaO in sandstone samples from sites NW037-2,3, NW029-1, and NE035-2 may be the result of the removal of Ca by leaching at the banks. Moreover, the slightly higher concentrations of CaO in the lower portions of the vertical profiles on the banks may

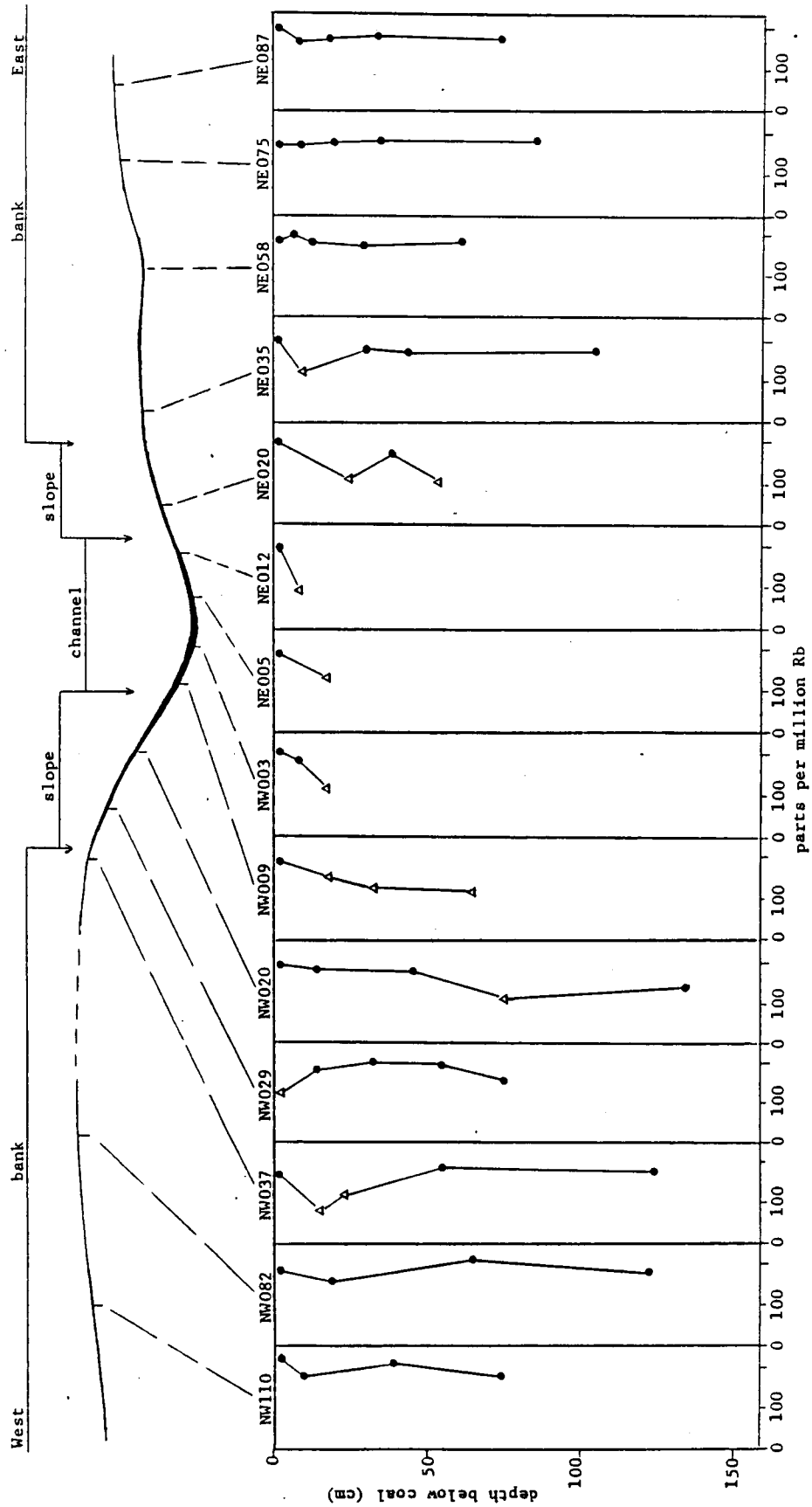


Figure 22. Trends in Rb with depth below the coal. Triangles represent sandstone samples.

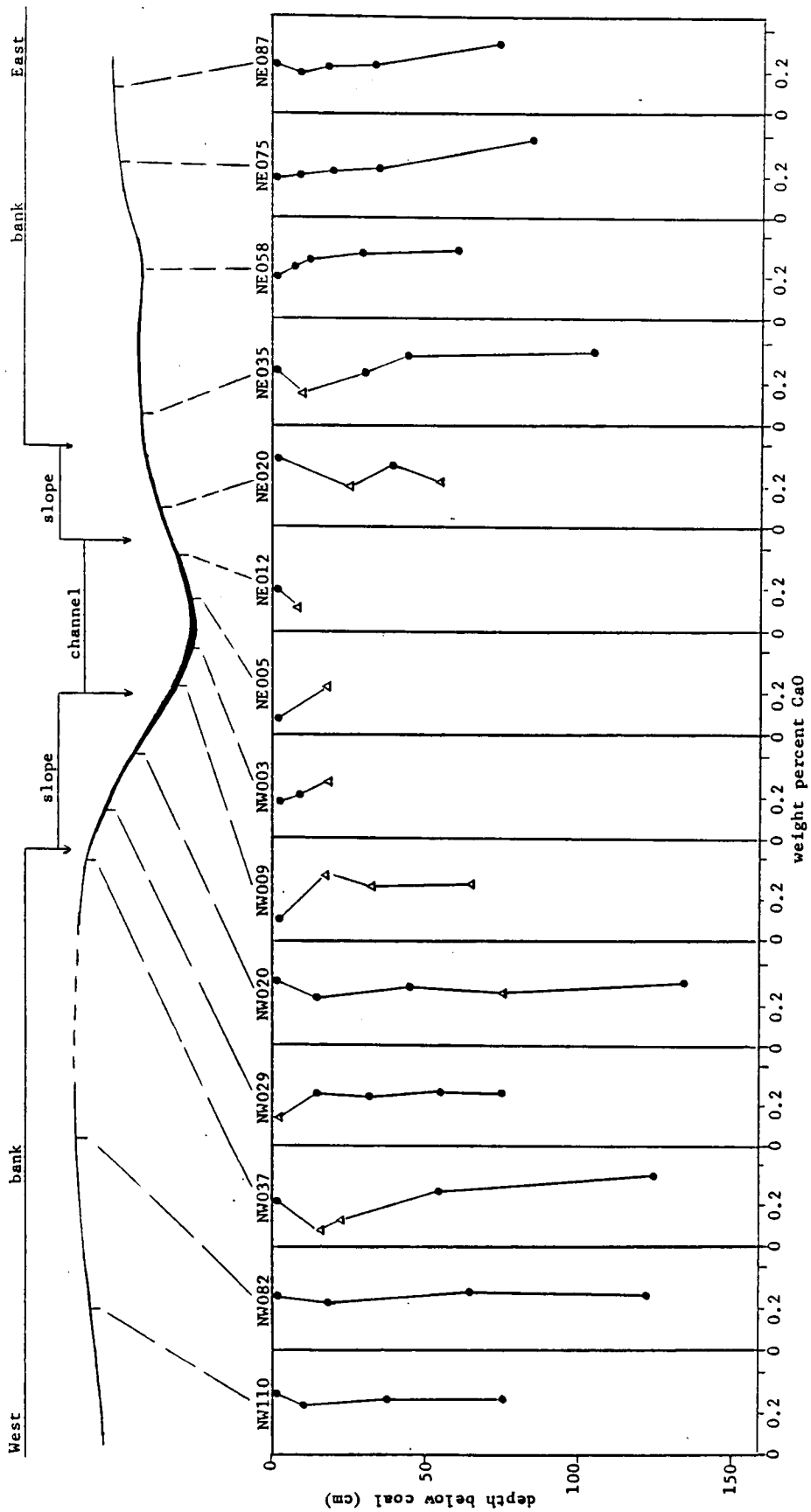


Figure 23. Trends in CaO with depth below the coal. Triangles represent sandstone samples.

also be evidence for leaching and the resultant accumulation of downward moving CaO.

A general similarity in trends exists between CaO (Fig. 23) and Sr (Fig. 24). However, a low correlation coefficient was calculated. Sr values range from 100-200 ppm, and slight increases are apparent in the 0-3 cm zone, where Sr may have been incorporated more readily into the organics or weathered (before or after deposition) clay structures.

Na_2O values are erratic and few trends are apparent (Fig. 25). However, the highest concentrations (up to 2.3%) are noted to be in the 0-3 cm zone in the channel and at site NE058 (1.0%). High Na_2O values are then possibly associated with topographic lows, and perhaps were derived from standing brackish water. Na_2O probably was incorporated in the organics and clays of the 0-3 cm zone of the channel seat rocks.

Values for TiO_2 are consistent in pattern and abundance (Fig. 26). With few exceptions (only 3 out of 14 sites), the highest concentrations exist in the 0-3 cm zone. Beneath this zone, values typically are laterally and vertically consistent. The highest values occur in the 0-3 cm zone (NE005 - 1.35%, in the channel; and NE037 - 1.31%, on the northwest bank). Three possibilities might account for higher concentrations of TiO_2: 1) more abundant clay minerals containing TiO_2, 2) a (residual) concentration of

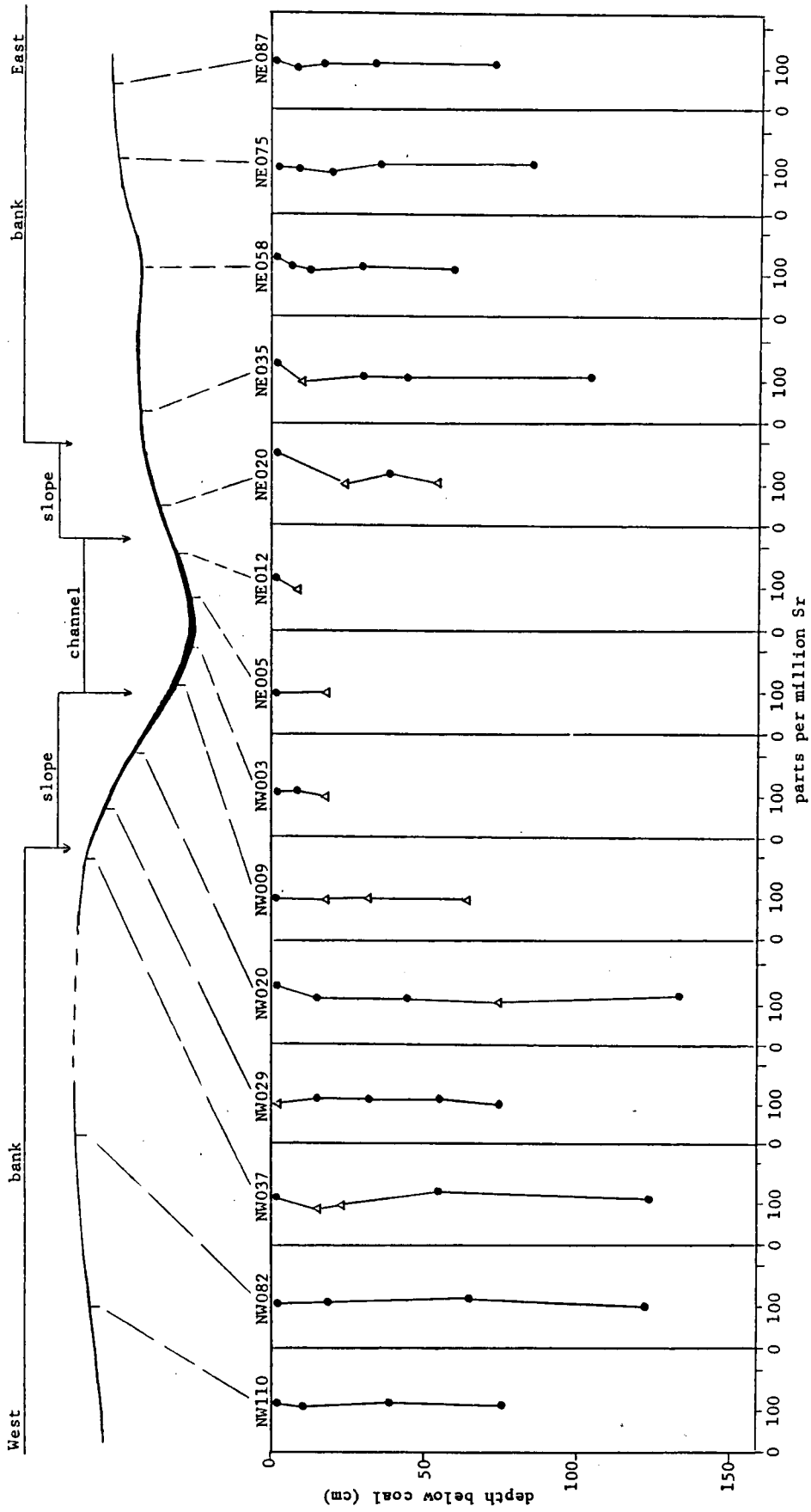


Figure 24. Trends in Sr with depth below the coal. Triangles represent sandstone samples.

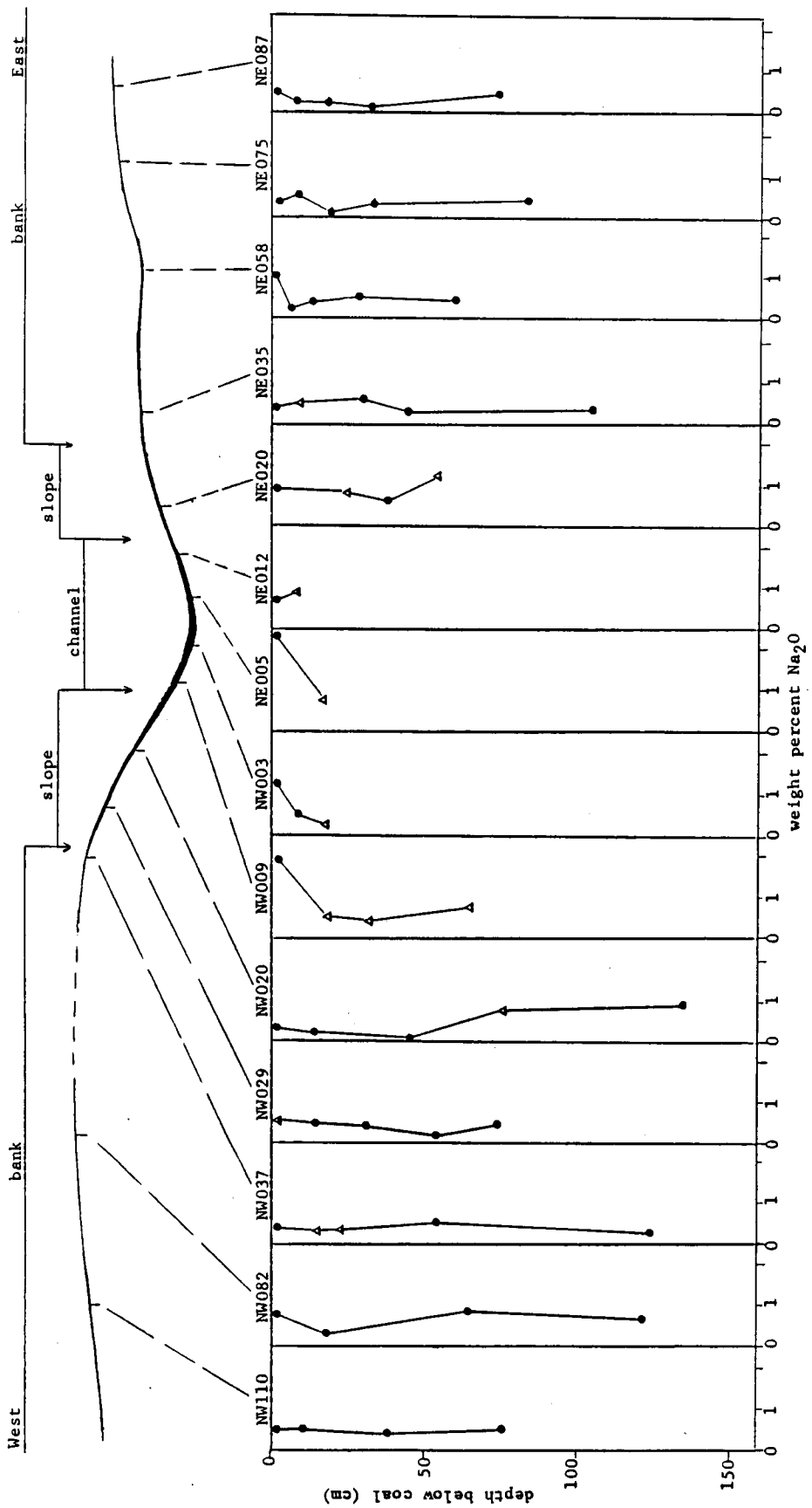


Figure 25. Trends in Na_2O with depth below the coal. Triangles represent sandstone samples.

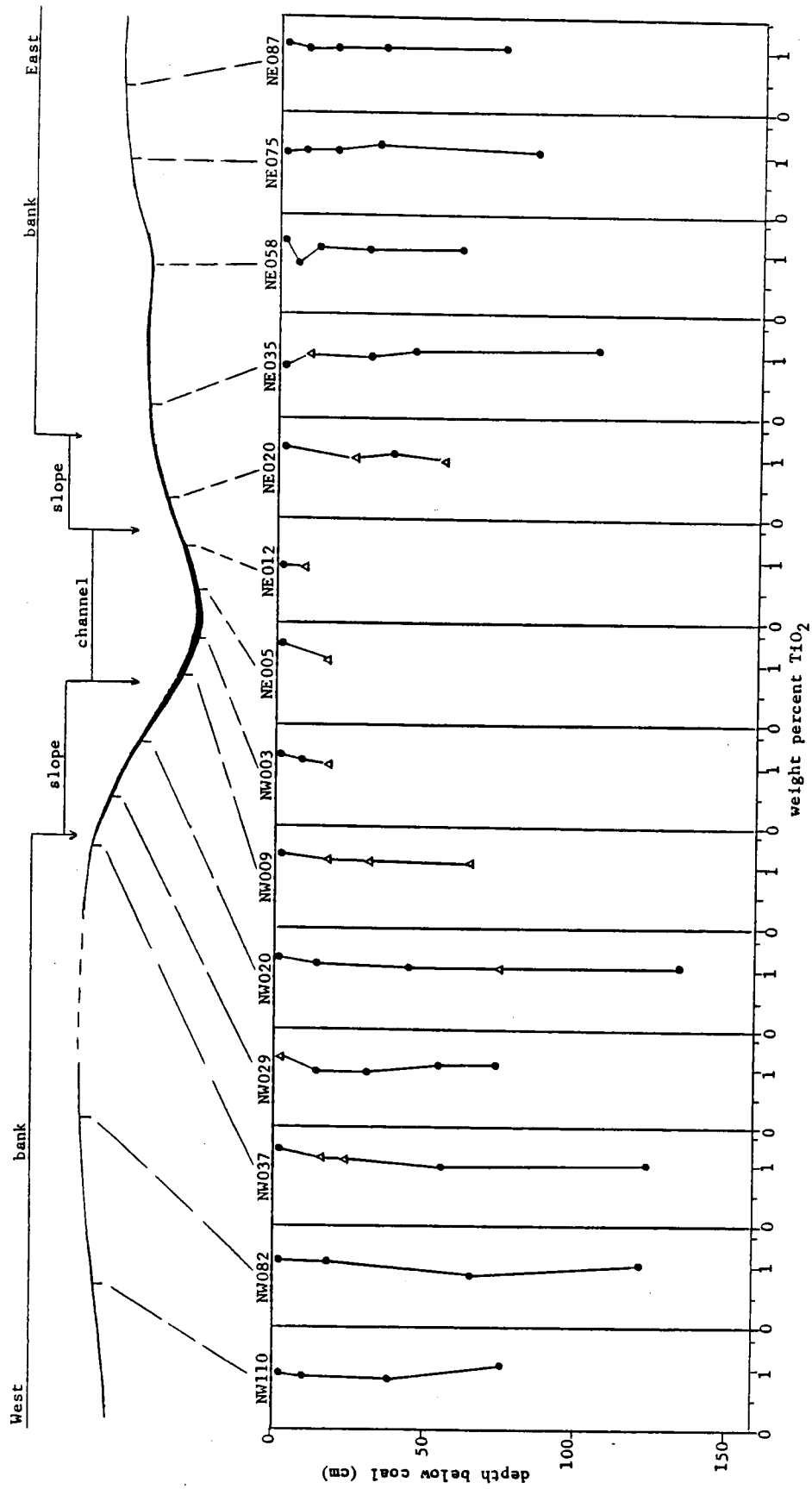


Figure 26. Trends in TiO_2 with depth below the coal. Triangles represent sandstone samples.

resistant TiO_2 minerals such as ilmenite or rutile, and 3) coarser-grained rocks which may contain a higher amount of Ti-bearing, heavy minerals. Such possible factors are difficult to discriminate between in the trends of TiO_2 (Fig. 26). However, because the higher TiO_2 values occur in the finer-grained rocks of the 0-3 cm zone, it is likely that TiO_2 is present in the clay minerals and organic matter.

Percent Ba (Fig. 27) and P_2O_5 (Fig. 28) have similar trends. Below the 0-3 cm zone, values decrease slightly on the banks and slopes, but are laterally consistent. The highest values for both elements occur in the channel (NE005) in the 0-3 cm zone, where P_2O_5 reaches 1.41% and Ba 0.25%. Ba differs from P_2O_5 in that high Ba concentrations also exist on the banks in the 0-3 cm zone. Ba is probably held in clays and organic matter, and therefore is more abundant in the 0-3 cm zone. A brackish water source in the channel may also have contributed Ba. P_2O_5, however, shows significant increases only in the 0-3 cm zone of the channel, and at NE058 (the low point on the northeast bank). The average P_2O_5 value in the 0-3 cm zone on the slopes and banks (excluding NE058) is 0.08%, whereas for the four channel sites and NE058, the average % P_2O_5 is 0.73, over 9X the average for samples from the bank and slope. A possible source for the concentrations could be the inclusion of phosphatic material derived from bones or fish in the

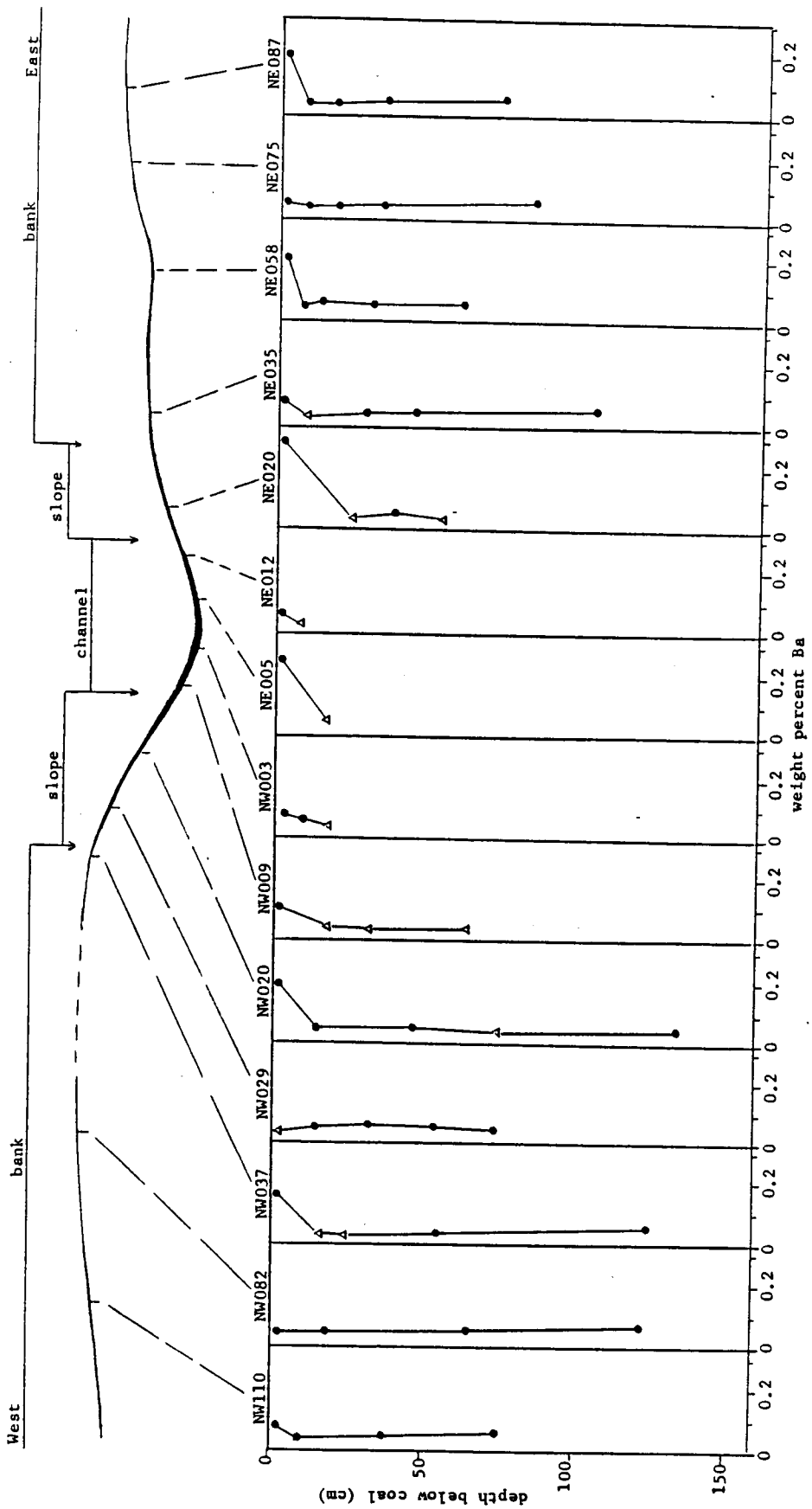


Figure 27. Trends in Ba with depth below the coal. Triangles represent sandstone samples.

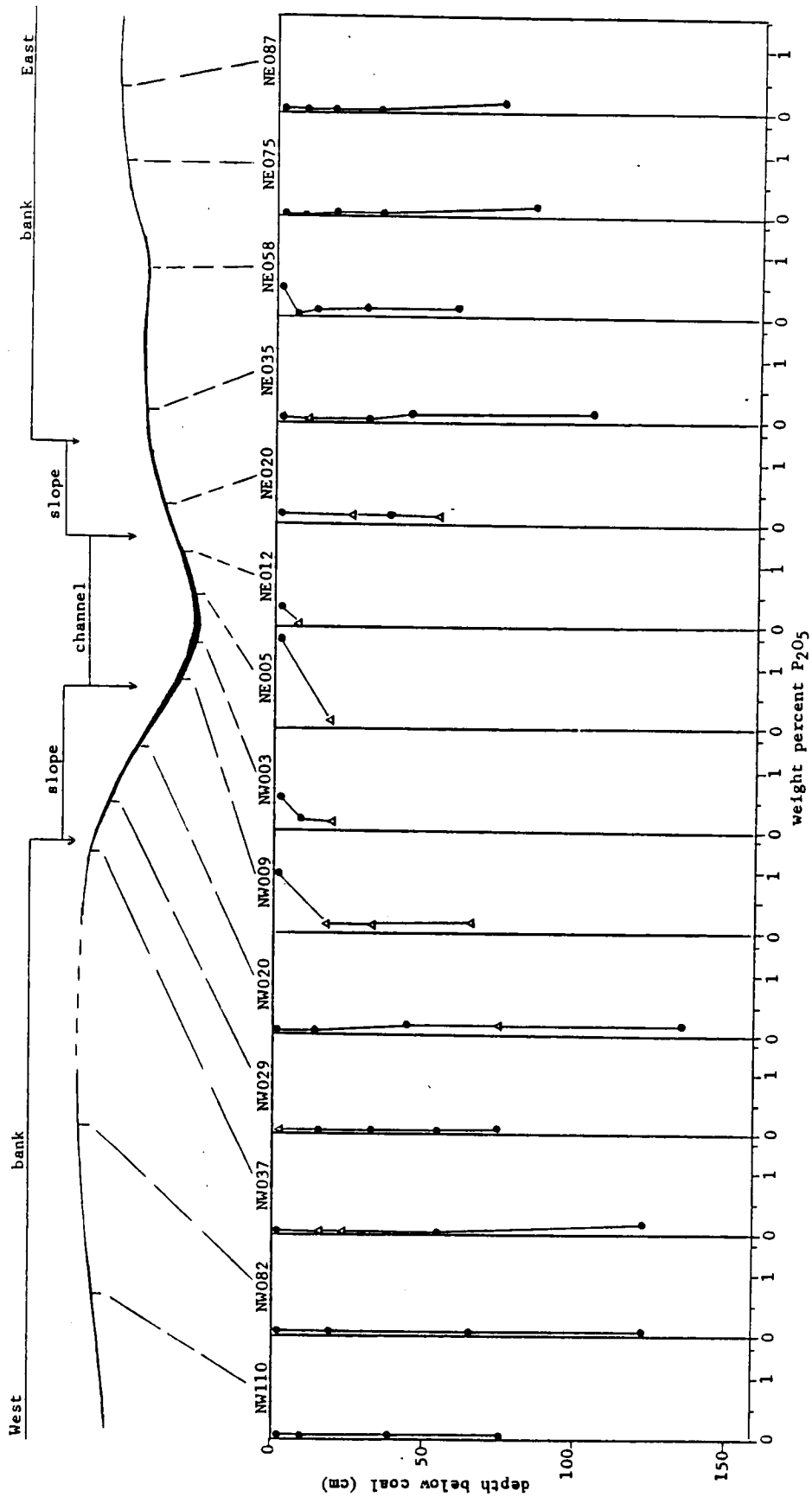


Figure 28. Trends in P_2O_5 with depth below the coal. Triangles represent sandstone samples.

deposits at the bottom of the channel. Because of the fine-grained nature of all the rocks in the 0-3 cm zone, it is hard to imagine a mechanism to produce a fractionation of phosphatic minerals (like apatite) to the channel and site NE058 only.

