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# Chemical analysis and geochemical associations in Devonian black shale core samples from Martin County, Kentucky; Carroll and Washington Counties, Ohio; Wise County, Virginia; and Overton County, Tennessee

by

Joel S. Leventhal

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## Contents

Page

Abstract.............................................................. 1

Introduction.......................................................... 2

Literature review..................................................... 2

Sample localities..................................................... 6

Experimental methods and techniques................................... 6

Results of analytical determinations.................................. 8

Covariance between elements........................................... 8

  S and other trace elements.......................................... 17

  Organic C and trace elements........................................ 20

  Other element pairs................................................. 28

Associations of trace elements with C and S........................... 28

  Down-hole plots..................................................... 28

  $CaCO_3$ and $PO_4$................................................. 36

  Closely-spaced samples showing black to gray transitions............ 38

Sediment deposition rate relative to trace-element contents........... 42

Discussion of statistical treatment and misleading results............ 44

References............................................................ 50

# Illustrations

Page

Figure 1. Map showing regional distribution of Upper Devonian black shale (dot pattern) in eastern United States and locations of samples: Co and Wo, Carroll and Washington Counties, Ohio; T, Overton County, Tenn.; M, Martin County, Ky.; W, Wise County, Va. Solid line or dashed line is approximate limit of Upper Devonian sedimentary rocks.............................. 7

2. Mean abundances of selected constituents of Devonian black shales............................................ 15

3. Diagram showing plot of $Fe_2O_3$ vs. S. Solid line is the linear-least-squares-fit of the data. The dashed line is the stoichiometry for $FeS_2$ (pyrite)............ 18

4. Diagram showing plot of Wise County, Va., see fig. 3 caption.............................................. 18

5. Diagram showing plot of S vs. Zn for samples from Martin County, Ky. The line is the linear-least-square fit of the data............................ 19

6. Diagram showing plot of S vs. Hg for samples from Wise County, Va. The line is the linear-least-square fit of the data............................ 19

7. Diagram showing plot of S vs. Mo for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.................... 21

Illustrations--continued

Page

8. Diagram showing plot of S vs. As for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.................... 21

9. Diagram showing plot of organic C vs. V for samples from Wise County, Va. The line is the linear-least-square fit of the data................................ 22

10. Diagram showing plot of organic C vs. Mo for samples from Wise County, Va. The line is the linear-least-square fit of the data................................ 22

11. Diagram showing plot of organic C vs. Mo for samples from Martin County, Ky. The line is the linear-least-square fit of the data................................ 23

12. Diagram showing plot of organic C vs. Zn for samples from Martin County, Ky. The line is the linear-least square fit of the data................................ 23

13. Diagram showing plot of organic C vs. Hg for samples from Overton County, Tenn. The line is the linear-least-square fit of the data......................... 25

14. Diagram showing plot of organic C vs. Hg for samples from Wise County, Va. The line is the linear-least square fit of the data................................ 25

15. Diagram showing plot of organic C vs. As for samples from Overton County, Tenn. The line is the linear-least-square fit of the data......................... 26

Illustrations--continued

Page

16. Diagram showing plot of organic C vs. Ni for samples from Martin County Ky. The line is the linear-least-square fit of the data.................................... 26

17. Diagram showing plot of organic C vs. Ni for samples from Overton County, Tenn. The line is the linear-least-square fit of the data............................ 27

18. Diagram showing plot of organic C vs. Ni for samples from Perry County, Ky. and Cattaraugus, County, N.Y. The line is the linear-least-square fit of the data..... 27

19. Diagram showing plot of Ni vs. $Fe_2O_3$ for samples from Overton County, Tenn. The line is the linear-least-square fit of the data............................ 29

20. Diagram showing plot of $SiO_2$ vs. $TiO_2$ for samples from Overton County, Tenn. The line is the linear-least-square fit of the data............................ 29

21. Diagram showing plot of carbonate C vs. MnO for samples from Martin, Wise and Overton Counties. The line is the linear-least-square fit of the data.............. 30

22. Down-hole plot of selected elements from Martin County, Ky. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration.................................... 31

Illustrations--continued

Page

23. Down-hole plot of selected elements from Wise County, Va. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration. Dashed lines indicate unsampled interval.................................... 32

24. Down-hole plot of selected elements from Washington County, Ohio. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration............. 33

25. Down-hole plot of selected elements from Overton County, Tenn. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration.................................. 34

26. Down-hole plot of selected elements from Carroll County, Ohio. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration Dashed lines indicate unsampled interval................................................ 35

27. Diagram showing several statistical results in samples from Wise County, Va., for organic C vs. V:............. 45

# Tables

Page

Table 1. Quantitative results of analyses of samples from Martin County, Kentucky.................................... 9

2. Quantitative results of analyses of samples from Washington, and Carroll Counties, Ohio...................... 10

3. Quantitative results of analyses of samples from Wise County, Va............................................. 11

4. Quantitative results of analyses of samples from Overton County, Tenn........ ............................... 12

5. Range in abundance and mean abundance of major constituents of Devonian shales............................. 13

6. Range in abundance and mean abundance of selected trace elements in Devonian shales...................... ....14

7. Semiquantitative determinations of selected elements (range and mean values) from samples of Devonian shales............ 16

8. Chemical analysis for certain elements of interest in samples from Overton County, Tenn.......................... 37

9. Element values and ratios of elements in samples from each side of two black shale-gray shale boundaries, Carroll County, Ohio.................................. 39

10. Ratio of trace elements to organic C and S in Devonian shale samples from five cores........................ 43

11. Statistical relationship for certain elements in Devonian shales............................................ 47

12. Statistical data for elements in shale from Leventhal (1978a)............................................... 48

13. Correlation coefficients (r) for pairs of elements from the samples studied from five locations................. 49

# Chemical analysis of and geochemical associations in Devonian black-shale core samples from Martin County, Kentucky; Carroll and Washington Counties, Ohio; Wise County, Virginia; and Overton County, Tennessee

by Joel S. