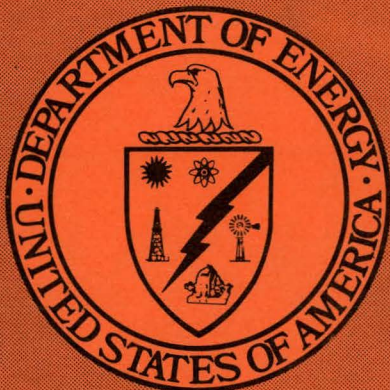


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INORGANIC GEOCHEMISTRY OF DEVONIAN SHALES IN SOUTHERN
WEST VIRGINIA: GEOGRAPHIC AND STRATIGRAPHIC TRENDS

By

Michael Ed. Hohn, Donald W. Neal, and J. J. Renton

April 1980

Prepared for

UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
Morgantown, West Virginia

TECHNICAL INFORMATION CENTER
UNITED STATES DEPARTMENT OF ENERGY

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Michael Ed. Hohn¹, Donald W. Neal¹, and J. J. Renton¹

ABSTRACT

Samples of cuttings from twenty-one wells and a core from a single well in southern West Virginia were analyzed for major and minor elements: silicon, aluminum, iron, magnesium, calcium, sodium, titanium, phosphorus, manganese, sulfur, zinc, and strontium. Stratigraphic and geographic controls on elemental abundances were studied through canonical correlations, factor analyses, and trend surface analyses.

The most abundant elements, silicon and aluminum, show gradual trends through the stratigraphic column of most wells, with silicon increasing and aluminum decreasing up-section. Other elements such as calcium, sulfur, and titanium change abruptly in abundance at certain stratigraphic boundaries. Important geographic trends run east-west: for instance, one can see an increase in sulfur and a decrease in titanium to the west; and a decrease in silicon from the east to the central part of the study area, then an increase further west. Although observed vertical trends in detrital minerals and geographic patterns in elemental abundances agree with the accepted view of a prograding delta complex during Late Devonian time, geographically-local, time restricted depositional processes influenced elemental percentages in subsets of the wells and the stratigraphic intervals studied. The black shales of lower Huron age do not represent simply a return of depositional conditions present in the earlier Rhinestreet time; nor do the gray shales of the Ohio Shale represent the same environmental conditions as the Big White Slate.

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INTRODUCTION

A recent study of stratigraphic relationships within the Devonian shale of southern West Virginia was accompanied by the sampling of cuttings from selected wells for elemental analyses (Neal, 1979). Observed distributions of major and minor elements provide means for confirming the stratigraphic work and for constructing a depositional model of the Devonian sediments in the study areas and adjacent regions. The sampling procedure exhibits elemental distributions within stratigraphic units over a geographic area, and among stratigraphic units in some of the wells. Possible trends or patterns in element distributions include: 1) abrupt changes at stratigraphic boundaries; 2) agreement between stratigraphic units and elemental distributions; 3) consistent increase or decrease in elemental percentages through the stratigraphic range studied; 4) constant matrix of correlation coefficients among elements throughout the stratigraphic or geographic range; and 5) geographic trends that parallel lithologic facies. Blackburn et al (1977) mapped the distribution of elements in outcrops of Devonian shales in Kentucky. The large number of data in the present study required use of multivariate statistics in addition to the mapping of element distributions.

METHODS

Samples of well cuttings were taken at fifty-foot intervals when possible; each well cutting represents ten to fifteen feet of vertical succession of rock. Elemental analyses were performed by X-ray fluorescence of pelletized powders according to the method of Nuhfer et al., (1979). Results were expressed as the oxide percent such that the elements silicon, aluminum, iron, magnesium, calcium, sodium, titanium, phosphorus, and manganese sum to 100 percent. Zinc and strontium were expressed as parts per million of the whole rock, and sulfur as percentage of the whole rock.

X-ray diffraction was used to determine mineralogical composition of each sample. Mineral abundances were expressed as percentages of total integrated peak height. Although not a weight or volume percentage of the respective minerals in the rock, the percent total intensity data have been shown to be numerically equivalent to weight percent of mineral phase (Renton, 1979) and are adequate for the kind of internal comparisons used in this study.

Statistical analysis was carried out using SAS (Statistical Analysis System; Barr et al., 1976). Procedure STEPWISE computed coefficients for polynomial equations representing trend surfaces.

Third-order polynomials were calculated, then a step-down procedure was used for dropping out terms until all of the independent variables remaining in the polynomial regression equation were significant at the 0.1 level. Because we were interested in broad trends, using either trend surfaces comprising all terms of third order and lower, or trend surfaces comprising a subset of significant terms gave comparable results. In general, the terms of low significance eliminated by the step-down procedure possessed little visual impact. Trend surfaces drawn from the reduced equations were preferred on the basis of greater simplicity, ease of verbal summary, and ease of comparison among analyses and subsets of samples.

BACKGROUND

The data used in statistical analyses and mapping included cuttings from 20 wells and samples from a cored well in Lincoln County (Fig. 1). The core from Lincoln County (permit number 1637) was sampled at irregular intervals and studied in detail (Erwin, 1978).

Sampling covered the interval of rocks between the Onondaga Limestone and the Bedford Shale (Fig. 2), but not all wells could be sampled through the whole of this interval.

GEOCHEMICAL SAMPLE CONTROL

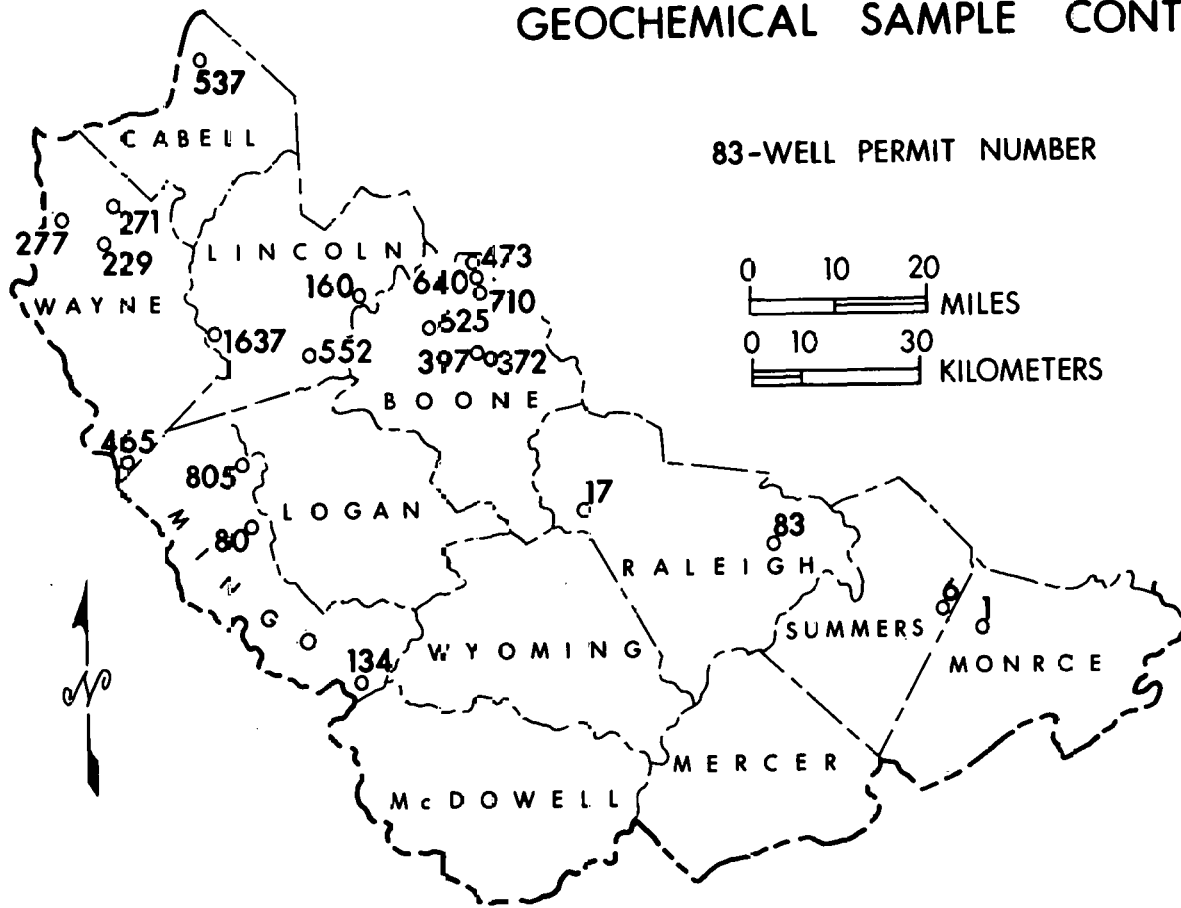


Figure 1. Location map of wells studied, identified by well permit numbers.

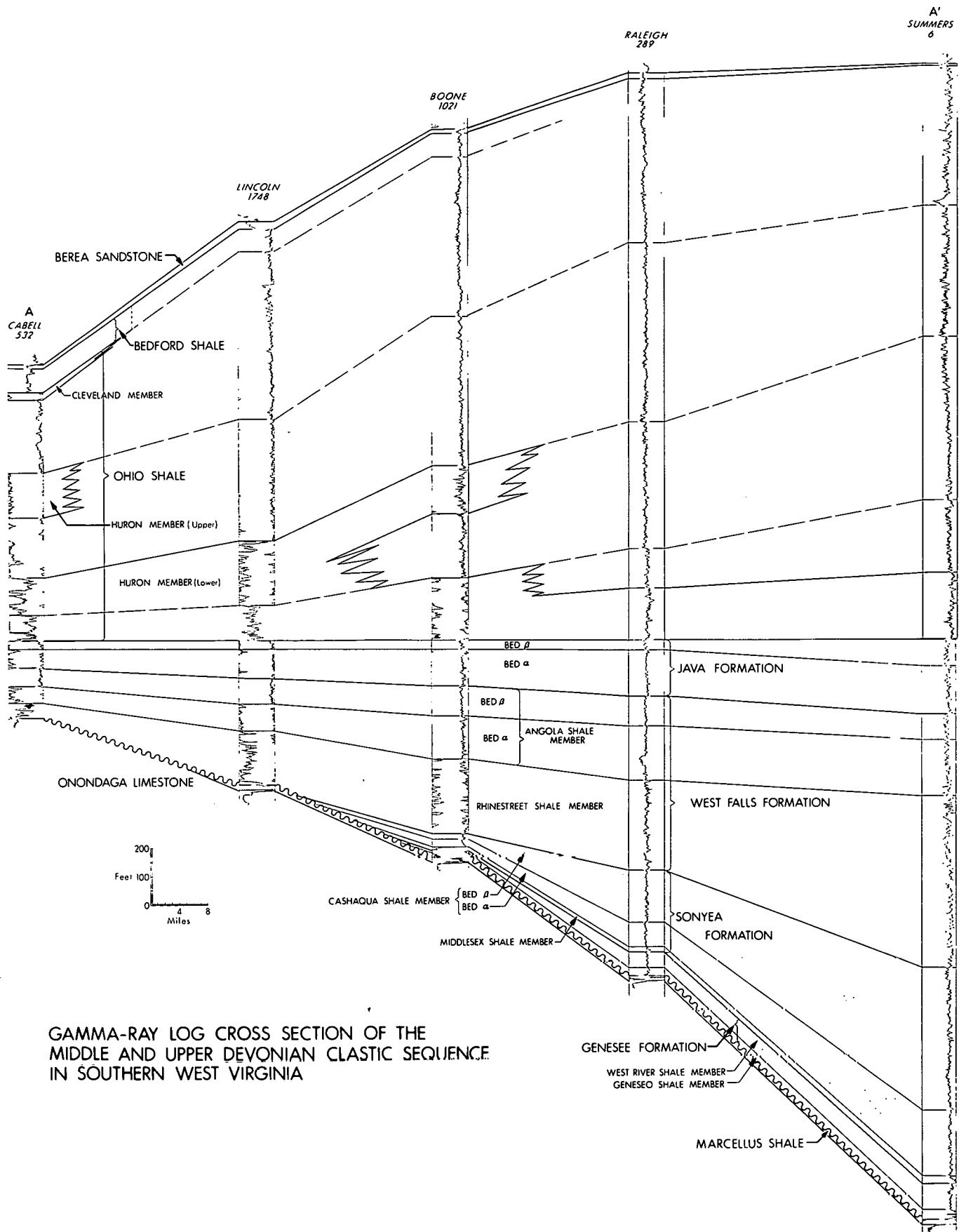


Figure 2. Stratigraphic units in the study area. Figure from Neal (1979).