Most or all of the Zr present probably occurs as the resistant mineral zircon. In the channel, Zr decreases upward (Fig. 29), which may be the result of the decreasing grain size of the rocks. The values in the 0-3 cm zone are the lowest recorded (with some values below detectable limits) for each of the four sample profiles of the channel. Low Zr values might have resulted from a masking effect by the high concentration of organic matter present in these samples. On the slopes and banks, Zr typically increases upward, although values are somewhat erratic. High values of Zr occur in sandstone samples (average ppm Zr in 13 sandstone samples is 660), but upward increases in Zr are still evident after eliminating these samples (such as NW037-2,3, NW029-1, and NW020-4 on the northwest bank and slope). Zr typically increases upward from 300 to 600 ppm. Increases upward on the banks may indicate a residual concentration of zircon, which was virtually unaffected by leaching processes. The decreases upward in the channel may have resulted from the deposition of finer-grained sediments upward with less heavy minerals, and a lack of leaching.

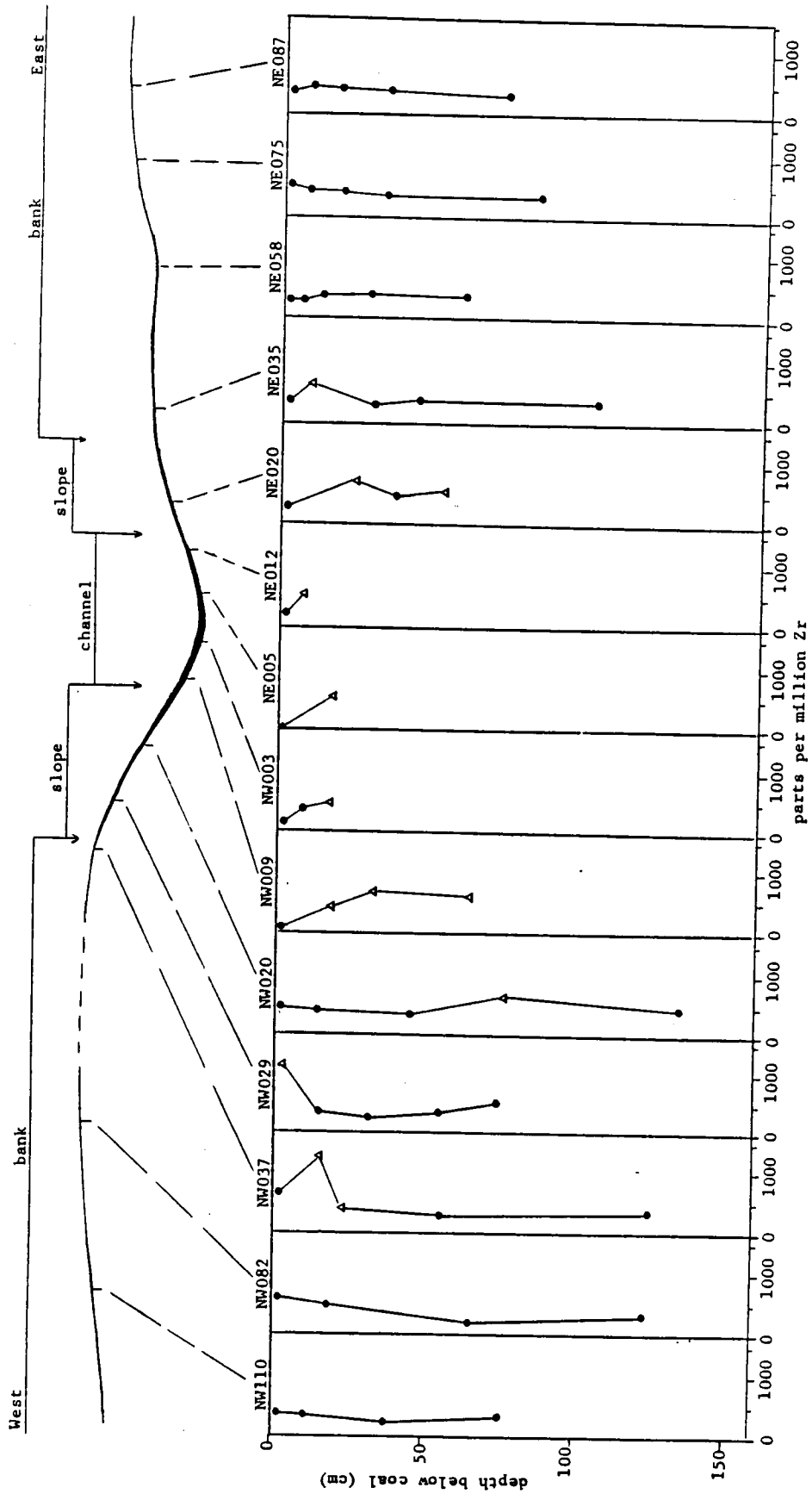


Figure 29. Trends in Zr with depth below the coal. Triangles represent sandstone samples.

Cr values (Fig. 30) range from values too low to be detected to 230 ppm. A high standard error of calibration (±80 ppm) exists for Cr. Therefore, any trends below the 0-3 cm zone, where little change is recorded, cannot be supported statistically. The highest values typically occur in the 0-3 cm zone. Higher concentrations of Cr may be contained in these clays. Resultant low concentrations of Cr in the 0-3 cm zone of the channel may have been affected by the increased concentrations of organics in these samples.

Bulk Mineralogy

Bulk mineralogical analyses by XRD were performed on all 58 seat rock samples using the pack-mount technique. The overall mineralogy was determined to be essentially quartz, 10A illite (muscovite), kaolinite, and chlorite. Additional minerals (typically in minor amounts) include microcline feldspar and pyrite. The 10A mineral is dominantly a 2_m muscovite. This is evidenced by the presence of the 2.99A peak at 29.8° 2θ for the 2_m polymorph, and the absence of 3.10A peak at 29.06° 2θ for 1_{md} muscovite (illite). Microcline is present in all samples, as indicated by a 3.24A peak at 27.5° 2θ. The 3.24A/4.26A ratio was calculated using bulk XRD patterns. The 4.26A peak is the (100) reflection for quartz, and is a well-defined peak at 20.8° 2θ. The ratio revealed minor

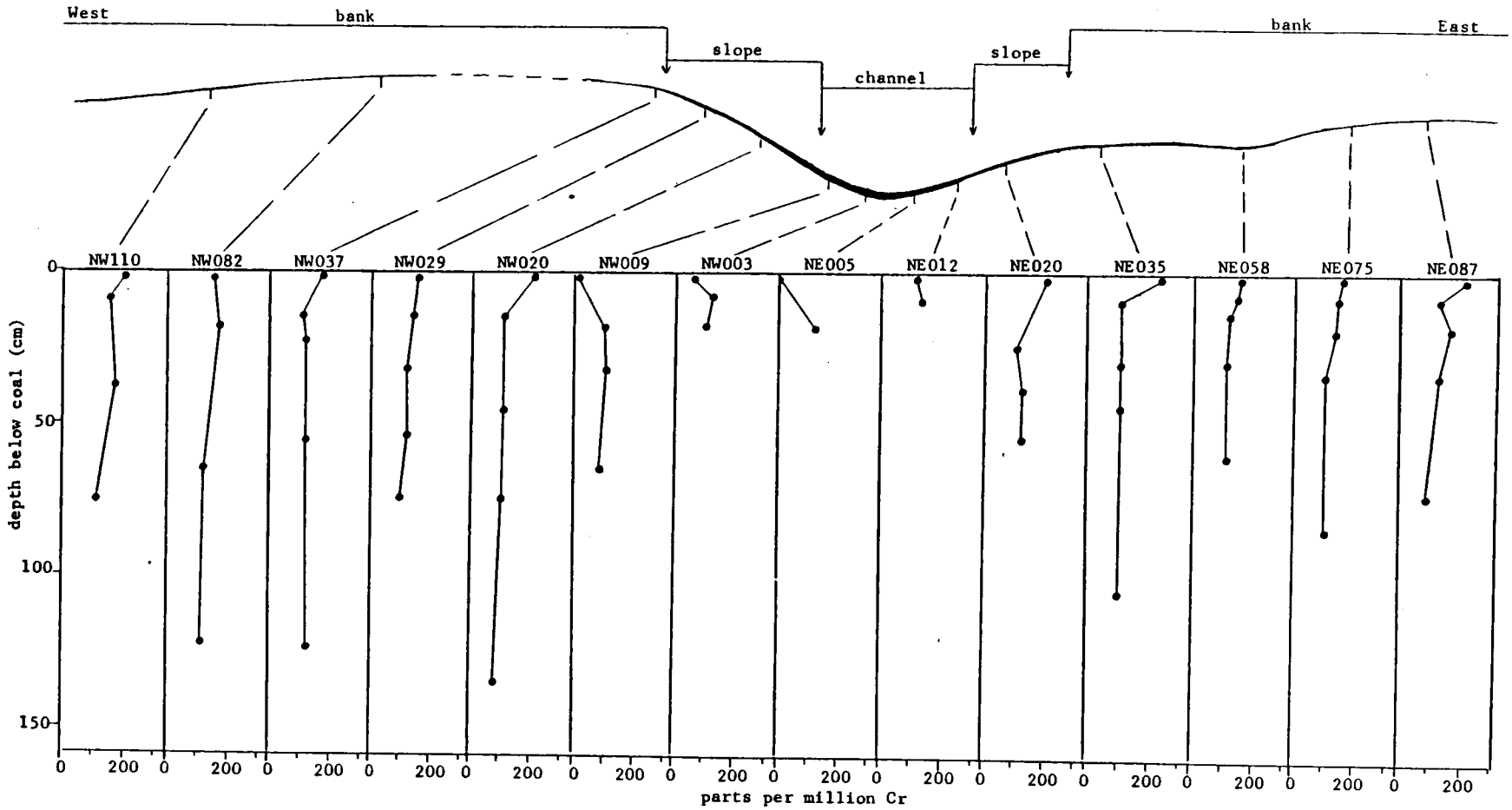


Figure 30. Trends in Cr with depth below the coal. Triangles represent sandstone samples.

variations vertically and laterally (Appendix 6). Slightly higher ratios were obtained for samples from the channel. The general lack of variation argues against extreme leaching which might have totally eliminated feldspars in some areas; however, minor leaching of the feldspars may have taken place. The average 3.24A/4.26A ratio for the 11 samples from the channel is 0.3. On the banks, the average is 0.2 for 33 samples. This may indicate better preservation of feldspars in the channel. Sandstone samples NW037-2,3, NW029-1, and NE035-2 were expected to have higher ratios, but values vary from 0.1 to 0.2. This may indicate that some leaching of the feldspars in these samples occurred. In vertical profiles, the 3.24A/4.26A ratios commonly decrease upward on the banks, and increase upward in the channel.

Pyrite is present in substantial amounts only in the 0-3 cm zone in the following samples: NW009, NW003, NE005, NE012 (which are in the channel), NE020 (on the northeast slope), and NE058 (which is the depression on the northeast bank). This suggests that reducing conditions existed at these locations.

Clay Mineralogy

Kaolinite, 10A muscovite and illite/mixed-layer material, and chlorite were the clay minerals identified by XRD. No discrete vermiculite or smectite clays were found.

X-ray patterns of the <2-μm fractions reveal a decrease in amount or absence of chlorite on the banks just beneath the coal, most notably on the northwest sites. Observations of the intensity of the 14A peak, using the <2-μm XRD patterns, are reported in Figure 31. The 14A peak was typically indistinguishable from the background (values reported as "0") in samples from the 0-3 cm zone. Indiscernable 14A peaks occur in the regions at the top of the profiles, especially on the northwest bank. More intense peaks are noted for almost all samples located at least 30 cm beneath the base of the coal. Samples lying in the zone less than 20 cm from the base of the coal do not show chlorite or typically have low intensities, except near or in the channel where intensities are higher. Chlorite thus appears to be more abundant and/or better preserved in the channel and in the lower portions of the vertical profiles. The probable cause was destruction of chlorite by leaching at the topographically higher environments. Chlorite in the channel may be either detrital in origin or possibly was later regenerated or transformed from mixed-layer clays following its destruction by acidic peat bog waters.

The 10A peak appears to be a combined peak from two different materials, discrete illite (muscovite) and illite/mixed-layer clays. Muscovite flakes are visible in hand specimens. XRD patterns typically revealed a sharp 9.9-10A peak as a crest above an asymmetrical, jagged

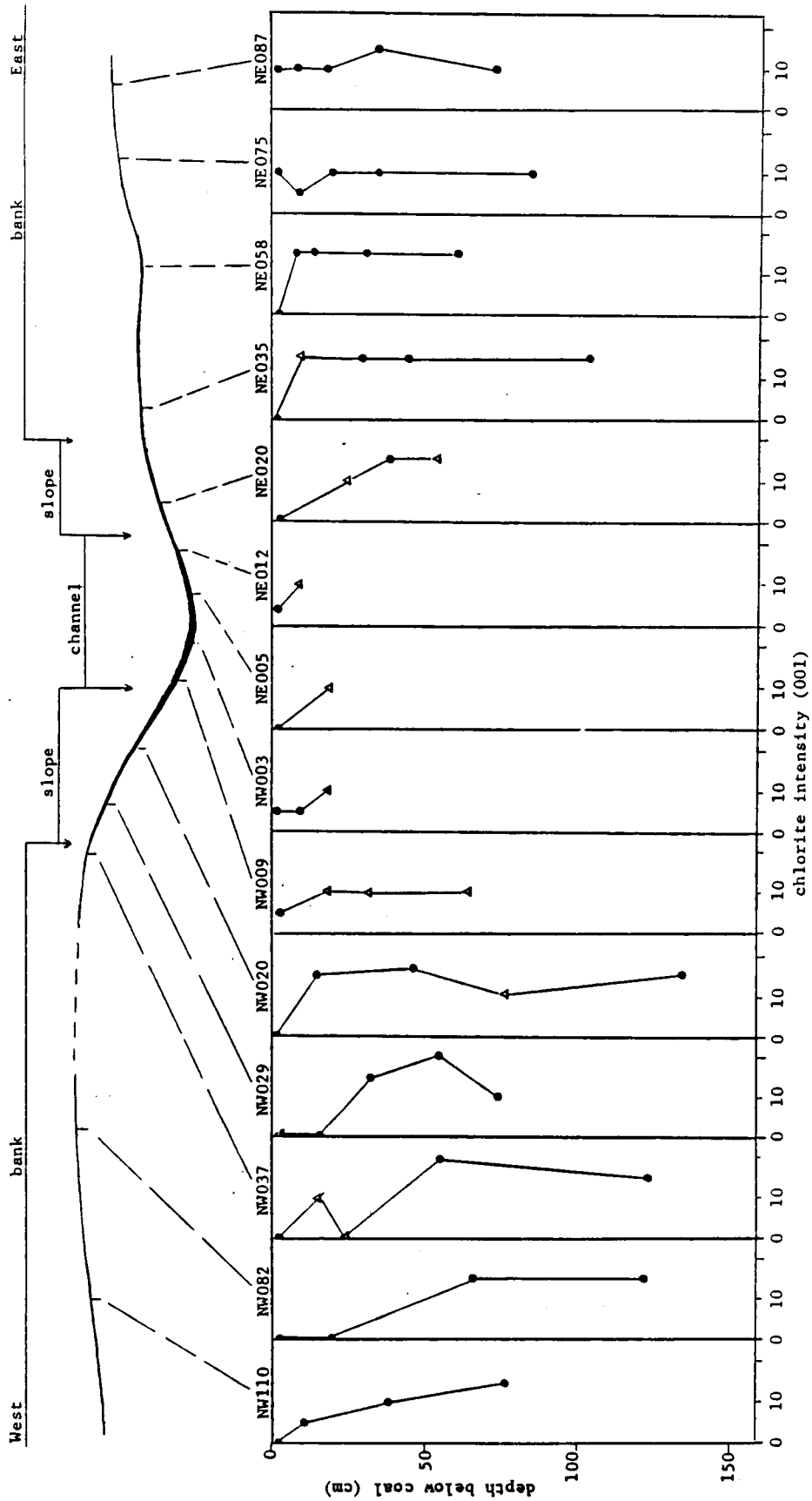


Figure 31. Intensity of 14A peak for seat rock samples.

segment on the right side (Fig. 32). The latter component is illite/mixed-layer material between 10 and 12A (Weaver, 1956).