The stratigraphic units studied in most detail include the West Falls Formation, the Java Formation, and the Ohio Shale. In West Virginia, Neal (1979) recognized two units in the West Falls Formation: a basal black shale, the Rhinestreet Shale Member, and a gray, silty shale with scattered siltstone, the Angola Shale Member. The Rhinestreet varies from black shale with little siltstone in the southwest, to a grayish-black shale with more siltstone in the southeast. The Java Formation consists of dark gray to grayish-black shale with abundant olive-gray to medium-dark gray, calcareous siltstone. The Ohio Shale is a grayish-black to black silty shale that includes two members: the basal Huron Member and the Cleveland Member, separated by the gray, silty shale and siltstone of the Chagrin Shale. The lower portion of the Huron Member is composed of black shale containing increasing quantities of gray shale near the top. An increasing quantity of intertonguing between gray and black shale is seen from west to east. A tongue of black shale separated by gray, silty shale from the lower Huron black shale defines the upper limit of the Huron Member (Fig. 2). Other tongues of black shale split off from the main body of the Huron Member; the Huron Member is defined as including rocks from the base of the main body of the black shales to the top of the uppermost tongue of thick, black shale. As defined, the upper limit is almost certainly not synchronous. Neal (1979) correlates gray shale and siltstone in the eastern sections with black shale to the west. We have designated this interval "X" on the figures. A simplified diagram of the Upper Devonian rocks in southern West Virginia (Fig. 3) also illustrates the three, main units used in the trend surface calculations below: the Rhinestreet, the "Big White Slate," and the Huron. The "Big White Slate" includes the Java Formation and the Angola Member of the West Falls Formation. The name comes from drillers' logs in West Virginia and is useful in sections where the division between the Java and Angola rocks is unclear.

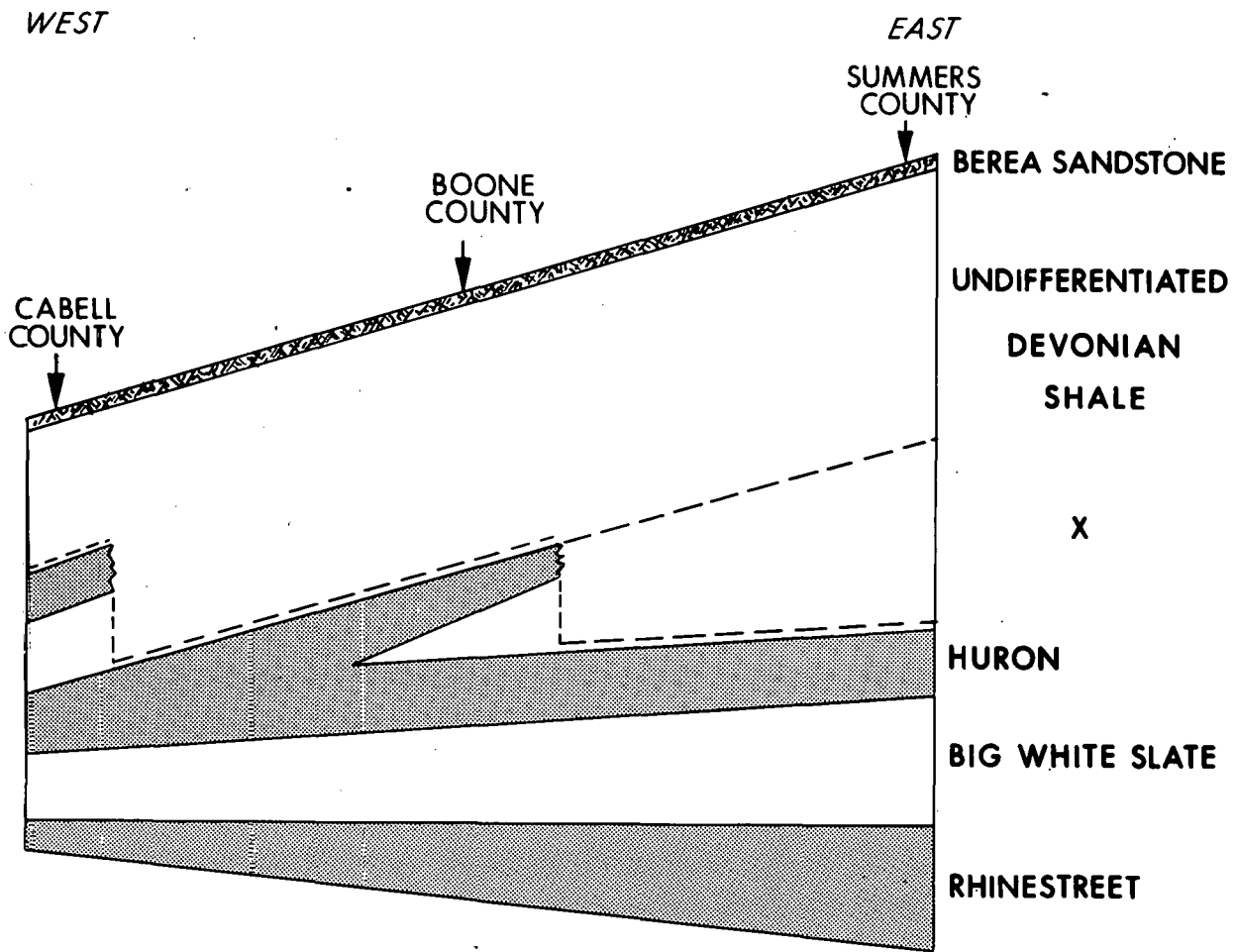


Figure 3. Simplified stratigraphic profile from eastern to western parts of study area, naming stratigraphic units discussed in most detail in the text.

STRATIGRAPHIC ANALYSIS

Canonical correlation of the elemental analyses with the mineralogical data allows one to check a priori assumptions about the correlation between given elemental and mineralogical variables, and to detect unsuspected correlations both within and between the two groups of variables. Confirmation of assumed interrelationships acts as a check of the integrity of the data. Standardization of all variables is implicit in the calculations for obtaining canonical correlations. The calculations yield two sets of canonical variates corresponding to the two sets of measured variables; a table of correlations between each variable and each canonical variate provides two sets of coordinates that can be graphed together on two or more axes. The resulting diagram shows the within- and between-set correlations, represented as angles between vectors drawn from the origin to points determined by the coordinates described above.

The Raleigh 83 well was chosen for analysis because of the modest sample size of 53, and the representation of strata from the Marcellus Shale to undifferentiated shales above the Huron Member of the Ohio Shale. Because the analysis requires inversion of the matrices of variance and covariance, these matrices must have full rank. Therefore, at least one variable must be dropped from each set of variables; otherwise, the n variables that sum to 100 possess a rank of $n-1$, and the matrices are noninvertible. The quantitatively important minerals were retained and silicon was dropped for the analysis. The placement of silicon can be inferred roughly from the position of quartz on the resulting diagram (Figure 4). Correlations between variables are expressed as angles between lines drawn from the origin to points representing each element or mineral. Angles of 0° , 90° , and 180° correspond to correlations of 1, 0, and -1. In the figure, elements and minerals are denoted respectively as points and arrows for clarity. Lengths of arrows or distances of points from the origin are proportional to the variation in each variable explained by the

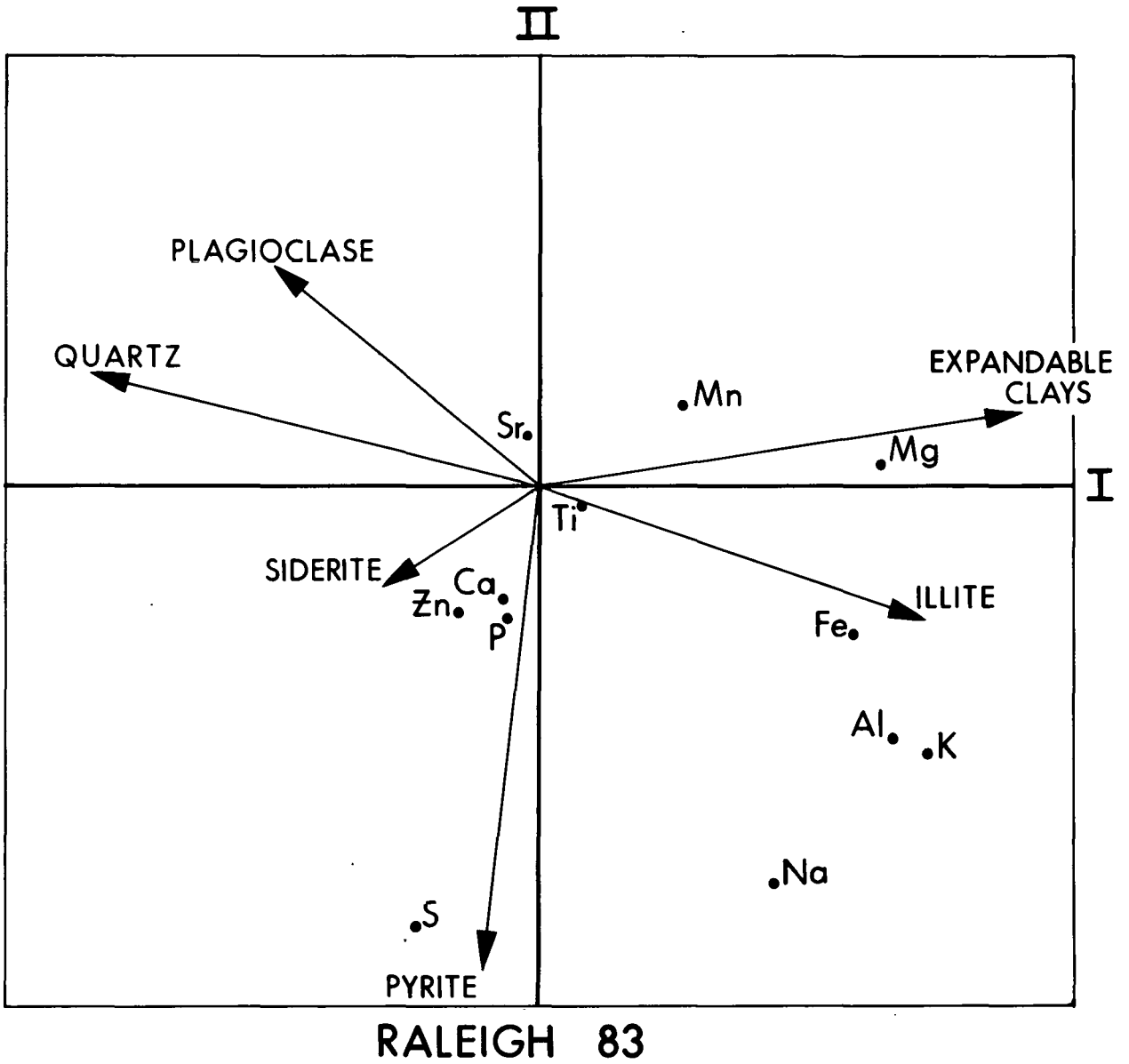


Figure 4. Results of canonical correlation analysis of 53 samples from well 83 in Raleigh County.

canonical variates. Therefore, one must interpret points near the origin with caution; these have been projected from additional dimensions not graphed. For instance, calcium and siderite describe a small angle with respect to the origin, but they are in fact correlated negatively. Points representing calcium and siderite lie in opposite directions along a canonical variate orthogonal to those in Figure 4. In general, one pays closest attention to variables arrayed about the margins of a canonical variates plot. The same principle holds for the interpretation of factor analysis such as those below.

Expected or easily-explained associations include: 1) sulfur and pyrite; 2) potassium with illite; 3) aluminum and the clay minerals; 4) magnesium with the expandable clays, and 5) quartz and plagioclase. Correlations can result from physical occurrence of an element in a particular mineral, or similar response to environmental processes. Sulfur and pyrite comprise a physical association for instance. Iron lies between the expandable clays and pyrite, two iron-containing mineral phases. Evidently, magnesium concentrations are controlled more by the relative percentages of 14 Å clays (chlorite) than the quantity of calcium. Dolomite occurs in only minor quantities. Calcite does not appear as a mineral phase because the quantities are generally below detection. Quartz and plagioclase comprise detrital minerals that increase in percentage high in the section, thus reflecting the lesser maturity of the undifferentiated shale and siltstone of the Ohio Shale (Figure 5) in comparison with sediments lower in the section.

Quartz and illite make up a large proportion of any given sample, with the result that they correlate inversely with each other. The stratigraphic distribution of potassium and silicon likewise vary inversely with respect to each other (Figure 6), displaying an increasing ratio of silicon to potassium with decrease in depth. The patterns in quartz, illite and plagioclase percentages reveal a clear picture of prograding delta or delta complex during Late Devonian

RALEIGH 83

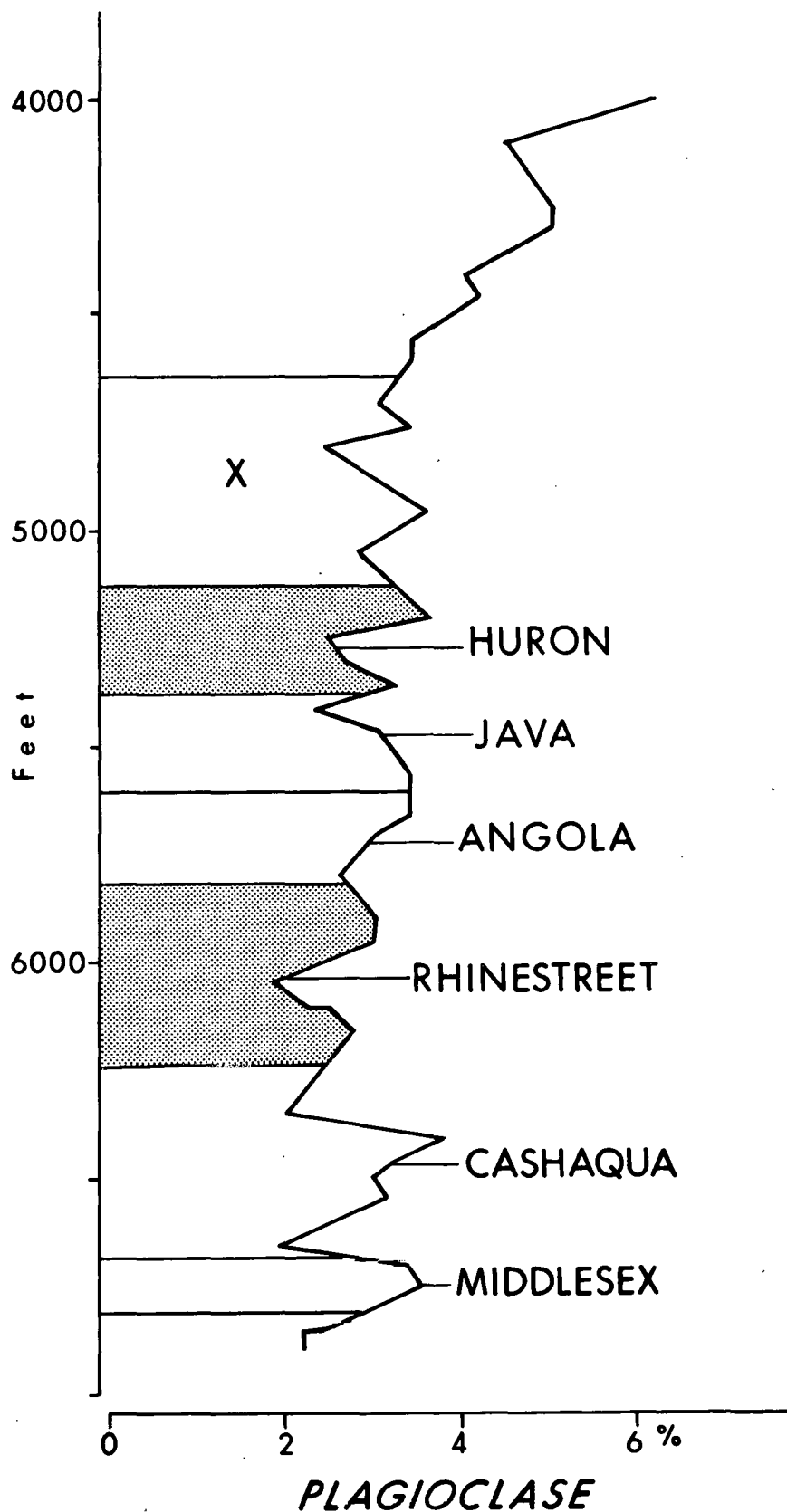


Figure 5. Vertical variation in plagioclase in the Raleigh 83 well.

RALEIGH 83

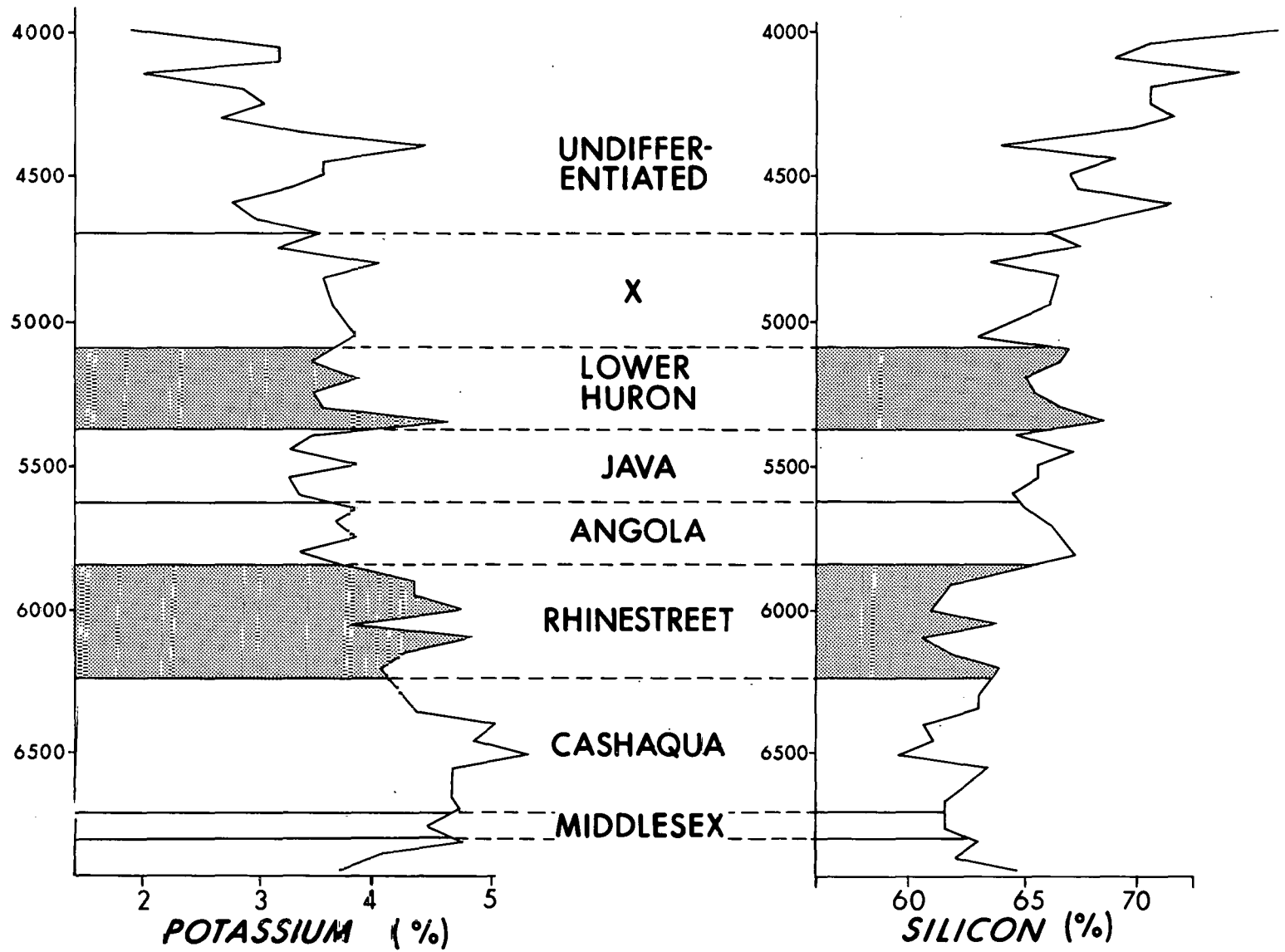


Figure 6. Vertical variation in potassium and silicon in the Raleigh 83 well.

time.

Calcium and phosphorus correlate highly, but show no correlation with any mineral phase other than a negative correlation with siderite along a sixth canonical variate (not graphed). The association of calcium and phosphorus presumably indicates the presence of apatite, but in quantities below detectable limits.

Titanium, manganese, zinc, and sodium do not correlate in any meaningful or useful way with either other elements or mineral phases. Sodium can be associated with clay minerals, but the observed correlations are weak. Sodium may be present in organic matter containing sulfur, and thus falls in a position intermediate to the expandable clays and sulfur.

Canonical correlations of samples from a cored well on Lincoln County (1637) reveal the same general relationships. One can conclude that magnesium, aluminum, potassium, and sulfur are indicative of specific mineral phases and may be useful in mapping. Elements such as iron and sodium are less specific, and probably not useful in mapping. Some elements such as titanium are not associated with any mineral phases studied, and await further treatment to yield meaningful patterns.