Mixed-layer clays have an interstratification (which may be random or ordered) of alternating clay mineral layers. A characteristic mixed-layer clay has two different layers, although there may be three or four separate types present (Millot, 1970). The mixed-layer clays at the study site appear to be randomly interstratified, and may have three components. The XRD patterns are complicated by the presence of discrete illite (muscovite), which is for the most part unaffected by glycolation and heat treatments. In each case glycolation reveals expansion of 10-12A material, which indicates the presence of some expandable layers in the mixed-layer clays (Fig. 33). Figure 33 (B) is typical for all glycolated slides. After glycolation, no peaks were found at 17A, which would not be the case if enough expandable layers were present. Another possibility is that the mixed-layer components are illite (10A), chlorite (14A), and smectite (14A), which is not unusual in shales (Weaver, 1956). Glycolation would expand the smectite layers, but would not affect the chlorite and illite layers. The result might be to diffuse the 10-12A mixed-layer material between 10 and 17A. Obviously, smectite layers are not abundant (probably less than 30%), but some expandable layers are present. Heat treatment to 550^{o} C (Fig. 33, C) produces an

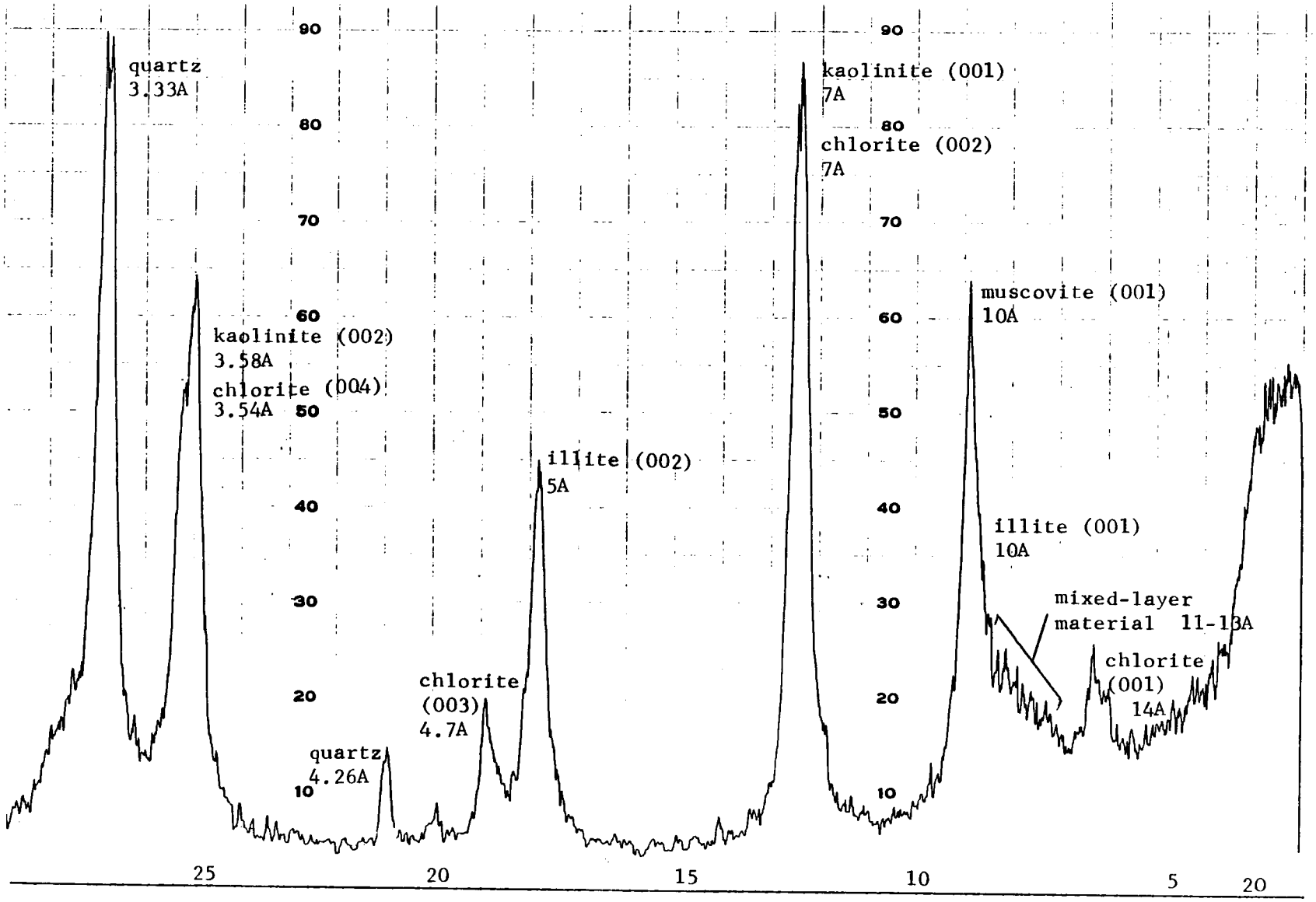
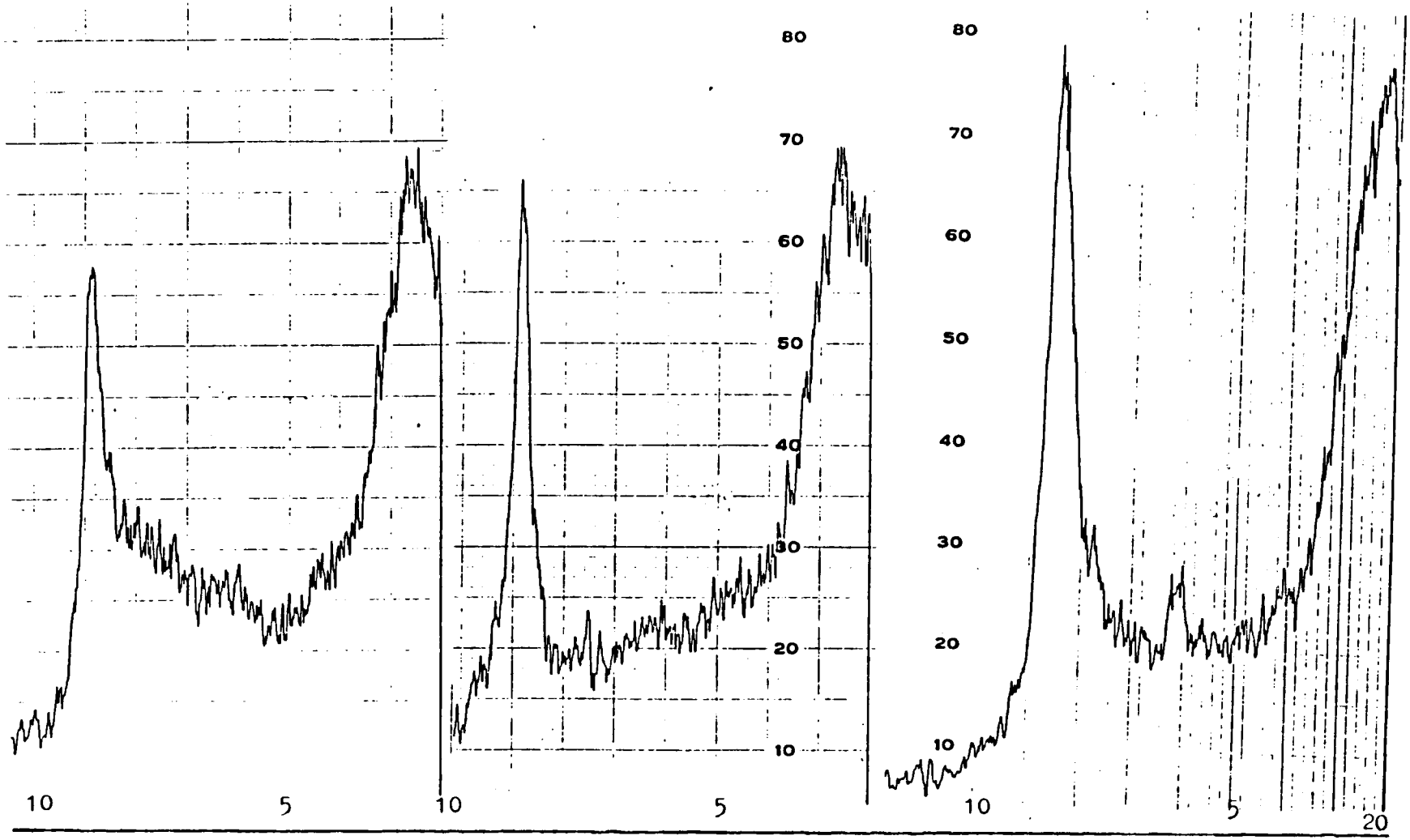


Figure 32. Typical XRD pattern from 2-30° 2θ.



A - Untreated sample B - Glycolated C - Heat treated (550° C)

Figure 33. Effects of glycolation and heat treatment. Sample is from the northwest bank (NW082-2).

increase in the 10A peak intensity in each case. This increase is directly attributable to collapsed smectite layers (Austin and Leininger, 1976). Moreover, after heat treatments (Fig. 33) or saturation with K^+ (Fig. 34), some peak asymmetry is retained. Saturation with K^+ should collapse expandable layers. A possible explanation is the existence of a 14A mixed-layer component that has not collapsed, which would be chlorite. Both vermiculite and smectite layers collapse to 10A when heated to temperatures of 550° C. Illite is probably the dominant phase of the mixed-layering, as evidenced by the proximity of the reflections to 10A. The overall position of the 10A peak does not change with glycolation, heat treatments, and/or K^+ saturation, verifying the presence of discrete 10A muscovite.

The identification of discrete chlorite was confirmed by heat treatments. Vermiculite (14A) collapses to 10A when heated to 550° C. All samples subjected to this temperature show an increase in intensity at 14A, which is typical of chlorite.

Kaolinite is present in all seat rock samples as confirmed by the (001) 7A peak at 12.5° 2θ and the (002) 3.58A peak at 24.9° 2θ. The (001) reflection of kaolinite at 7A coincides with the (002) of chlorite. Kaolinite is unaffected by glycolation and K^+ saturation, whereas heat treatment to 550° C destroys kaolinite. In summary, the

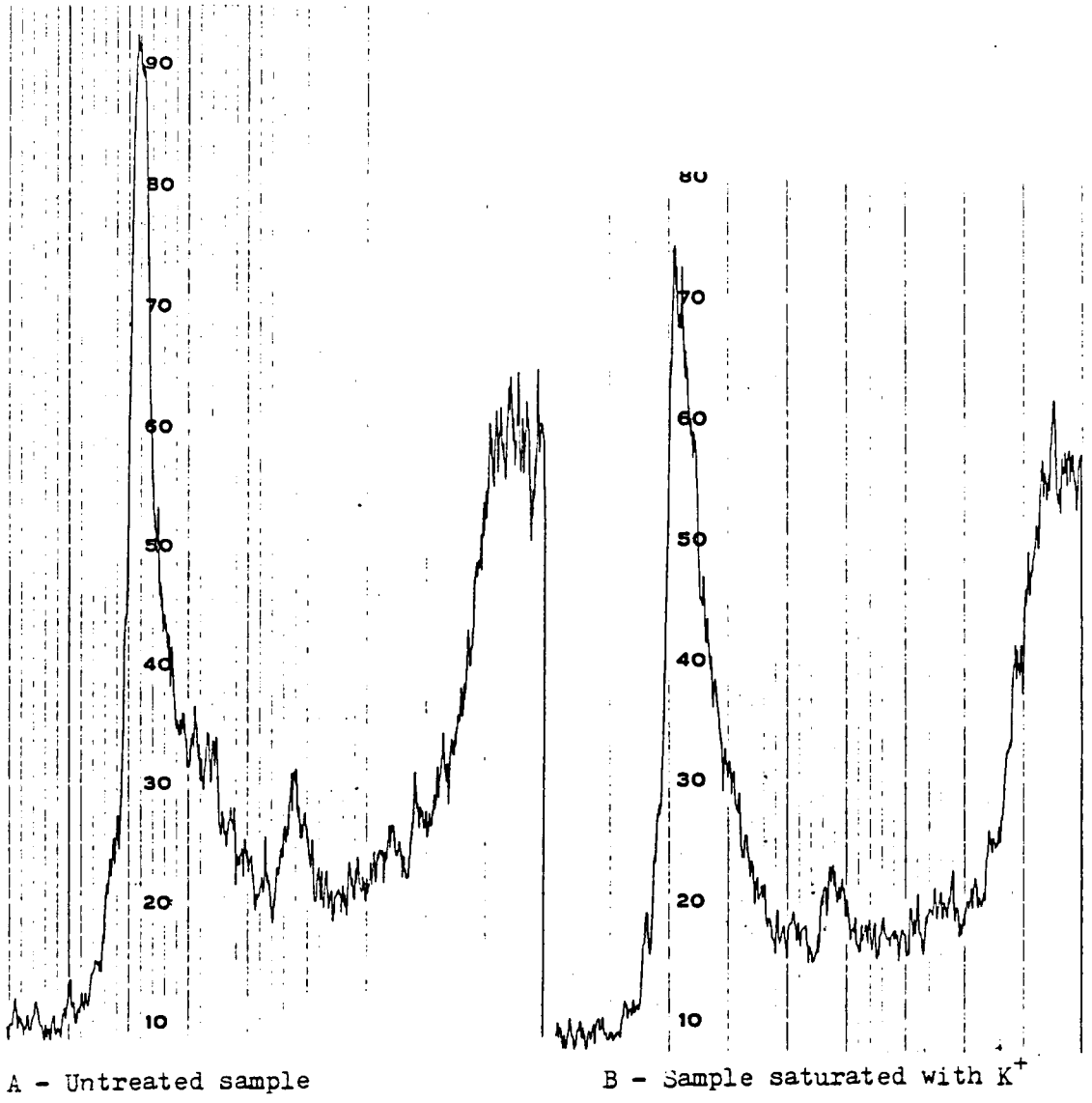


Figure 34. Effects of saturation with K^+. Sample is NW029-2.

phyllosilicates present include kaolinite, chlorite, muscovite, and illite/mixed-layer clays, which are most likely randomly interstratified illite-chlorite-smectite.