SELECTED STRATIGRAPHIC PROFILES

In order to evaluate the stratigraphic work of Neal (1979), the variation of elements with the stratigraphic boundaries determined from geophysical well logs were studied. Sulfur provides one element important in such comparison because it has been found to be high in the black shales of the Huron and Rhinestreet Shale Members. The distribution of sulfur does show higher values in the black Huron and Rhinestreet Shale Members (Fig. 7), as compared with intervening gray shale. The interval designated "X" in Fig. 7 comprises gray shale that correlated with black shale in sections to the west; note that sulfur displays high values in these rocks despite the relative paucity of true "black shale". Environmental conditions must have been nearly the same across the whole of the study area during the time interval represented by these rocks, but the deposition or preservation of organic matter was insufficient to create extensive black shale facies in the east. Black shale is not necessarily high in organic matter, but within the interval studied, this shale shows a high organic content (Erwin, 1978).

Calcium exhibits lower values in the black shale than in the intervening gray shale of the Big White Slate (Fig. 8), particularly in the western-most sections. The presence of calcium could reflect an alkaline environment, not conducive to the preservation of organic matter because of induced bacterial action. The gray shale and siltstone above the black shale of the Huron Member do not have high percentages of calcite. As indicated by the canonical correlations, phosphorus correlates highly with calcium. Therefore, the stratigraphic profiles for phosphorus look very similar to those for calcite, and provide redundant information.

Silicon and elements comprising clay minerals show little stratigraphic variation worthy of attention, other than vertical trends noted above, and profiles

SULFUR

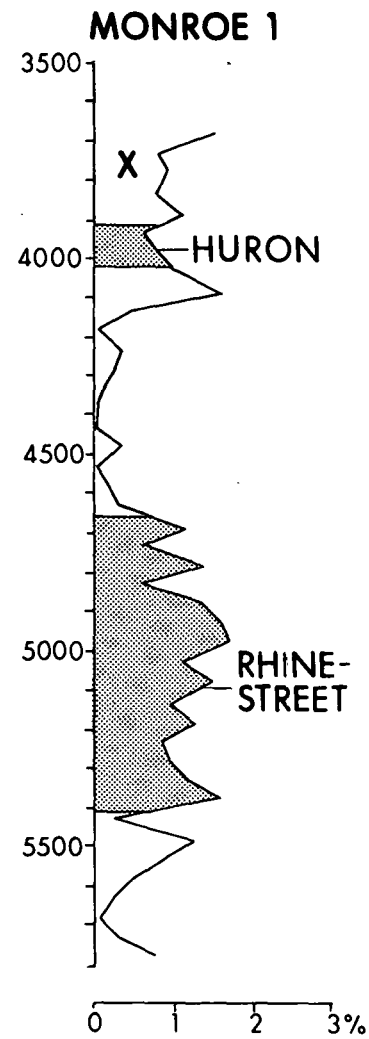
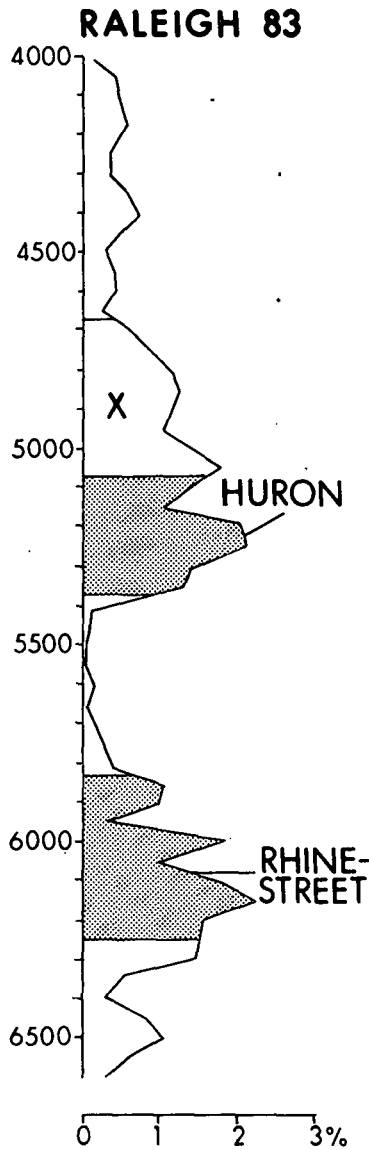
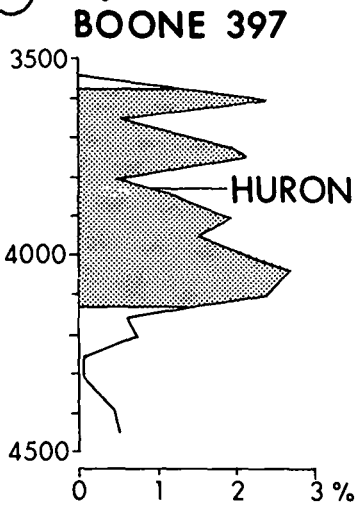
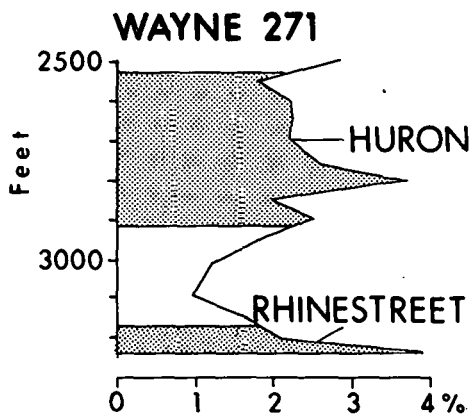
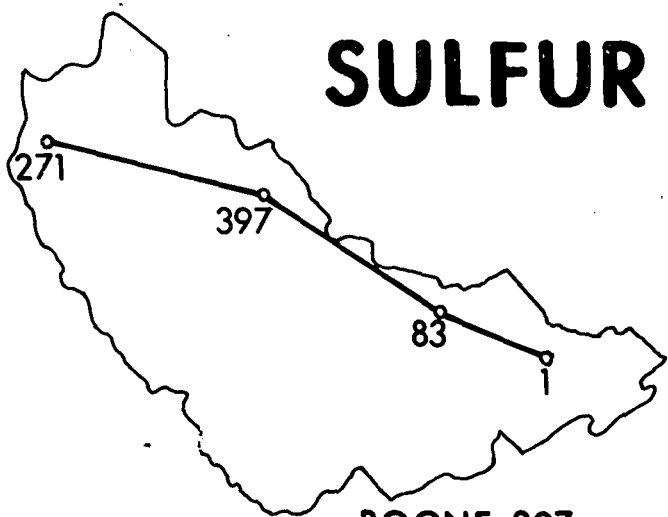
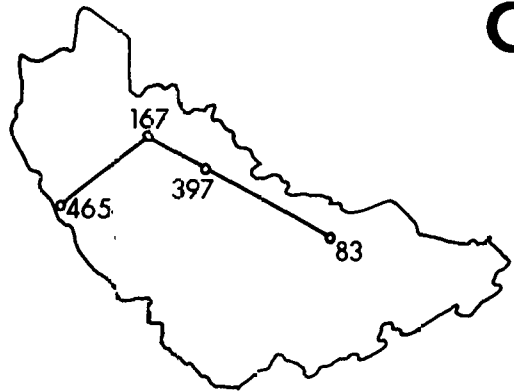
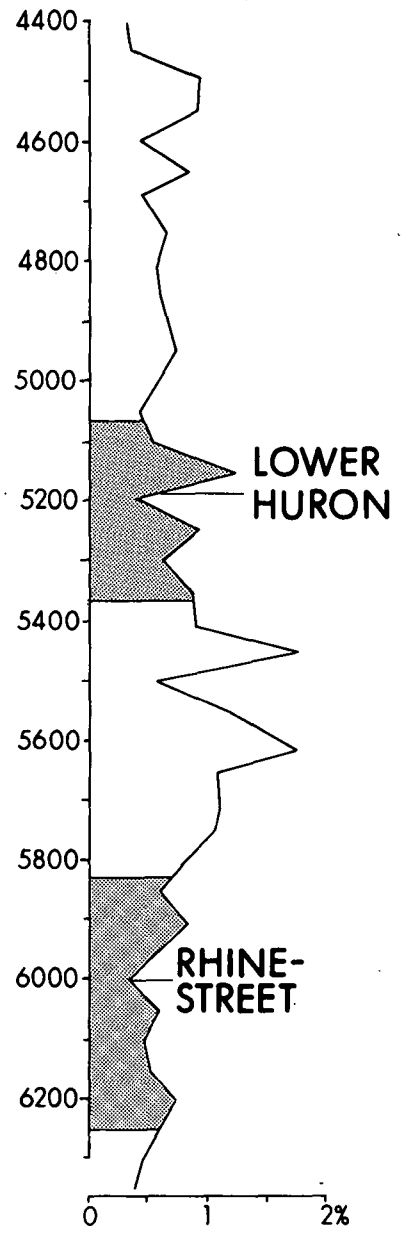


Figure 7. Vertical variation in sulfur measured in selected wells in southern West Virginia.

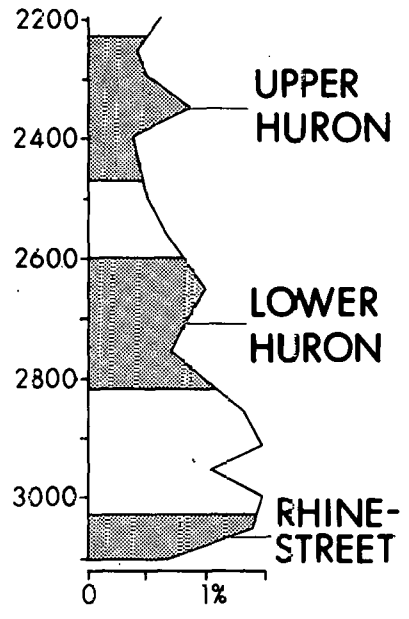
CALCIUM



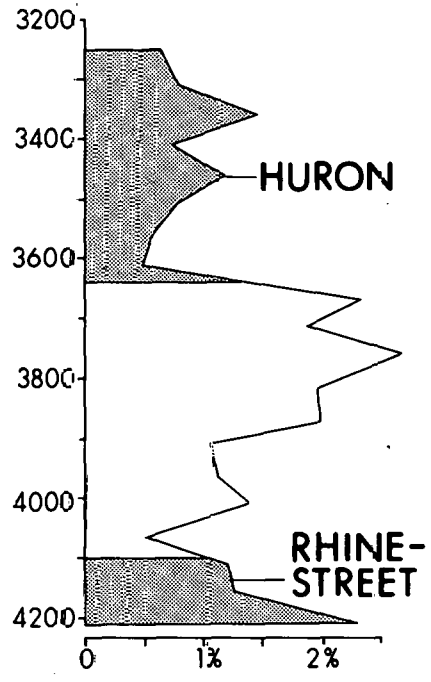
RALEIGH 83



WAYNE 465



LINCOLN 167



BOONE 397

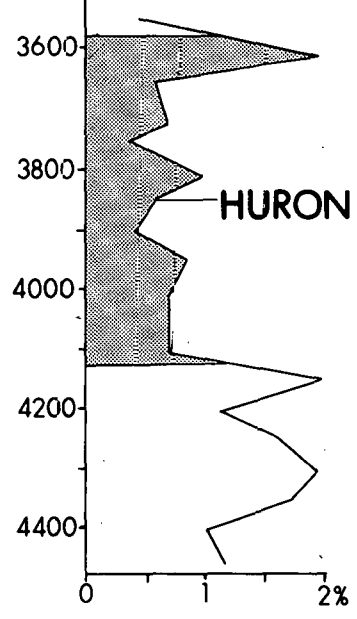
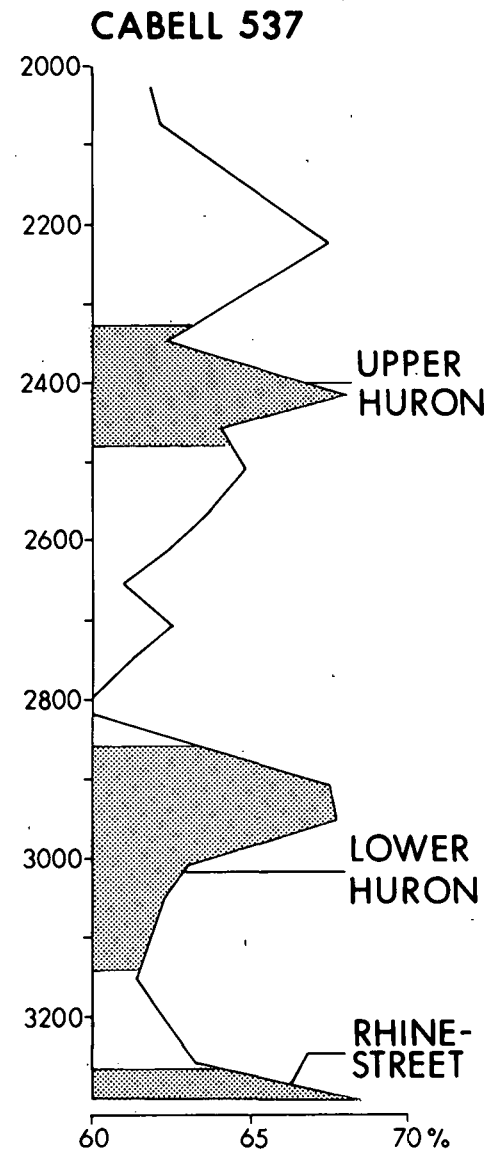
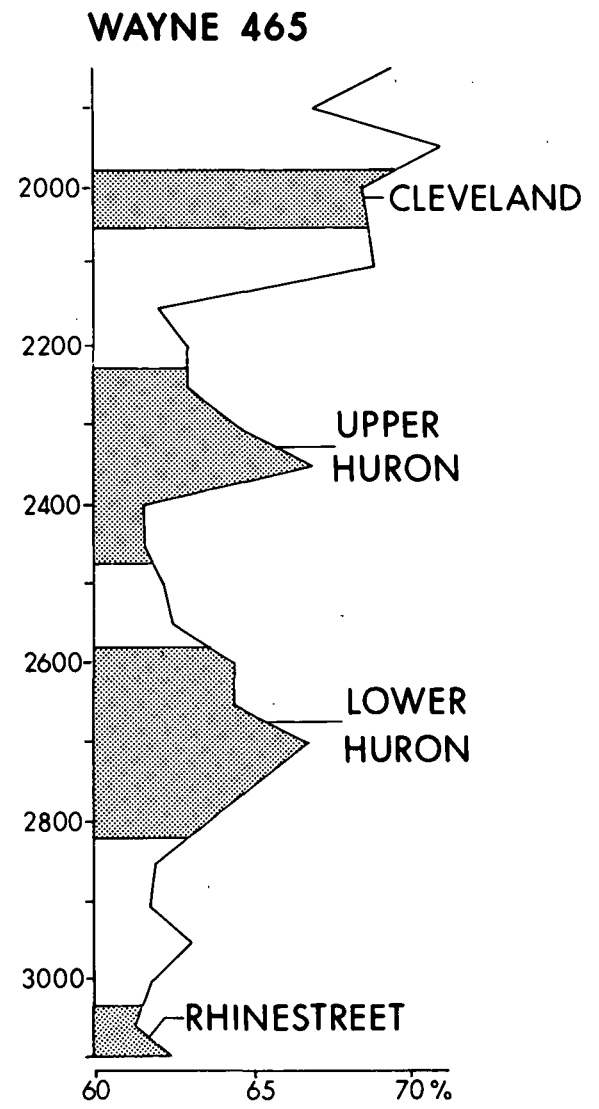
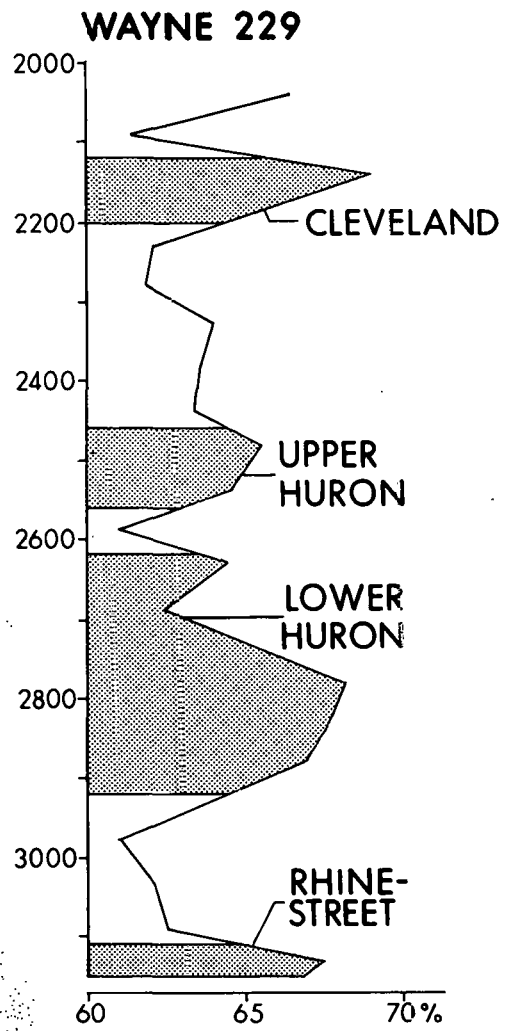


Figure 8. Vertical variation in calcium measured in selected wells in southern West Virginia.

SILICON

Figure 9. Vertical variation in silicon measured in selected wells in southern West Virginia.



in Wayne and Cabell Counties (Figure 9). In these wells, the percentage of silicon has maxima in the black shale throughout the section. This pattern cannot be observed in sections east of Lincoln County. These maxima appear to be related to higher quartz percentages in the black shale.

Titanium has a consistently high correlation with detrital minerals (Vine and Tourtelot, 1970), either in heavy minerals or in clays. Profiles in the eastern part of the study area exhibit some decrease in titanium with increasing depths (Fig. 10). However, the sections in Wayne County and the core in Lincoln County show a break between the gray shale of the Big White Slate and the overlying black shale. The Rhinestreet Shale Member and the lower black shale of the Huron Member possess the lower percentages; but grade into overlying gray shale. These observations suggest a cyclic-like pattern of deposition, one cycle comprising a basal black shale and overlying gray shale and siltstone. This pattern and that in quartz noted above might be manifest only in the west because of a break in sedimentation between the Big White Slate and the lower Huron, or because the western sections do not possess the siltstone found in the Rhinestreet and Big White Slate to the East. Neal (1979) suggests this siltstone to be of turbidite origin.

TITANIUM

①

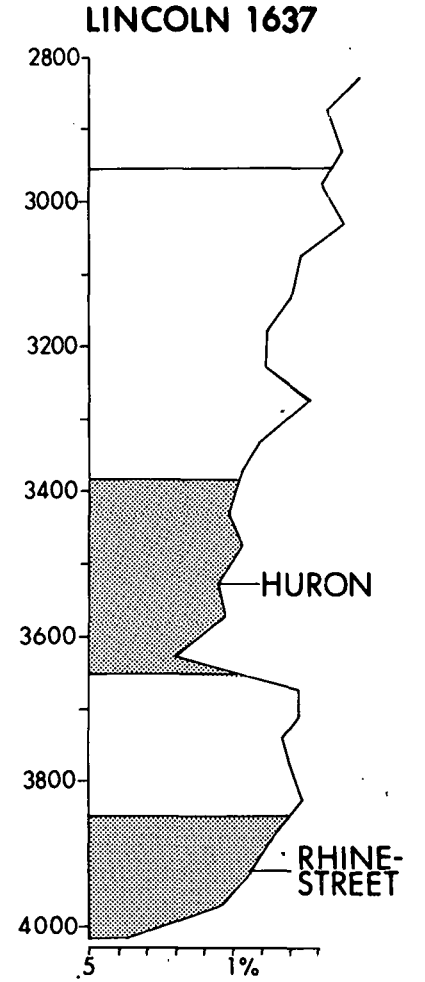
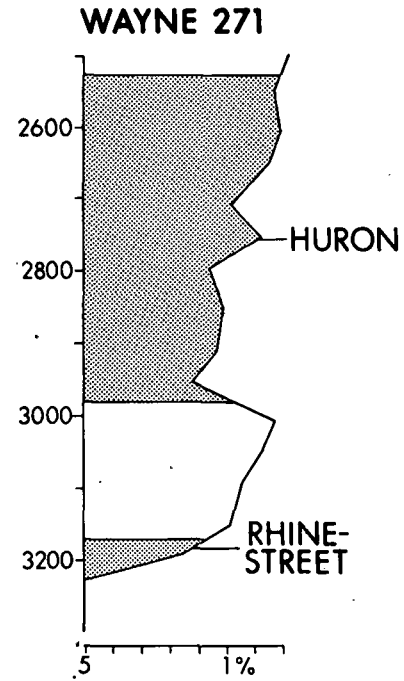
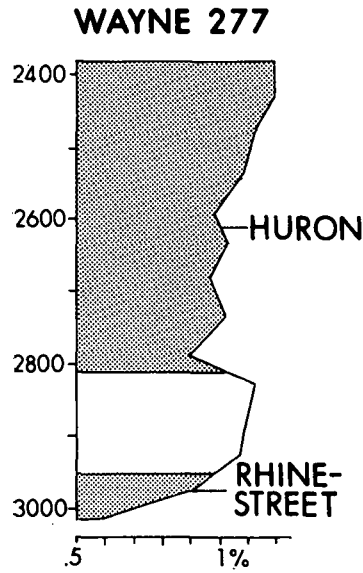
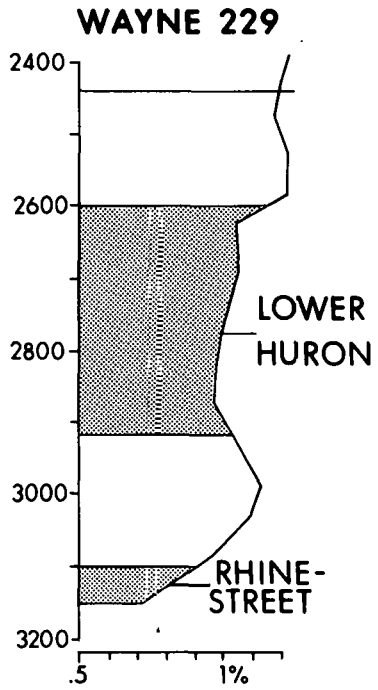
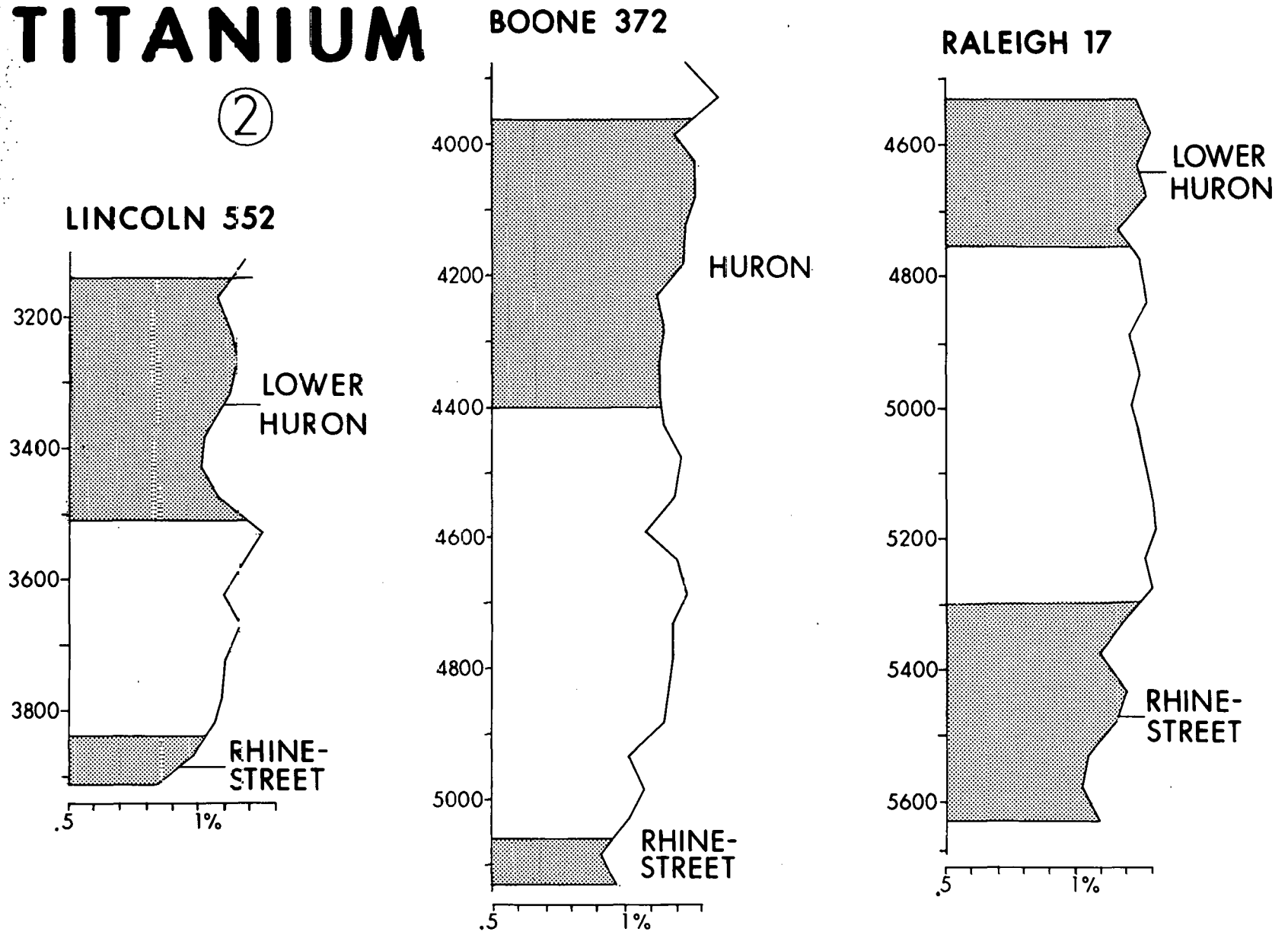