Sharpness ratios (SR) were calculated in an attempt to quantify the degree of crystallinity of the 10A peak (Weaver, 1961). The method used was to divide the peak height by its width at one-half the height. Sharpness ratios (Figure 35) show a decrease upward in vertical profiles. The northwest bank exhibits better defined trends than the northeast bank. For sites NE087, NE075, NE058, NE035, and NE020, values are consistently >20. Notable exceptions are in the 0-3 cm zone at NE020 and NE058. These two sites are paleotopographically the lowest of the northeast slope and bank sample profiles. The other low areas (NW009, NW003, NE005, and NE012) also exhibit SR values <15 in the 0-3 cm zone. In the channel (NE012-NW009), SR values decrease toward the coal (Fig. 35). Sites NW082 and NW037 (the paleotopographic highs) have lower ratios in the upper part of the profile than the other northwest sites. The northwest bank as a whole exibits more vertical change than the northeast bank. Two different processes may have been responsible for the tendency for 10A material to be more poorly crystallized toward the tops of the vertical profiles. The deposition of finer-grained material upward may have resulted in poorly crystallized clays at the tops of the sample profiles. Alternatively,

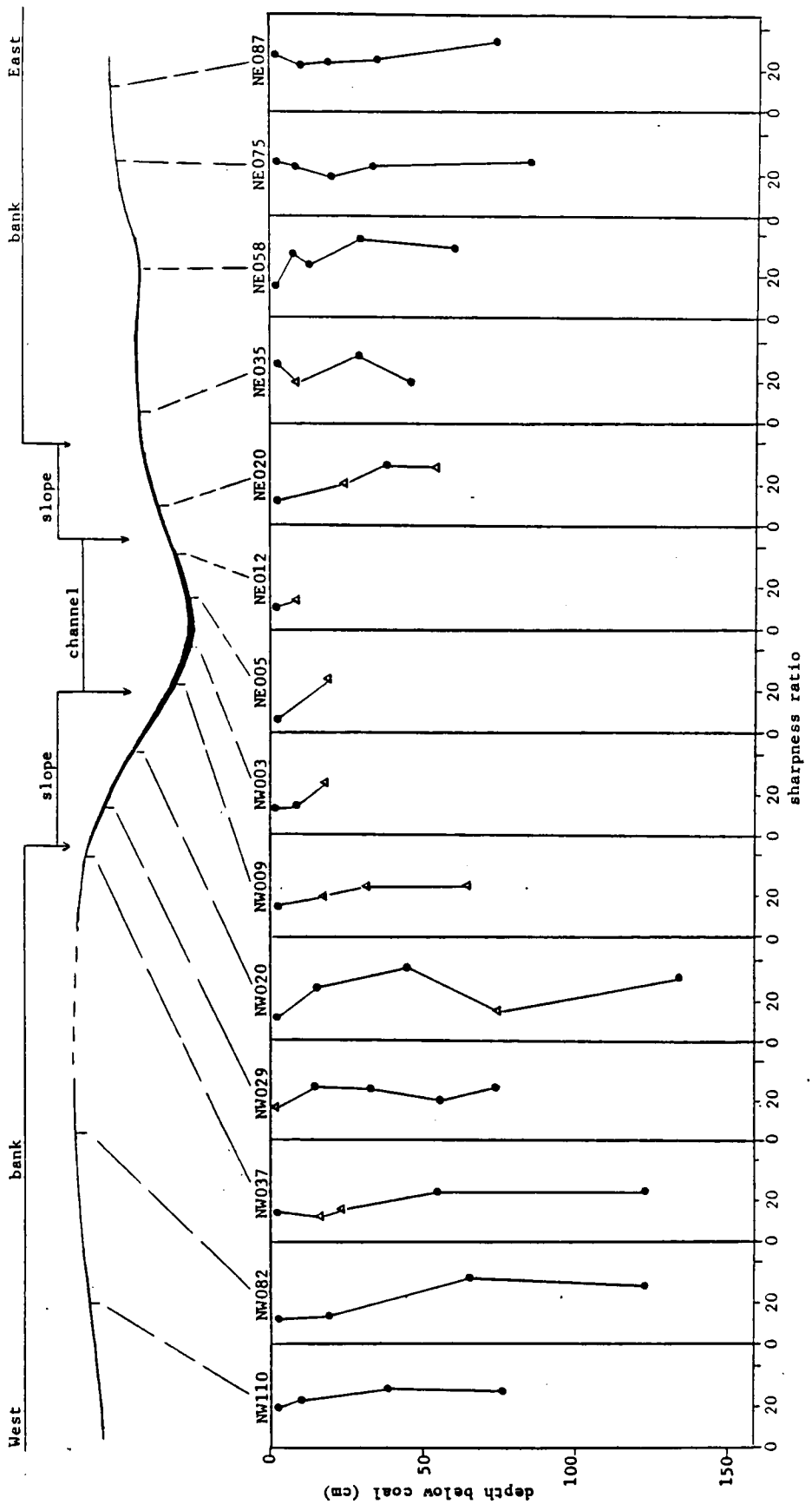


Figure 35. Sharpness ratios for 10A material.

leaching by acidic waters may have affected the structure of illite. Because SR values typically decrease upward, the most probable cause is the upward increase of finer-grained, more poorly crystallized clay minerals. The lower values of the paleotopographic highs (NW037 and NW082) may be evidence for leaching at these sites.

Values were computed for relative clay mineral percentages, using peak height ratios (Fig. 36, and Appendix 5). For equal peak heights, illite at 10A was assumed to be 2.5X more abundant than the 7A peak. An assumed ratio of 1.7 for the (001)/(002) peak ratio of chlorite allowed the effect of the (002) peak of chlorite to be subtracted from the (001) peak of kaolinite. A sample calculation is shown in Appendix 4. Several generalizations may be made concerning the clay mineral percentages (Fig. 36). Chlorite typically is less than 10% of the clays. In the channel, percent chlorite commonly rises upward in vertical profile. On the banks, percent chlorite decreases upward to less than 5%. Laterally to the channel, values in the 0-3 cm zone increase to 10%. The highest illite percentages typically occur in the 0-3 cm zone. In the channel, illite increases upward, whereas percent kaolinite values decrease. On the banks below the 0-3 cm zone, percent kaolinite reveals some tendency to increase upward, with exceptions at sites NE058 and NE087. Illite values typically are steady on the northeast bank below the 0-3 cm zone. On the northwest

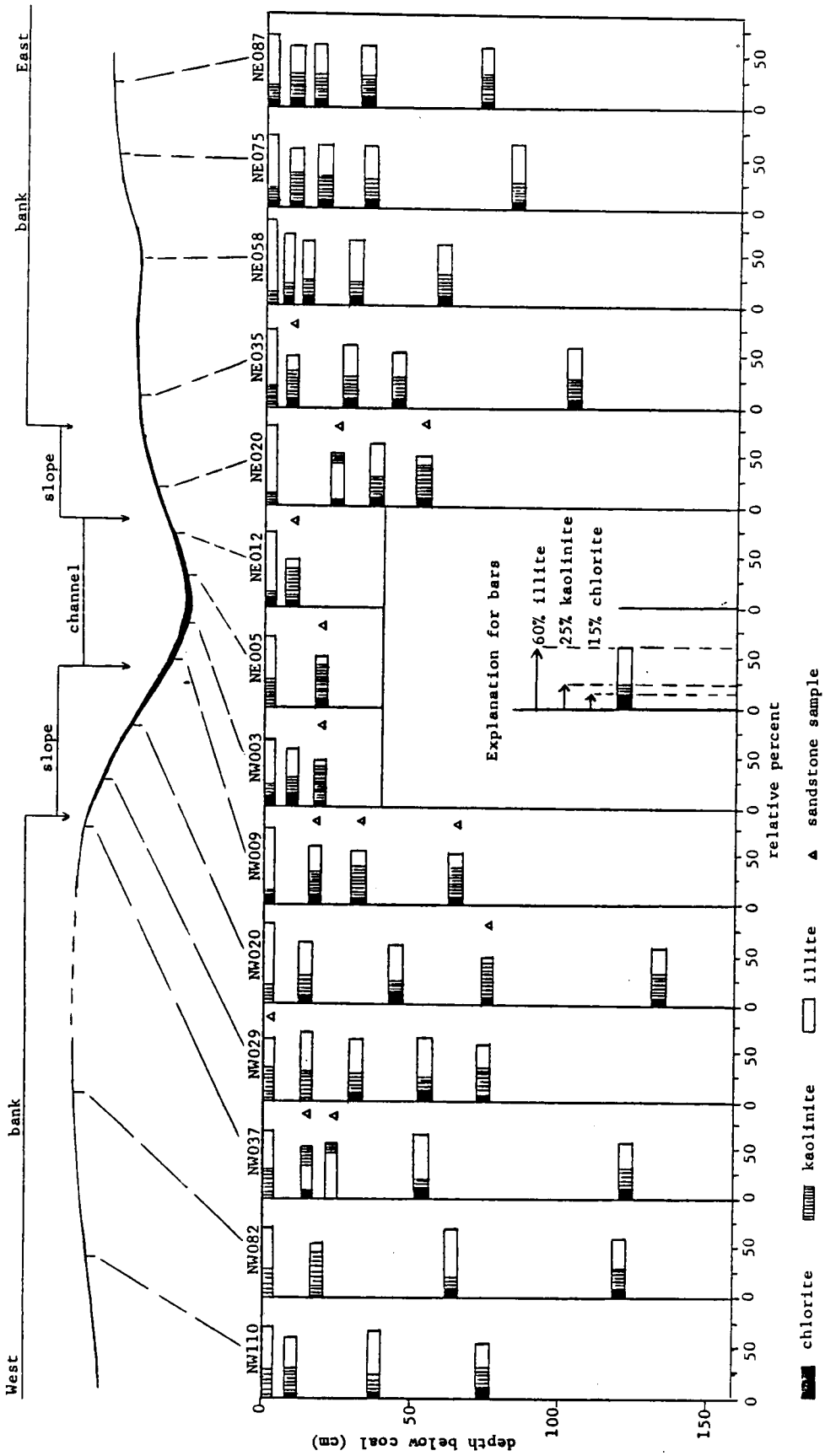


Figure 36. Calculated relative clay mineral percentages. Triangles denote sandstone samples.

bank, illite values do not show any consistent trends below the 0-3 cm zone.

The trends of kaolinite and illite may be expressed in the kaolinite/illite ratios (Fig. 37). K/I ratios do not vary greatly, although there is a tendency for K/I ratio to decrease upward in the channel. This may be a reflection of the association of kaolinite with coarse-grained rocks, and illite with finer-grained rocks. Sandstone samples (NW037-2,3, NW029-1, NW020-4, NW009-2,3,4, NW003-3, NE005-2, NE012-2, NE020-2,4, and NE035-2) have uniformly higher K/I ratios. Fine-grained rocks in the 0-3 cm zone have uniformly low K/I ratios, indicating the dominance of illite. Laterally in the 0-3 cm zone, the K/I ratios are higher on the banks than in the channel. Also, the K/I ratios from the northwest bank are slightly higher than those from the northeast bank. This may be a reflection of the increased concentration of kaolinite in the 0-3 cm zone on the northwest bank, and both banks in general. Below the 0-3 cm zone on the northwest bank, K/I ratios increase slightly upward. For the northeast bank, values are typically steady with the exception of those from site NE058, where K/I ratios decrease upward. It is apparent that the northwest bank exhibits higher kaolinite amounts, especially in the upper parts of the profiles. Chlorite amounts are low in the upper portions of the vertical profiles. Whereas kaolinite might be expected to have

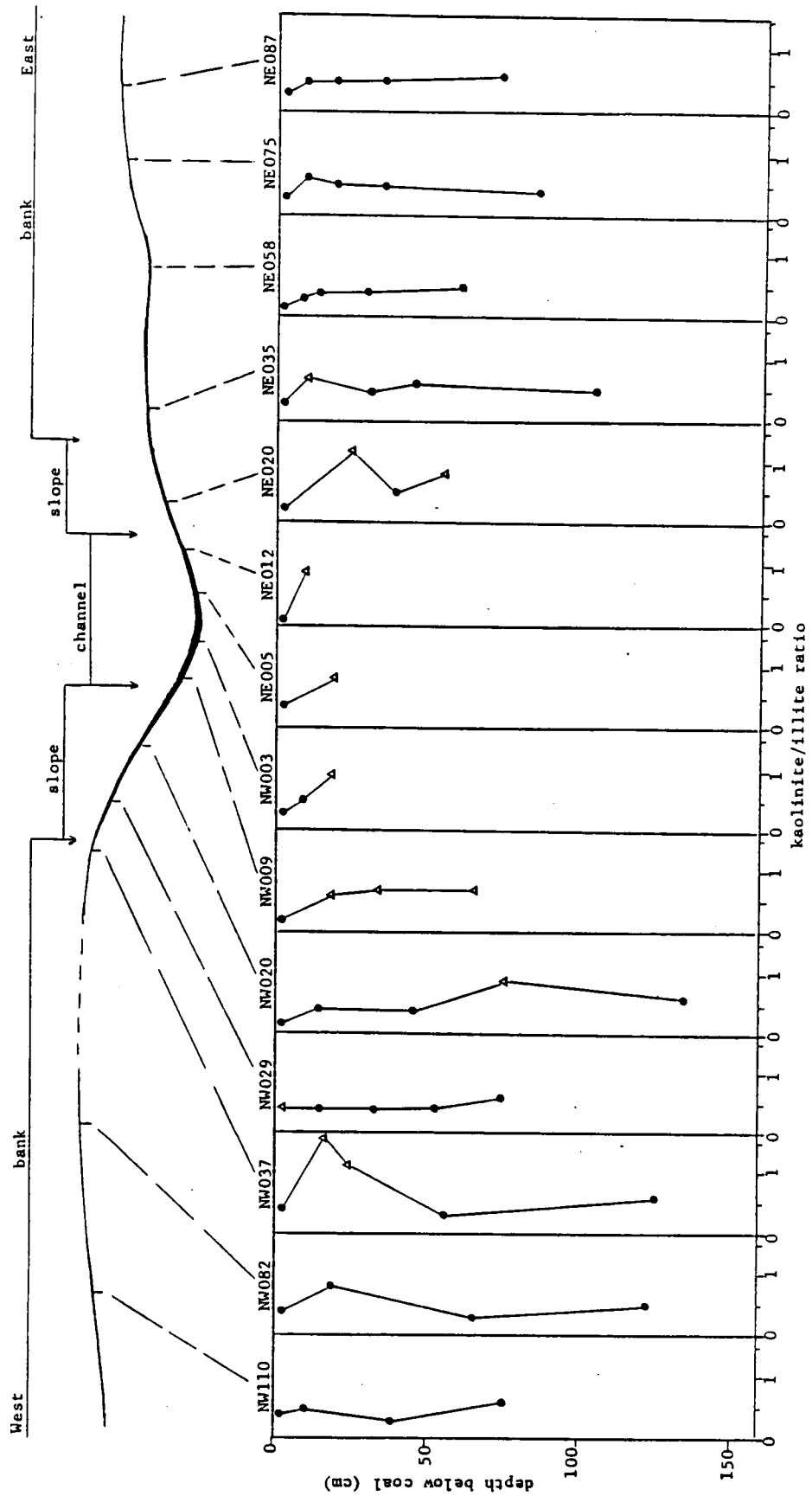


Figure 37. K/I ratios for seat rock samples. Triangles represent sandstone samples.

higher concentrations in the coarse-grained rocks, this is not necessarily expected for the bank samples from the 0-3 cm zone. Based on these observations, leaching of chlorite and weathering reactions to produce some kaolinite enrichment seems plausible for the rocks on the banks (especially the northwest side). These possible changes in clay mineralogy would then be an overprint on the original depositional sequence.

Coal Analyses

Petrographic analyses for five representative coal samples are presented in Table 1. Values are reported in volume percent (referred to as %). Except for coal NW037 (on the bank), vitrinite is the dominant maceral group with values over 83%. Low pyrite values (<2%) are characteristic of each coal. Coal sample NW003 (in the channel) and the northeast coals are similar in composition. Coal NW037, on the paleotopographic high, stands out with higher values for exinites (13.1% and 14.7%), inertinites (8.3% and 9.0%), and detritus (49.6% and 52.8%).

XRF values compliment the petrographic analyses (Table 2). Coals NW037 and NW082 show relatively high values for SiO_2 (8-10%), Al_2O_3 (23-27%), TiO_2 (0.9-1.0%), P_2O_5 (1.4-1.7%), and Fe (0.4-0.9%). Sites NW003, NE005, NE020, and NE035 vary little in SiO_2, although Coal NE035 has slightly higher percentages in SiO_2 and Al_2O_3. Percent

Table 1. Maceral, pyrite, and terrigenous clastic (detritus) contents (in volume %) of selected coal samples.

Coal	Sample Site	% Vitrinite	% Exinite	% Inertinite	% Detritus	% Pyrite
NW037A[a]	bank	27.0 ± 2.8	14.7 ± 2.2	8.3 ± 1.7	49.6 ± 3.2	0.4 ± 0.2
NW037B	bank	24.2 ± 2.7	13.1 ± 2.2	9.0 ± 1.8	52.8 ± 3.2	0.9 ± 0.4
NW003	channel	88.9 ± 2.0	7.6 ± 1.7	0.6 ± 0.3	1.3 ± 0.5	1.6 ± 0.8
NE005	channel	83.2 ± 2.3	11.6 ± 2.1	1.7 ± 0.7	2.8 ± 1.4	0.7 ± 0.4
NE020A[a]	slope	87.6 ± 2.0	8.8 ± 1.8	1.8 ± 0.7	0.7 ± 0.4	1.1 ± 0.5
NE020B	slope	89.5 ± 1.9	6.2 ± 1.4	1.0 ± 0.5	2.3 ± 0.8	1.0 ± 0.5
NE035	bank	86.7 ± 2.1	10.2 ± 1.9	0.2 ± 0.1	2.0 ± 0.7	0.9 ± 0.4

[a] duplicate samples made.

Table 2. Chemical analyses for selected coal samples.

	B NW082	B NW037	C NW003	C NE005	S NE020	B NE035
% Al_2O_3	10.16	8.59	1.98	2.23	1.79	2.77
% SiO_2	27.84	23.77	2.49	3.27	2.09	4.46
% P_2O_5	1.74	1.37	0.04	0.05	0.04	0.07
% S	1.07	0.69	0.73	0.65	0.74	0.64
% K_2O	0.39	0.27	0.03	0.02	0.02	0.04
% CaO	0.02	0.00	0.12	0.09	0.10	0.07
% TiO_2	0.91	1.00	0.04	0.10	0.02	0.12
% Fe	0.89	0.41	0.23	0.12	0.14	0.00

B - bank

C - channel

S - slope

sulfur is low at every site, only NW082 (1.1% S) has sulfur values above 0.7%.

Coals NW003, NE005, NE020, and NE035 are banded coals, and similar in chemistry and maceral composition, which is evidence for similar depositional environments. Coals NW037 and NW082, megascopically dull coals on the paleotopographic highs of the northwest bank, are significantly different than the other coals examined. The high percentages of inertinites and the low percentages of vitrinite macerals argue for periodic drying conditions. High values of Al_2O_3, TiO_2, and SiO_2 are a result of an influx of terrigenous clastic material, that was most likely the result of subaerial exposure. Overall, low S values of the coals argue against a marine influence. Most of the S may be in the form of organic sulfur. Coal NE035 has very little Fe present (0.002%), therefore the sulfur cannot be present as pyrite. Low CaO values eliminate gypsum as the source of the sulfur.

In summary, swamp water levels almost certainly remained above the channel, and probably above the northeast slope and bank for much of the time. The northwest bank probably existed much of the time in aerated conditions, which resulted in the higher percentages of inertinite macerals and terrigenous clastic material.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Introduction

Field observations of the study site have indicated that the rocks beneath the coal bed were at one time exposed to the surface for a period of unknown length. At the time of exposure, the site was an abandoned channel that was developing into a peat swamp. Topographic highs (the banks) and lows (the channel) existed, which apparently became two separate and distinct environments. It is likely that the presence and movement of groundwater and surface water, and the type and amount of organic matter, was primarily controlled by paleotopography. It is possible that the paleotopography was the chief factor in any alteration of the rocks. The highs might be expected to have had more groundwater movement downward and therefore more leaching. The lows, where it has been shown that reducing conditions existed, might have been less affected because of less water movement. Also, the low areas may have been zones of concentration of mobilized material from leached areas, or from ionic species held in the surface water.

Therefore, the mineralogy and chemistry of the rocks below the coal are functions of both inherited characteristics and any changes that may have occurred after deposition. Inherited characteristics resulted from

sedimentologic processes and the provenance of sediments deposited. At the study site, this included the flow velocity of the water, i.e., the type and proportions of minerals deposited. Higher flow velocities would have resulted in more silt and sand (quartz), whereas slower velocities would have resulted in more clays. Thus, one factor of the subsequent chemistry is the mineral suite proportions. Trends which probably reflect the original mineralogy and chemistry can be seen in Al_2O_3/SiO_2 ratios, K_2O, Rb (contained in detrital muscovite), and in part TiO_2. Because of the limited vertical and horizontal extent of the study area, the provenance of the rocks below the coal-seat rock contact is considered to have been unchanging, as would have been the chemistry of the basin waters, and climatic conditions.

Changes that took place after the deposition of sediments and the formation of the channel by erosion may include leaching of the rocks (sediments) by moving groundwater. Because a swamp was established in the abandoned channel, the effects of organic matter, acid waters, and possible presence of surface water may have contributed to any alteration of the rocks beneath the coal. Moreover, the surface water, which possibly existed as a vestige of the channel-carving event, may have been initially brackish or marine.

Channel Samples

Chemical and mineralogical analyses of the seat rocks and coal analyses support field observations that the banks and the channel represented two different environments. The channel, the zone from NW010 to NE015, contains sample sites NW009, NW003, NE005, and NE012. The following trends consistently occur for each of the four channel sites:

1. Fe increases upward, even after an amount of Fe has been allotted to FeS_2.

2. High S concentrations (2-12%) in the 0-3 cm zone.

3. High concentrations of P_2O_5, Na_2O, and Ba in the 0-3 cm zone.

4. General upward increases of Al_2O_3, K_2O, MgO, Na_2O, TiO_2, CaO, Rb, and the Al_2O_3/SiO_2 ratio.

5. A reduction upward in SiO_2, Zr, and Cr.

6. Higher 3.24A/4.26A ratios than those from the banks.

7. Substantial amounts of pyrite in the 0-3 cm zone.

8. Presence of chlorite in nearly all channel samples.

9. Low SR values in the 0-3 cm zone.

10. A decrease upward in relative % kaolinite, and an increase upwards in relative % illite.

11. Lower K/I ratios in the 0-3 cm zone than those from the same zone on the banks.

12. High % vitrinite and low % inertinites and terrigenous clastic material for coals NE005 and NW003.

13. Low amounts of S, Al_2O_3, SiO_2, K_2O, etc., for coals NW003 and NE005.

It has been documented that overlying sediments and their depositional environments control the concentration of sulfur in coal, much more so than the underlying sediments (Horne, et al., 1978). Coals of the study site are low in % S (<1%), which indicates a non-marine affiliation for the rocks deposited above the coal (Horne et al., 1978). The maceral compositions of the coals from the channel indicate little or no aeration took place. Exposure of the coal (peat) to the air would have resulted in the degradation of vitrinite macerals (the woody tissues), and thus the relative increase of the more resistent inertinite (carbonized, degraded parts), and exinite macerals (resinous materials). Maceral compositions and chemistry similar to those of the channel were observed for coals NE020 and NE035. The peat swamp probably existed uniformly over the channel and the northeast slope and bank, which were topographically lower than the northwest bank, where the coal is much thinner. Pyritized Calamites fossils are further evidence for consistently wet conditions in the channel.

The high concentrations of S, Na_2O, and MgO in the 0-3 cm zone of the channel seat rocks may indicate an initially brackish or marine influence after the erosion which formed the channel. The elements, perhaps as ionic complexes in

standing water, may have been adsorbed onto the clays and organic matter at the base of the peat bog. Possibly, the source of Fe for pyrite formation was mobilized Fe^{+++} complexes which remained in solution in the acidic waters of the swamp, or migrated in groundwater from the topographic highs downward to lower levels on the banks or laterally to the channel. Organic matter creating acidic swamp water may have allowed the Fe to remain in solution. Subsequently, the Fe was reduced and immobilized as pyrite, where enough S and the right Eh/pH conditions existed.

The hypothesis that the channel seat rocks were not leached is supported by the presence of chlorite, which is easily destroyed under weathering conditions (Schultz, 1958). Also, the relatively higher 3.24A/4.26A (microcline/quartz) ratio, and lower K/I ratios for the 0-3 cm zone than those of the banks, may also be evidence for little or minor leaching processes having affected the seat rock samples of the channnel. However, the chlorite present may have been regenerated as the result of later addition of Mg to relict chlorite structures or mixed-layer clays. Detrital chlorite in the seat rock samples may have been altered by acidic waters. Low SR ratios for 10A material in the 0-3 cm zone may have been produced by the acidic waters (which affected the crystallinity) rather than a result of originally weathered fine-grained material.

Discussions in literature of acidic conditions and leaching effects of organic acids that were released from the peat, along with the subjects of original mineralogy, are common. Studies of present-day bogs have shown that low pH values do exist, typically less than 4.5 (Gorham, 1985, cited in Stumm 1985). Staub and Cohen (1978) concluded that peat accumulation (and resultant organic acids) affects seat rocks, hypothesizing that enrichment of kaolinite in the seat rocks of the Snuggedy Swamp, South Carolina was a result of leaching by organic acids originating from the overlying peat. Studies of Pennsylvanian underclays have also suggested that acidic waters influenced the mineralogy below the coal (Staub and Cohan, 1978; Huddle and Patterson, 1961).

Whereas much consideration has been given to the presence and effects of acidic solutions released by the peat, little attention has been given to the actual inorganic species composition of fluids expelled during peatification and coalification and their possible effects on the seat rocks. Alterations by organic acids are attributed only to the effects of acidity, and possible contributions of material in the fluids such as cations are virtually ignored. Parham (1964) assumed that coal formation (i.e., fluids released from the peat) had little effect on the clay minerals in underclays because: 1) groundwater flowed upward in bogs (Deevey, 1958) and 2)

plants removed only minor amounts of nutrients from the seat rocks, assuming modern-day bog plants are appropriate examples.

Schultz (1958) and Keller (1958) hypothesized that some changes in clay mineralogy may have occurred during coalification, and the formation of chlorite from degraded clays was also possible. Chlorite found in the channel samples may have regenerated in this manner. The possibility that the inorganic species composition of the fluids (rather than just the presence of organic acids) released during coalification processess affected the clay minerals and seat rock chemistry at the study site cannot be ignored. Elements originally contained in coal that were mobilized during coalification may have had a significant impact on the surrounding sediments. Such processess might have been responsible for the present-day existence of chlorite, and allows for the possibility that chlorite had been altered under original acidic conditions in the channel bottom at the time of peat accumulation.

A plausible source for the high P_2O_5 concentrations is the former deposition of phosphatic material such as bones, fish scales, etc., on the channel bottom. The reductions upward in SiO_2 and Zr and the increases in K_2O, Rb, Al_2O_3, and TiO_2 are probably a function of decreasing grain size (the increase in the amounts of clays present), i.e., the original mineralogy.

Bank Samples

The chemical and mineralogical trends of the seat rocks on the banks, and the results of coal analyses of NW037 and NW082, are distinctly different from the data of the channel samples. Bank samples include the sites NW110, NW082, NW037, NE035, NE058, NE075, and NE087. The following trends exist for samples from the banks:

1. Significant reductions upward in Fe, MgO, and MnO.

2. Low S values (<0.2%) in the 0-3 cm zone, with the exception of NE058.

3. Minor reductions upward below the 0-3 cm zone in Ba, P_2O_5, CaO, and Rb.

4. Relatively higher concentrations in the 0-3 cm zone of Cr, Zr, Ba, and Sr (more obvious for Sr on the northeast bank).

5. Minor increases upward in TiO_2, Al_2O_3, Cr, and Zr.

6. Reductions toward the coal in the amount of chlorite present.

7. Average lower 3.24A/4.26A ratios.

8. A decrease in SR values upward, most notable at sites NW082 and NW037.

9. Slightly higher K/I ratios, especially on the northwest bank.

10. High amounts of inertinite macerals and terrigenous clastic material in coals NW082 and NW037.

11. Relatively high amounts of SiO_2, Al_2O_3, P_2O_5, TiO_2, K_2O, etc., in coals NW037 and NW082.

The higher amounts of terrigenous clastic material in the northwest coals analyzed are reflected in XRF analyses. The high proportions of inertinite macerals indicate that the peat (coal) of NW082 and NW037 were deposited under aerated conditions. Detrital material most likely was contributed by being subaerially exposed. Because coal NE035 on the northeast bank is similar to the coals of the channel, swamp conditions on the northeast bank were probably maintained with little or no intervals of drying.

For the seat rocks on the banks, several mineralogical trends exist, which support a leaching hypothesis for the paleotopographically higher environments. Chlorite has apparently been destroyed in the upper portions of the vertical profiles (more readily observed on the northwest bank). Also, some kaolinite enrichment may have occurred (seen in K/I ratios and relative amounts of kaolinite) as a direct result of weathering. Also, the lower 3.24A/4.26A ratios on the banks suggests partial removal of microcline. Low SR ratios for the upper portions of the vertical profiles of NW082 and NW037 (paleotopographically the highest sites) may indicate that leaching affected the structure of mica (illite).

Reductions upward in Fe, MgO, and MnO most likely represent actual leaching as groundwater flowed through the

sediments. The downward (and probably lateral) migration of Fe probably resulted in the formation of siderite concretions where reducing conditions (like localized environments of decaying roots) existed on the banks and slopes. The boundary between the zone of siderite concretions (a reducing environment) and the rocks above (an oxidizing environment) may represent a former water table (Gardner and Williams, 1985). The source in part for the Fe, Mn, and Mg probably was weathered chlorite and illite. Mobilized material in the oxidized zones probably moved downward and toward the channel in a natural flow of groundwater. The lack of sulfur in the 0-3 cm zone may also be an indication of oxidizing conditions and/or the lack of surface water that might have contained sulfate complexes.

Further chemical evidence for leaching is the upward increase in some elements like Zr, which is mostly present in the form of the resistant mineral zircon. A residual concentration by leaching might have been responsible for the trends. Other elements which may exemplify this are TiO_2 and Cr.