Figure 10-1. Vertical variation in titanium, measured in selected wells in southwestern West Virginia.

TITANIUM

②

Figure 10-2. Vertical variation in titanium, measured in selected wells in southwestern West Virginia.

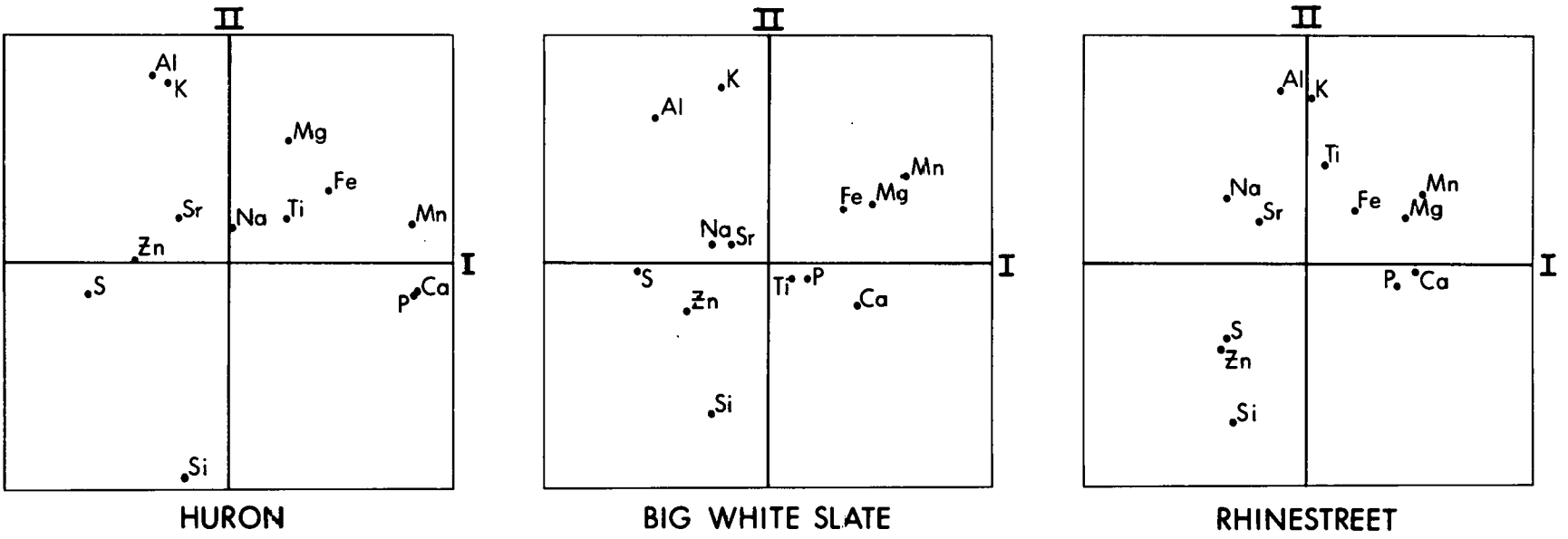


GEOGRAPHIC PATTERNS

FACTOR ANALYSIS The samples in the study area belonged to the three important stratigraphic intervals diagrammed in Figure 3. The multivariate statistical method of factor analysis provides a way to visualize correlations within a set of variables. Factor analysis of samples in each stratigraphic interval gives a visual measure of the stability of interdependencies among variables through time. The data used in these analyses included samples from wells in counties north of the study area, namely, Mason, Putnam, Kanawha, Jackson, Roane and Wood Counties. These wells provide statistically more meaning to the data through the use of larger sampling populations; and also eliminate "edge effects" along the northern regions of the study area in trend surfaces described below. Before the factor analysis and trend surface calculations, the uppermost sample in each stratigraphic interval at each well was dropped from the data set. These samples were likely to have been contaminated by caving of rock above the apparent collection depth of the well cutting. Our goal was to assemble the most representative sampling of each stratigraphic unit. The final data constituted 55 samples from the Rhinestreet Shale Member, 144 samples from the Big White Slate, and 184 samples from the Huron Member.

Before plotting the loadings of the thirteen variables or factors, a Procrustes rotation method (Gower, 1975) was used to rotate the factors to a position of mutual, closest fit. This rotation to a consensus configuration facilitates visual comparison of the results without modifying the angles among the vectors representing variables. The first four axes account for an average of seventy percent of the total variation in each of the three analyses; the major features of the solutions emerge from the first two axes of the rotated configurations (Fig. 11). The first axis has high negative loadings for sulfur and positive loadings for manganese, whereas the second axis separates silicon

Figure 11. Results of factor analyses of data representing three stratigraphic intervals.



from the elements found in clay minerals: aluminum, potassium, magnesium and iron. The observed negative correlation between manganese and sulfur could reflect remobilization and loss of manganese under negative redox potential. Sulfides are common constituents of reduced zones in sediments.

Phosphates, usually Ca-phosphates, are partially solubilized in the reduced zone, (Bonatti et al; 1971) but only the Huron samples showed a negative correlation between phosphorus and sulfur. Calcium and phosphorus correlate highly with each other in two intervals, but do not correlate above zero in the Big White Slate, the only interval with measurable quantities of calcite. Most of the calcium must be associated with phosphorus in the black shale intervals.

Titanium shows a high correlation with aluminum (0.59) in the Rhinestreet interval only. Titanium could substitute for iron or silicon in clay minerals, hence the association. However, the upper units include more immature sediments, and therefore more heavy minerals. In all three units, sulfur correlated negatively with Titanium.

TREND SURFACE ANALYSIS Most of the trend surfaces figured were significant at the .05 level (Table 1); the exceptions -- silicon and aluminum in the Big White Slate, and calcium in the Rhinestreet Shale Member -- were included in the figures for completeness. Final acceptance of these few, nonsignificant trends must await further sampling, but they are nevertheless useful in suggesting geologic trends.

The percentage of aluminum in the Big White Slate and Huron shale increases from east to west, and then declines in the western-most counties; aluminum in the Rhinestreet Shale decreases from the north-east to the west (Fig. 12). As expected, silicon exhibits an inverse relationship with aluminum because these are the two most abundant elements in the main detrital minerals (Fig. 13). Assuming that higher silicon reflects greater deposition of quartz, then during the time represented by Rhinestreet shale, more quartz was deposited in the west than in the eastern regions of the study area.

Table 1. Significance levels of trend surfaces shown in Figures 12-16, expressed as probability of obtaining a larger F statistic.

<u>Element</u>	<u>Stratigraphic units</u>		
	Huron Member	Big White Slate	Rhinestreet Shale Member
Si	.008	.08	.0001
Al	.001	.09	.002
Ca	.003	.0001	.25
Ti	.0001	.0001	.0001
S	.0001	.001	.003

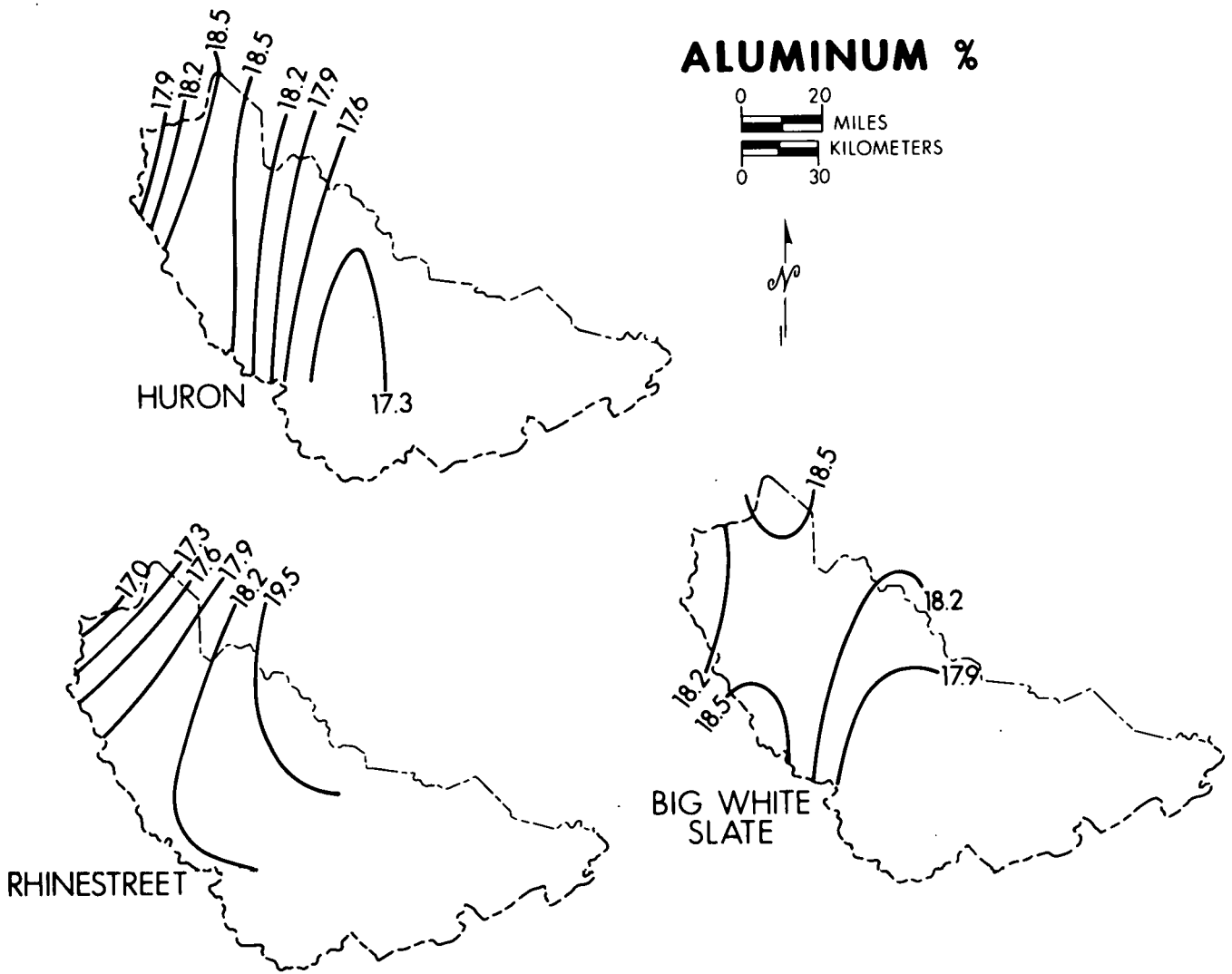


Figure 12. Trend surface of aluminum in each of three stratigraphic units.

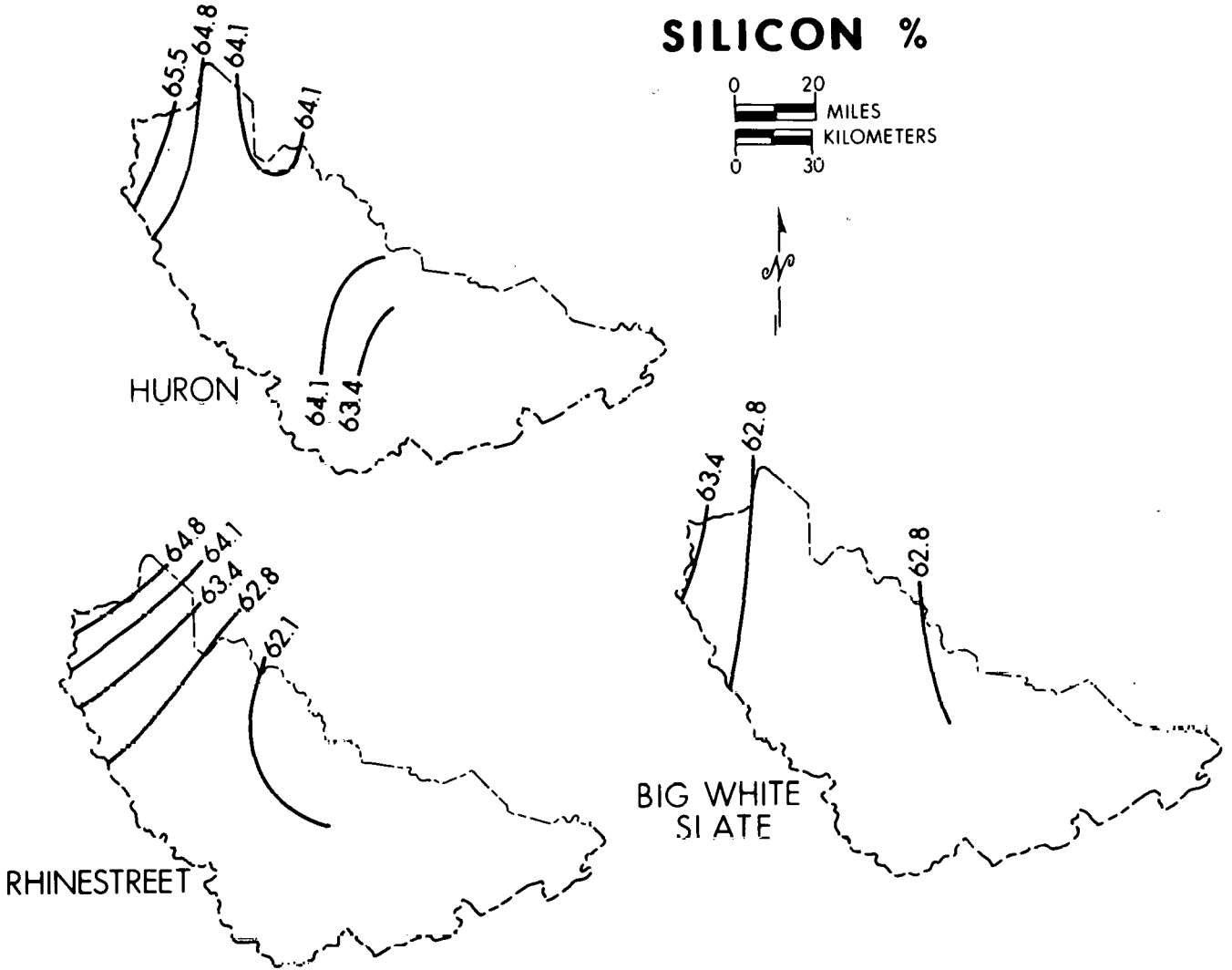


Figure 13. Trend surface of silicon in each of three stratigraphic units.

The Rhinestreet Shale Member rests unconformably on the Onondaga Limestone in Lincoln, Wayne and Cabell counties; to the west, sediments over the Cincinnati Arch may have been subaerially exposed during Rhinestreet deposition. Sediment thus exposed comprised Devonian limestone and Silurian dolomite and some sandstone. One must also consider the increase in silicon percentages in the black shale relative to gray shale in these same wells (Fig. 9). Neal (1979) and Schwietering (1977) argue that the black shales such as those of the Rhinestreet and lower Huron Members were deposited in shallow water; Schwietering (1979, personal communication) suggests the possibility of abundant plant life, acting as a sediment baffle to trap quartz grains. Terrestrial plants can incorporate silica in their tissues (Renton and Cecil, 1979), possibly leading to silica-rich coals; Calamites may have concentrated silica in its stems for subsequent release upon decay. On the other hand, petrographic work shows presence of authigenic chert filling voids in fossil spores (H. King, 1979), personal communication). No inferences about freshwater versus marine environments can be made, however.

The explanation might lie in complex time-relationships within the Rhinestreet Shale Member. Schwietering (1977) considered the black shales to be shallow marine sediments on a shelf far from the eastern source of sediments. During transgression, this black shale facies is deposited farther to the west, to be overlapped by prodeltaic mud and silt. Subsequent infilling of the epicontinental sea would lead to the eastern extent of the black shale facies migrating to the east. The western sections in the study area could include only very late Rhinestreet sediments, containing relatively high quartz percentages. However, one must then explain the actual decrease in silicon percentages with deposition of the gray shale of the overlying Angola Shale Member. The model predicts that those shales should have more quartz than the black shale.

Note that in the eastern part of the state, silicon percentages increase

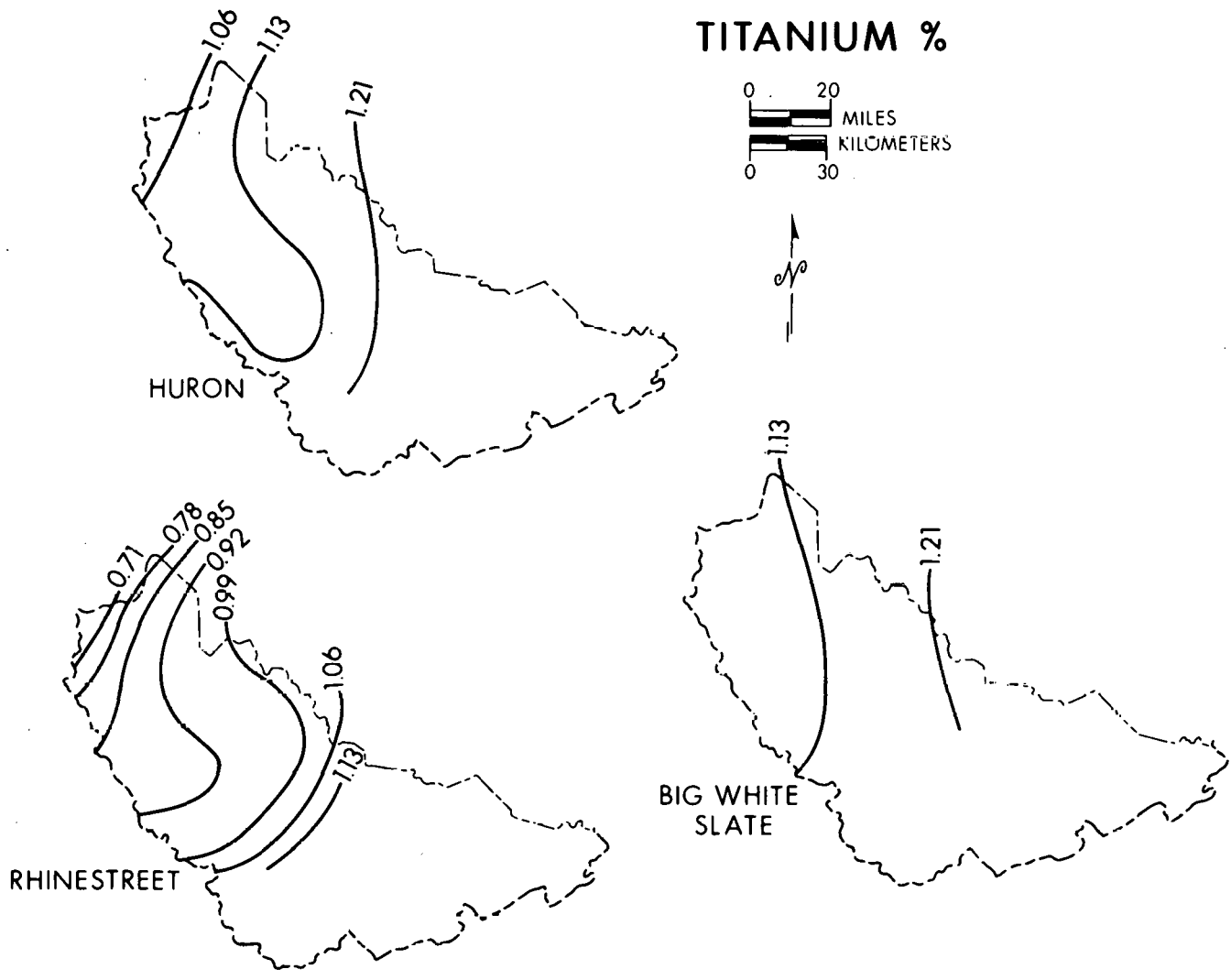


Figure 14. Trend surface of titanium in each of three stratigraphic units.