Local Pool

Site NE058, described as a paleotopographic low (possibly a pool) on the northeast bank, shows characteristics of both bank and channel sites. High concentrations in the 0-3 cm zone of S, TiO_2, Na_2O, Fe,

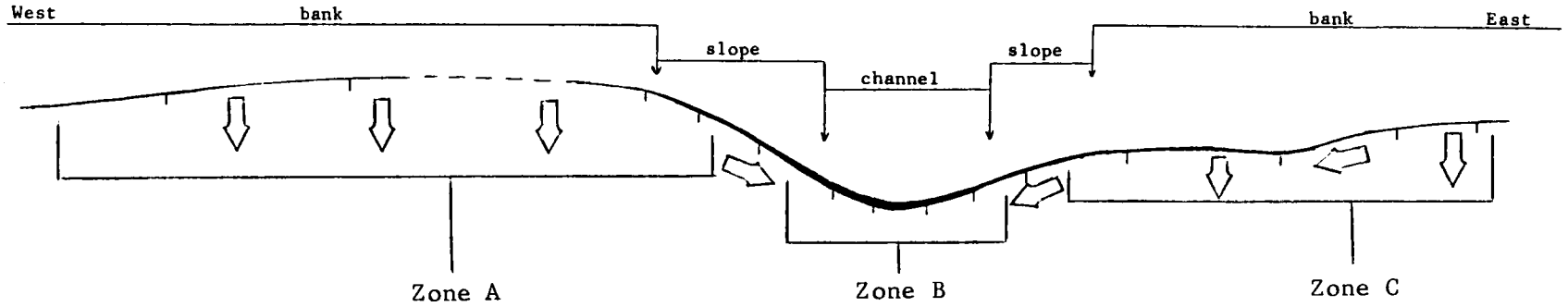
P_2O_5, and Ba argue for similar depositional conditions as the channel. Below the 0-3 cm zone, NE058 exhibits trends similar to the other bank sites. The area may have developed groundwater flow similar to that of the channel. Rocks underneath perhaps acted as a poorly drained soil.

Conclusions

Although the study site was originally divided into the micro-environments of banks, slopes, and channel, a more appropriate subdivision might be northwest bank, northeast bank, and channel (Fig. 38). The northwest bank was paleotopographically the highest. The zone beneath the coal could be considered a paleosol, as evidenced by root traces, unbedded character of the seat rocks, and chemical and mineralogical data. Leaching of the seat rocks and possibly the peat apparently occurred as groundwater flowed downward.

The northeast bank, which stood at half the relief of the northwest bank, most probably existed in wet conditions most of the time during peat deposition. The seat rocks most likely served as a poorly drained soil, which underwent some leaching effects to alter the chemistry and to a much lesser extent the mineralogy. The lower relief (paleotopography) probably resulted in less oxidation and water movement, resulting in less leaching.

The channel undoubtably remained submerged. The 0-3 cm zone below the coal, composed largely of clays and organic



	Zone A	Zone B	Zone C
INCREASES: (or high amounts in the 0-3 cm zone)	Zr, Cr, Al_2O_3, Ba, TiO_2, Al_2O_3/SiO_2, kaolinite, K/I ratio	S, Fe, Na, Mg, P, Mn, Ba, Al_2O_3, K_2O, Rb, Ca, TiO_2, Al_2O_3/SiO_2; pyrite	Zr, Cr, Al_2O_3, Ba, TiO_2, Al_2O_3/SiO_2
DECREASES: (or low amounts in the 0-3 cm zone)	Fe, Mg, Mn, P, S; chlorite, SR ratio, 3.24A/4.26A ratio	Zr, Cr, SiO_2; K/I ratio, SR ratio	Fe, Mg, Mn, Ca, P, S
SUMMARY:	Leached area - destruction of chlorite, possibly some enrichment of kaolinite.	Wet zone of concentration and reducing conditions; initial brackish standing water (?), chlorite regeneration (?).	Some leaching evident, mostly chemical trends; possibly represents a poorly drained horizon.

Figure 38. Summary of micro-depositional environments at the study site.

matter, apparently served as a zone of concentration under reducing conditions. Subsiding channel-carving waters may have deposited phosphatic material (fish scales, bones, etc.). The water may have been initially brackish, contributing ions to the organics and clays of the 0-3 cm zone. Subsequently, organic acids from the peat could have affected this 0-3 cm zone. Leached material from the paleotopographic highs may have also contributed material to the channel.

Therefore, paleotopography apparently had a noticeable effect on the mineralogy and chemistry of the rocks at the study site by controlling the flow of groundwater and the presence of standing water. Topographic highs were affected by leaching processes which altered somewhat the original rocks. Organic concentrations and surface water, which together controlled Eh/pH conditions, were also controlled by the ancient topography. The amount of organic matter and the conditions in which it accumulated were probably factors in the lateral variations in chemistry beneath the coal (especially in the 0-3 cm zone) as different Eh/pH conditions probably existed from the banks to the channel. Brackish standing water probably existed initially in the lows. The topographic lows as a result of this possible brackish influence, Eh/pH conditions, and groundwater flow, became zones of accumulation.

The composition of the sediments at the time of deposition controlled the present-day mineralogy and chemistry to some extent. These two factors, the original material and the leaching/concentration of elements and minerals because of different Eh/pH conditions and groundwater flow, probably had the greatest influence on the rocks we see today.

Suggestions for Further Study

A detailed examination of the chlorites from the channel in comparison with chlorites from other sites, may reveal differences in composition from which conclusions about their origins may be drawn. Did chlorite form after deposition? Was chlorite originally altered by the acidic bog waters? Also, fluids released during coalification may have traveled upward through the roof rocks, affecting the sediments immediately above the coal. Therefore, an investigation of the rocks above the coal might better define alteration associated with coalification processess.

The progress of the peat swamp development at the study site may be revealed by examining in detail the macroscopic coal banding and chemistry of coals, both laterally and vertically. Did the swamp exist in the channel and transgress over the banks, or was the swamp initially present over the entire area, including the topographically higher northwest bank? The timing of the leaching and peat accumulation might then be assessed.

Collection of samples from beneath the channel by (digging or coring) may prove beneficial to further establish trends. Detailed analyses of heavy minerals (their identity and distribution) might better explain chemical variations in elements such as phosphorous, zirconium, barium, and titanium. Examination of thin sections of sandstones from the northwest bank might reveal whether extensive feldspar leaching occurred.

Finally, the shale directly below the coal in the channel might be examined for phosphatic remains such as bones, fish scales, etc. (Spackman, W., 1985, Personal Communication). Such a find would be significant and would further establish the character of the depositional environment of this channel-fill coal.

LIST OF REFERENCES

LIST OF REFERENCES

Austin, G. S. and Leininger, R. K. (1976) The effect of heat-treating sedimented mixed-layer illite-smectite as related to quantitative clay mineral determinations: J. Sed. Pet., v. 46, p. 206-215.

Brown, G., ed. (1961) The X-ray Identification and Crystal Structure of Clay Minerals: Mineralogical Society of London, Jarrold and Sons, London, 544 p.

Chayes, F. (1956) Petrographic Modal Analysis: Wiley and Sons, New York, 113 p.

Chestnut, D. R. (1981) Marine zones of the Upper Carboniferous of eastern Kentucky: in Coal and Coal-Bearing Rocks of Eastern Kentucky, Haney, D. C. (Director), Kentucky Geological Survey, Lexington, KY, p. 57-66.

Deevey, E. S. (1958) Bogs: in Parham (1964) Lateral clay mineral variation in certain Pennsylvanian underclays: J. Sed. Pet., v. 34, p. 1179-1193.

Gardner, Thomas W. and Williams, E. G. (1985) Pedogenesis of some Pennsylvanian underclays: groundwater, topographic, and tectonic controls, Absracts with Programs, V. 17, No. 7, 1985 G.S.A. Annual Meeting, p. 588.

Garrels, R. M. and Christ, C. L. (1965) Solutions, Minerals, and Equalibria: Freeman, Cooper, and Company, San Francisco, 450 p.

Gorham, E. Eisenreich, S. T., Ford, J. Santelmann, M. V. (1985) The chemistry of bog waters: in Stumm, W., ed., Chemical Processess in Lakes, John Wiley & Sons, New York, 1985, 435 p.

Griffin, G. M. (1970) Interpretation of X-ray diffraction data: in Procedures of Sedimentary Petrology, Carver, R. E. (ed.), Wiley-Interscience, New York, 1970, p. 541-569.

Haney, D. C., director (1981) Coal and Coal-Bearing Rocks or Eastern Kentucky, Kentucky Geological Survey, Lexington, KY, p. 18.

Holbrook, P. W. (1973) Geologic and mineralogic factors controlling the properties and occurrence of ladle brick clays: unp. PhD thesis, Pennsylvania State Univ., 318 p.

Horne, J. C., Ferm, J. C., Caruccio, F. T., and Baganz, B. P. (1978) Depositional models in coal exploration and mine planning in Appalachian region: in Geology of Coal, Ross, C. A. and Ross, J. R. P. (eds.), Hutchison Ross Publishing Co., Strousburg, PA, 1984, p. 124-156.

Horne, J. C., and Ferm, J. C. (1978) Carboniferous Depositional Environments: Eastern Kentucky and Southern West Virginia: Department of Geology, Univ. of South Carolina, 151 p.

Huddle, J. W., and Patterson, S. H. (1961) Origin of Pennsylvania underclay and related seatrock: Geol. Soc. Amer. Bull., v. 72, p. 1643-1660.

Keller, W. D. (1970) Environmental aspects of clay minerals: Journ. Sed. Petrol., v. 40, p. 788-813.

Ketani, R. V. (1981) The Magoffin Member: in Coal and Coal-Bearing Rocks of Eastern Kentucky, Haney, D. C. (director), Kentucky Geological Survey, Lexington, KY, p. 160-161.

Logan, E. W. (1842) On the stigmaria (sic) clay in the Blossberg coalfield of Pennsylvania: in Origin of Pennsylvania underclay and related seatrocks, Huddle, J. W., and Patterson, S. H., 1961, Geol. Soc. Amer. Bull., v. 72, p. 1643-1660.

Lithgow, E. W. (1972) An analysis of the factors controlling the occurrence of bloating shales in the Pennsylvania System of western Pennsylvania: unp. M.S. Thesis, Pennsylvania State Univ., 209 p.

Muller, J. (1964) in Coal and Coal-Bearing Strata, Murchison, D. and Westoll, T. S. (eds.), 1968, Oliver and Boyd, London, 418 p.

Millot, G. (1970) Geology of Clays, Springer-Verlag, New York, 429 p.

Oldam, D. W. (1979) Analysis of the relationships between composition and occurrence of bloating shales and clays in the Pennsylvanian System of western Pennsylvania: unp. M.S. Thesis, The Pennsylvaia State Univ., 150 p.

Parham, W. E. (1964) Lateral clay mineral variation in certain Pennsylvania underclays: J. Sed. Pet., v. 34, p. 1179-1193.

Rimmer, S. M. and Eberl, D. D. (1982) Origin of underclay as revealed by vertical variations in mineralogy and chemistry: Clay and Clay Minerals, v. 30, no. 6, p. 420-430.

Roeschmann, G. (1971) Problems concerning investigations of paleosols in older sedimentary rocks: in Paleopedology - Origin, Nature, and Dating of Paleosols, Yaalon, D. H. (ed.), Isreal Universities Press, Jerusalem, p. 311-320.

Schultz, L. G. (1958) Petrology of underclays: Geol. Soc. Amer. Bull., v. 69, p. 363-402.

Spackman, W. (1985) Personal communication: Penn. State Univ., University Park, PA.

Staub, J. R. and Cohen, A. D., (1978) Kaolinite-enrichment beneath coal: a modern analogue, Snuggedy Swamp, South Carolina: Journ. Sed. Petrol., v. 48, no. 1, p. 203-210.

Stewart, W. N. (1983) Paleobotony and the Evolution of Plants, Cambrige University Press, Cambrige, 405 p.

Stumm, W., ed. (1985) Chemical Processess in Lakes, John Wiley & Sons, New York, 435 p.

Stutzer, O. (1940) Geology of Coal, University of Chicago Press, Chicago, 461 p.

Van der Plas, L. and Tobi, A. C. (1965) A chart for judging the reliability of point-counting results: Am. Journ. Science, v. 263, p. 87-90.

Wanless, H. R., Baroffio, J. R., and Trescott, P. C. (1969) Conditions of deposition of Pennsylvania coal beds: in Geology of Coal, Ross, C. A. and Ross, J. R. P. (eds.), 1984, Hutchison Ross Publishing Company, Strousburg, PA, p. 85-122.

Weaver, C.E. (1957) The distribution and identification of mixed-layer clays in sedimentary rocks: Amer. Mineralogist, v. 41, p. 202-221.

Weaver, C.E. (1961) Clay minerals of the Ouachita structural belt and adjacent foreland: in The Ouachita System, Flawn, P. T., Goldstein, A., King, P. B., and Weaver, C. E., University of Texas, Pub. No. 6120, p. 147-162.

Weaver, C. E. (1979) Geothermal Alteration of Clay Minerals and Shales: Diagenesis: Georgia Institute of Technology, Office of Nuclear Waste Isolation, 176 p.

Williams, E. G., Bergenback, R. E., Falla, W. S., and Vdagawa, S. (1968) Origin of some Pennsylvanian underclays in western Pennsylvania: J. Sed. Pet., v. 34, p. 1179-1193.

Williams, E. G. (1984) Personal communication: Penn. State Univ., University Park, PA.

APPENDIXES

APPENDIX 1

XRF PELLET PREPARATION

Steps

1. Crush rock sample into pea-sized fragments, avoiding contamination.

2. Grind 6 g of sample in the Shatterbox with the tungsten carbide mill for six minutes, using a few drops of freon as a grinding agent.

3. Place 3 g of pulverized material into pellet die.

4. Form pellet in hydraulic press, first under 10,000 PSI for 10 seconds, then under 30,000 PSI for one minute, using two teaspoons of boric acid as a base.

5. Store in desiccator, until ready for analysis.

APPENDIXES

APPENDIX 2

XRF ERROR ANALYSIS FOR CLAY PROTOCOL

Element	Std. Error of Calibration(%)[a]	Repeatability(%)[a]
Na_2O	±0.15	±0.26
MgO	±0.04	±0.05
Al_2O_3	±0.08	±0.11
SiO_2	±0.24	±0.15
P_2O_5	±0.01	±0.03
S	±0.01	±0.01
K_2O	±0.02	±0.01
CaO	±0.06	±0.02
TiO_2	±0.01	±0.03
Cr	±76ppm	± 6ppm
MnO	±43ppm	±21ppm
Fe_2O_3	±0.02	±0.08
Ba	±90ppm	±29ppm
Rb	± 6ppm	± 3ppm
Sr	± 7ppm	± 3ppm
Zr	±23ppm	±14ppm

[a]using standard SO2 with 9 replicate analyses. EG&G ORTEC's ATAC program and the Departmental (Dept. of Geol. Sciences at the Univ. of Tenn.) Clays Protocol.