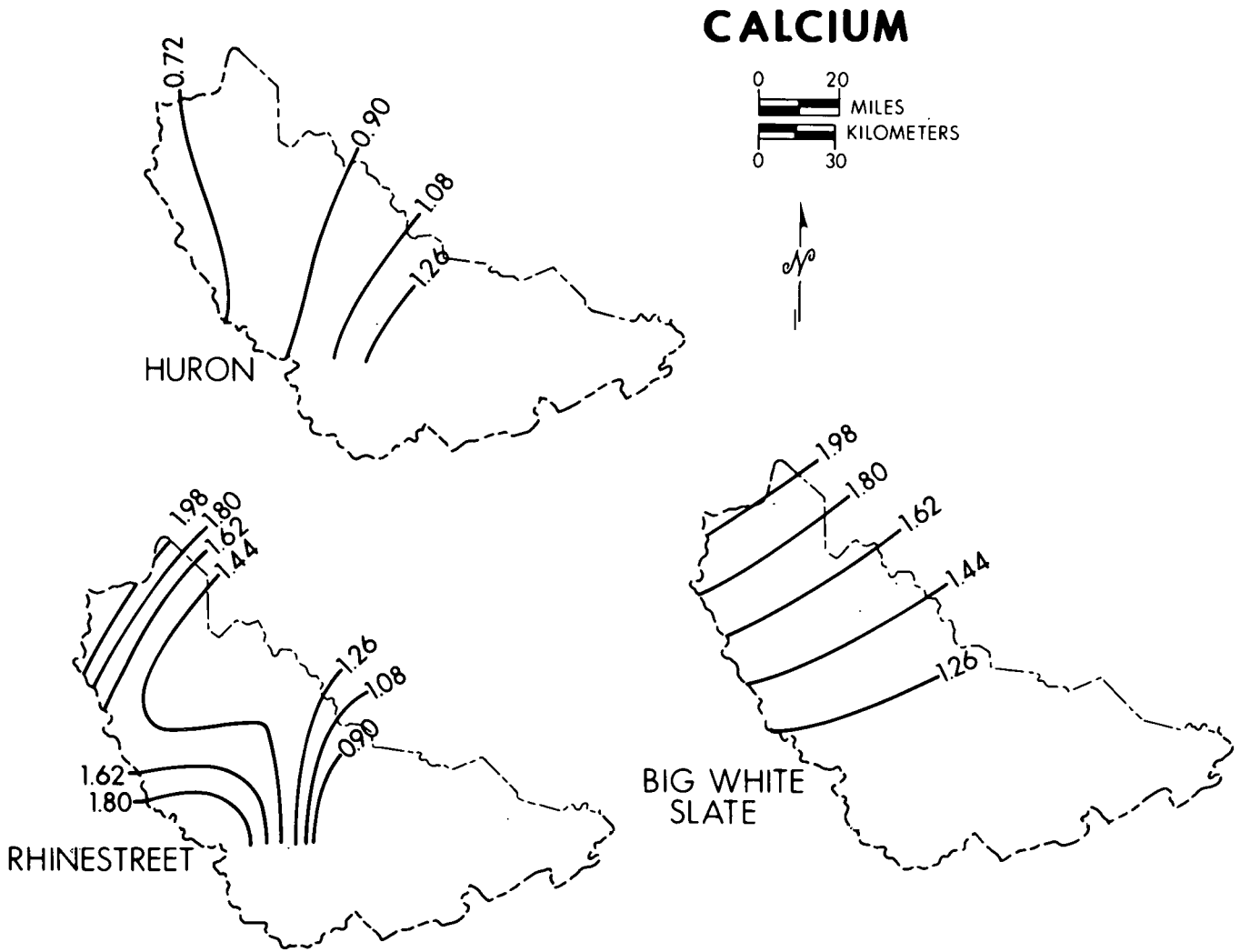


Figure 15. Trend surface of calcium in each of three stratigraphic units.

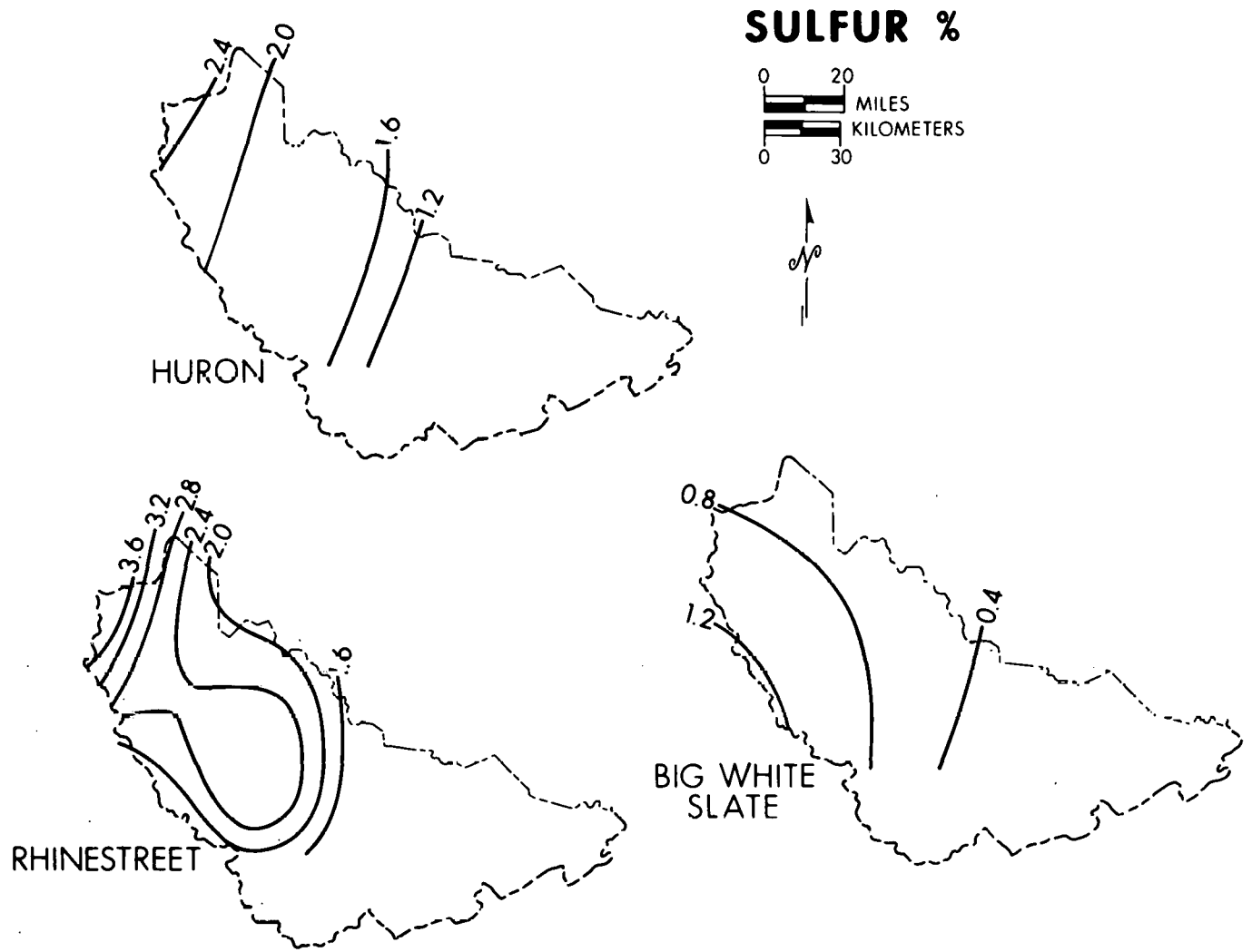


Figure 16. Trend surface of sulfur in each of three stratigraphic units.

upsection, with little or no influence by the "black shale" intervals, more nearly corresponding to the general model of a prograding delta complex. Trend surfaces for titanium, correlating with the detrital minerals, confirm this picture of a sediment source in the east providing heavy minerals (Fig. 14).

As predicted by the factor analysis, trend surfaces for potassium and magnesium parallel the distribution of aluminum. Similarly, phosphorus distributions resemble those for calcium.

A westward source of calcium appears reasonable from trend surface analysis of calcium percentages (Fig. 15) for the Rhinestreet and Big White Slate intervals. The more calcareous nature of the Big White Slate as compared with the black shales is apparent from the trend surface. Calcium shows an opposite trend in the black shales of the Huron Member, decreasing to the west.

Sulfur percentages correlate with quantities of organic matter in the Devonian shale, and can be used to study organic facies (Erwin, 1978). Most of the sulfur occurs in pyrite, although sphalerite has been observed (H. King, 1979, personal communication) and sulfur occurring in organic compounds is possible. Sulfur increases from southeast to northwest throughout the section, except in the sulfur-poor Big White Slate, in which the trend is still increasing from east to west (Fig. 16). Sulfur bears a nearly inverse relationship with calcium in the Huron interval. These trends do not necessarily mean that the deposition of organic matter was slower in the eastern part of the study area, but could reflect a greater influx of silt by turbidity currents. In Boone County, the black shale of the lower Huron Member forms two main tongues above and below a tongue of gray siltstone and shale (Fig. 3). As noted in the discussion on stratigraphic patterns, sulfur exhibits high percentages in gray shale correlative with black shale to the west. If sulfur percentages correspond to patterns in the biotic communities during the lower Huron deposition, the environmental conditions favoring sulfur deposition extended across the whole of the study area and alternated in the east with episodes of differing biotic or depositional character.

SUMMARY AND CONCLUSIONS

The distributions of the ubiquitous elements, silicon and aluminum, show gradual trends through the stratigraphic column of most wells. Other elements such as calcite, sulfur, and titanium show abrupt changes in abundance at stratigraphic boundaries. Those boundaries that do not coincide with abrupt elemental changes may instruct as much as those that do, for instance, the gradual increase in titanium from the Rhinestreet through the Big White Slate. Important geographic trends appear to be east to west; e.g. decrease in titanium and an increase in sulfur to the west; decrease in silicon from the east to the central part of the study area, then an increase further west. The north-south-trending contours of the polynomial surfaces parallel roughly the axis of the Appalachian basin, from northeast to southwest. In conjunction with observed vertical trends in detrital minerals, these trends support the accepted picture of a prograding delta complex during Late Devonian time. The observed patterns in elemental abundances leave unresolved the controversy of whether the black shale of the Rhinestreet Shale Member and the lower Huron Member represent shallow or deep water sedimentation.

The spacing of the samples wells does not permit the geochemical evaluation of specific wells favorable to production of gas. Instead, the data collected give a database for comparison of local anomalies or trends related to production. On a regional basis, the westwardly increase in sulfur to levels much greater than in the eastern counties of Summers and Monroe mirrors the presence of abundant gas fields in the western counties. However, the trend in sulfur content corresponds as well with the areas of thick black shales, a necessary prerequisite to gas production (Neal, 1979). Insofar as knowledge of the mode of formation of the black shale aids exploration, the geochemical data pose some intriguing questions e.g. the increase in silicon abundance west of Boone

County, counter to the usual evidences of an eastward source of sediments. Does this silicon represent detrital quartz, or authigenic chert, or a plant origin?

The geochemical analyses of very fine-grained sediments provide the type objective survey that petrographic work cannot give even with many more days or weeks of labor. Although one cannot assign elements to specific mineral phases, elemental analyses possess a much higher accuracy and precision than the determination of actual mineralogical abundances through X-ray diffraction or petrographic methods. Petrography becomes important once the elemental analyses suggest specific problems.

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