APPENDIX 3

XRF VALUES FOR SEAT ROCK SAMPLES

Element	Sample NW110-1	Sample NW110-2	Sample NW110-3	Sample NW110-4	Sample NW082-1	Sample NW082-2
Na_2O	0.57	0.54	0.38	0.56	0.75	0.30
MgO	1.19	1.21	1.50	1.79	1.08	1.14
Al_2O_3	27.18	26.02	25.69	22.02	23.22	25.49
SiO_2	58.41	59.32	59.46	60.63	61.97	61.77
P_2O_5	0.08	0.02	0.06	0.08	0.07	0.06
S	0.09	-	0.00	0.01	0.14	0.02
K_2O	5.73	4.98	5.36	4.46	4.94	4.53
CaO	0.30	0.24	0.27	0.27	0.27	0.23
TiO_2	0.96	0.90	0.85	1.06	1.11	1.05
Cr	200	150	170	110	150	170
MnO	100	120	220	530	90	120
Fe_2O_3	2.91	3.03	4.46	6.29	2.74	2.86
Ba	810	400	470	520	430	430
Rb	220	180	210	180	180	160
Sr	120	110	120	110	110	110
Zr	370	320	230	320	580	480

Element	Sample NW082-3	Sample NW082-4	Sample NW037-1	Sample NW037-2	Sample NW037-3	Sample NW037-4
Na_2O	0.78	0.64	0.43	0.30	0.34	0.51
MgO	1.76	1.89	0.95	0.93	0.85	1.68
Al_2O_3	25.00	22.04	19.20	13.43	18.84	21.55
SiO_2	58.29	61.45	60.80	73.47	69.25	62.11
P_2O_5	0.05	0.07	0.06	0.03	0.04	0.04
S	-	-	0.31	-	-	-
K_2O	5.36	4.48	4.15	2.13	3.18	4.72
CaO	0.28	0.27	0.22	0.08	0.13	0.27
TiO	0.85	1.04	1.31	1.13	1.10	0.98
Cr	120	110	180	110	120	120
MnO	340	540	100	180	120	350
Fe_2O_3	5.75	6.17	3.17	3.15	2.44	5.56
Ba	550	650	1600	240	270	340
Rb	210	180	170	80	120	190
Sr	120	100	120	90	100	130
Zr	200	320	630	1280	370	280

Element	Sample NW037-5	Sample NW029-1	Sample NW029-2	Sample NW029-3	Sample NW029-4	Sample NW029-5
Na_2O	0.23	0.55	0.46	0.40	0.22	0.38
MgO	1.87	1.04	1.42	1.58	1.83	1.46
Al_2O_3	22.34	14.64	25.22	24.29	22.93	18.70
SiO_2	60.36	68.01	61.15	59.36	60.00	64.90
P_2O_5	0.14	0.05	0.05	0.05	0.06	0.11
S	-	0.13	-	-	0.01	-
K_2O	4.30	3.13	5.05	4.84	4.70	3.57
CaO	0.35	0.13	0.26	0.24	0.26	0.26
TiO_2	1.04	1.23	0.93	0.94	1.05	1.07
Cr	120	150	140	120	120	100
MnO	650	140	230	360	470	480
Fe_2O_3	6.31	2.68	3.99	5.46	6.14	5.49
Ba	490	330	450	540	500	420
Rb	180	120	180	200	190	150
Sr	110	100	110	110	110	100
Zr	300	1170	310	240	320	500

Element	Sample NW020-1	Sample NW020-2	Sample NW020-3	Sample NW020-4	Sample NW020-5	Sample NW009-1
Na_2O	0.32	0.17	0.05	0.71	0.87	1.88
MgO	1.22	1.59	1.82	1.32	1.66	2.04
Al_2O_3	24.42	22.36	22.30	15.23	18.31	21.46
SiO_2	54.92	59.91	61.64	71.39	64.41	25.98
P_2O_5	0.09	0.04	0.11	0.15	0.15	0.92
S	0.46	-	-	-	0.02	6.95
K_2O	5.48	4.38	4.34	2.83	3.59	6.95
CaO	0.26	0.22	0.28	0.25	0.31	0.10
TiO	1.17	1.03	1.06	1.02	1.08	1.23
Cr	200	110	110	100	80	20
MnO	150	380	480	300	560	330
Fe_2O_3	3.37	5.48	6.14	4.13	5.93	12.94
Ba	1870	470	470	320	470	1040
Rb	190	180	180	110	140	190
Sr	140	110	110	100	110	100
Zr	420	370	310	650	410	70

Element	Sample NW009-2	Sample NW009-3	Sample NW009-4	Sample NW003-1	Sample NW003-2	Sample NW003-3
Na_2O	0.49	0.44	0.78	1.23	0.48	0.25
MgO	1.53	1.36	1.26	2.02	1.62	1.23
Al_2O_3	18.19	16.72	16.17	23.94	22.71	14.67
SiO_2	64.69	69.21	70.44	38.02	56.65	69.96
P_2O_5	0.14	0.16	0.17	0.53	0.13	0.14
S	0.01	0.01	0.01	3.58	0.55	0.04
K_2O	3.53	3.11	2.99	4.36	4.36	2.68
CaO	0.32	0.27	0.27	0.17	0.20	0.27
TiO_2	1.12	1.10	1.07	1.18	1.08	1.03
Cr	100	110	90	60	120	100
MnO	100	320	300	430	400	450
Fe_2O_3	6.49	4.63	4.35	9.90	6.17	5.20
Ba	440	340	350	670	590	350
Rb	150	130	120	200	180	110
Sr	100	100	100	110	110	100
Zr	420	670	600	130	330	440

Element	Sample NE005-1	Sample NE005-2	Sample NE012-1	Sample NE012-2	Sample NE020-1	Sample NE020-2
Na_2O	2.31	0.75	0.69	0.92	0.90	0.81
MgO	2.60	1.36	1.52	1.02	1.30	1.15
Al_2O_3	18.87	16.99	24.12	15.42	24.45	14.59
SiO_2	13.30	69.18	46.61	72.54	46.39	73.36
P_2O_5	1.41	0.14	0.32	0.08	0.17	0.13
S	12.05	0.04	1.81	0.01	0.94	0.01
K_2O	2.59	3.22	4.82	2.65	5.68	2.60
CaO	0.07	0.24	0.20	0.12	0.33	0.19
TiO	1.35	1.08	0.97	0.91	1.18	1.00
Cr	-	120	120	130	200	100
MnO	380	350	270	240	170	290
Fe_2O_3	18.40	4.73	6.74	3.50	5.35	4.05
Ba	2490	380	680	260	2820	300
Rb	190	130	200	100	200	110
Sr	100	100	120	90	170	100
Zr	-	550	250	540	250	690

Element	Sample NE020-3	Sample NE020-4	Sample NE035-1	Sample NE035-2	Sample NE035-3	Sample NE035-4
Na_2O	0.60	1.17	0.42	0.56	0.60	0.28
MgO	1.61	1.22	1.23	1.11	1.72	1.85
Al_2O_3	21.29	14.91	24.69	18.02	22.91	21.73
SiO_2	61.99	71.78	60.80	69.00	60.16	61.09
P_2O_5	0.14	0.13	0.08	0.07	0.08	0.13
S	0.04	0.10	0.07	0.01	-	0.05
K_2O	4.28	2.74	5.21	3.18	4.61	4.30
CaO	0.30	0.21	0.27	0.16	0.25	0.33
TiO_2	1.08	1.00	0.89	1.03	1.04	1.13
Cr	120	120	230	110	110	110
MnO	380	270	120	240	390	440
Fe_2O_3	5.83	4.21	3.01	3.72	6.02	6.28
Ba	510	310	870	340	500	480
Rb	170	100	200	120	180	170
Sr	120	100	140	100	110	110
Zr	440	520	370	680	310	380

Element	Sample NE035-5	Sample NE058-1	Sample NE058-2	Sample NE058-3	Sample NE058-4	Sample NE058-5
Na_2O	0.35	1.03	0.23	0.40	0.50	0.42
MgO	1.76	1.49	1.45	1.72	1.78	1.91
Al_2O_3	19.42	21.21	25.51	22.31	21.53	22.00
SiO_2	60.98	37.58	58.75	61.21	61.34	60.50
P_2O_5	0.14	0.47	0.05	0.10	0.14	0.14
S	0.01	3.47	0.07	0.04	0.05	0.04
K_2O	3.85	4.60	5.18	4.46	4.50	4.46
CaO	0.35	0.21	0.25	0.28	0.31	0.33
TiO	1.12	1.20	0.85	1.09	1.04	1.07
Cr	100	140	150	110	110	110
MnO	780	170	260	410	420	450
Fe_2O_3	7.09	7.28	4.68	6.06	6.17	6.48
Ba	530	1970	440	560	500	540
Rb	170	190	200	180	170	180
Sr	110	140	120	110	120	110
Zr	320	260	230	340	340	330

Element	Sample NE075-1	Sample NE075-2	Sample NE075-3	Sample NE075-4	Sample NE075-5	Sample NE087-1
Na_2O	0.39	0.51	0.10	0.30	0.45	0.47
MgO	1.28	1.33	1.56	1.71	1.81	1.23
Al_2O_3	22.70	24.21	22.56	22.63	20.54	23.91
SiO_2	64.30	61.68	62.64	60.20	61.22	58.13
P_2O_5	0.04	0.02	0.04	0.05	0.16	0.07
S	0.02	0.01	0.00	0.00	0.04	0.23
K_2O	4.64	4.44	4.40	4.46	4.18	5.17
CaO	0.20	0.21	0.22	0.24	0.38	0.23
TiO_2	1.02	1.03	1.05	1.13	1.05	1.13
Cr	150	140	130	100	100	210
MnO	150	270	340	400	700	170
Fe_2O_3	3.19	4.04	5.11	5.86	7.12	3.49
Ba	540	380	440	470	540	1950
Rb	170	170	180	180	180	200
Sr	110	110	100	120	120	120
Zr	520	450	420	350	320	380

Element	Sample NE087-2	Sample NE087-3	Sample NE087-4	Sample NE087-5
Na_2O	0.24	0.25	0.14	0.40
MgO	1.43	1.46	1.66	1.84
Al_2O_3	23.64	23.20	22.08	20.85
SiO_2	61.61	61.95	62.10	61.31
P_2O_5	0.04	0.04	0.03	0.14
S	0.01	0.01	0.02	0.03
K_2O	4.34	4.49	4.31	4.09
CaO	0.19	0.22	0.23	0.33
TiO	1.06	1.06	1.07	1.07
Cr	130	160	120	90
MnO	280	280	380	650
Fe_2O_3	4.32	4.54	5.53	6.92
Ba	380	410	480	540
Rb	170	170	180	170
Sr	100	110	110	110
Zr	430	400	380	320

APPENDIX 4

SAMPLE CALCULATION OF RELATIVE CLAY MINERAL PERCENTAGES

1. Measure peak heights (Ph), corrected for background.
   14A (C) - 11
   10A (I) - 64
   7A (K+C) - 101

2. $$\%(K+C) = \frac{\frac{Ph7A}{2.5}}{\frac{Ph7A}{2.5} + Ph10A} \times 100 = \frac{\frac{101}{2.5}}{\frac{101}{2.5} + 64} \times 100 = 39\%$$

3. $$\%K = \frac{Ph7A - (Ph14A \times 1.7)}{100} \times \%(K+C) = \frac{101 - (11 \times 1.7)}{100} \times 39 = 32\%$$

4. $$\%C = \%(K+C) - \%K = 39 - 32 = 7\%$$

5. $$\%I = \frac{Ph10A}{\frac{Ph7A}{2.5} + Ph10A} \times 100 = \frac{64}{\frac{101}{2.5} + 64} \times 100 = 61\%$$

6. %K = 32
   %C = 7
   %I = 61

APPENDIX 5

RELATIVE CLAY MINERAL PERCENTAGES

[illegible]	Location	% K	% C	% I	[illegible]
[illegible]W110-1		28	0	72	0.4
[illegible]W110-2	bank	32	6	62	0.5
[illegible]W110-3		24	6	70	0.3
[illegible]W110-4		32	11	57	0.6
[illegible]W082-1		29	0	71	0.4
[illegible]W082-2	bank	46	0	54	0.8
[illegible]W082-3		20	9	71	0.3
[illegible]W082-4		32	9	59	0.5
[illegible]W037-1		31	0	69	0.4
[illegible]W037-2		56	9	35	1.6
[illegible]W037-3	bank	53	0	47	1.1
[illegible]W037-4		21	12	67	0.3
[illegible]W037-5		33	11	56	0.6
[illegible]W029-1		29	0	64	0.4
[illegible]W029-2		30	0	70	0.4
[illegible]W029-3	slope	28	9	63	0.4
[illegible]W029-4		25	12	63	0.4
[illegible]W029-5		35	7	58	0.6
[illegible]W020-1		18	0	82	0.2
[illegible]W020-2		28	10	62	0.4
[illegible]W020-3	slope	25	14	61	0.4
[illegible]W020-4		43	8	49	0.9
[illegible]W020-5		33	8	59	0.6
[illegible]W009-1		13	10	77	0.2
[illegible]W009-2	channel	33	8	59	0.6
[illegible]W009-3		39	7	54	0.7
[illegible]W009-4		39	8	53	0.7
[illegible]W003-1		22	11	67	0.3
[illegible]W003-2	channel	28	14	58	0.5
[illegible]003-3		41	6	47	[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]5-1	channel	29	0	71	0.4
[illegible]5-2		42	8	50	0.8
[illegible]012-1	channel	5	10	75	0.1
[illegible]012-2		54	6	40	1.4
[illegible]020-1	slope	12	0	78	0.2
[illegible]020-2		51	7	42	1.2
[illegible]020-3		29	9	62	0.5
[illegible]020-4		42	8	50	0.8
[illegible]035-1	bank	22	0	78	0.3
[illegible]035-2		38	9	53	0.7
[illegible]035-3		31	8	61	0.5
[illegible]035-4		32	10	58	0.6
[illegible]035-5		29	9	62	0.5
[illegible]058-1	bank	14	0	86	0.2
[illegible]058-2		21	8	71	0.3
[illegible]058-3		26	10	64	0.4
[illegible]058-4		24	10	66	0.4
[illegible]058-5		31	9	60	0.5
[illegible]075-1	bank	21	7	72	0.3
[illegible]075-2		34	6	60	0.6
[illegible]075-3		31	7	62	0.5
[illegible]075-4		29	9	62	0.5
[illegible]075-5		26	8	66	0.4
[illegible]087-1	bank	19	8	73	0.3
[illegible]087-2		32	8	60	0.5
[illegible]087-3		32	7	61	0.5
[illegible]087-4		30	10	60	0.5
[illegible]087-5		33	7	60	0.6

[illegible] - Kaolinite C - Chlorite I - Illite

APPENDIX 6

3.24A/4.26A RATIOS FOR SEAT ROCK SAMPLES

Sample	Site	#1	#2	#3	#4	#5
NW110	B	0.2	0.2	0.3	0.2	
NW082	B	0.2	0.2	0.3	0.2	
NW037	B	0.1	0.2	0.1	0.2	0.2
NW029	S	0.1	0.2	0.2	0.2	0.2
NW020	S	0.2	0.3	0.3	0.2	0.2
NW009	C	0.2	0.4	0.2	0.1	
NW003	C	0.4	0.3	0.2		
NE005	C	0.7	0.4			
NE012	C	0.2	0.3			
NE020	S	0.2	0.3	0.2	0.2	
NE035	B	0.2	0.1	0.8	0.2	0.2
NE058	B	0.0	0.1	0.2	0.3	0.1
NE075	B	0.1	0.1	0.2	0.3	0.2
NE087	B	0.1	0.1	0.2	0.2	0.1

B - Bank
S - Slope
C - Channel

VITA

Stuart Oliver Reese was born in Tyrone, PA on March 28, 1961. He attended Port Matilda Elementary School, and later graduated from Bald Eagle Area High School at Wingate, PA in 1979. In September of 1979, he entered Juniata College, located at Huntingdon, PA. There he majored in geology and received his Bachelor of Science degree in May, 1983.

In the autumn of 1983, he accepted a full-time Graduate Assistantship from the Department of Geological Sciences at the University of Tennessee in Knoxville, TN. In the Fall of 1985, he was awarded his Master of Science degree. The author is a member of the American Association of Petroleum Geologists, and the Society of Mining Engineers of AIME.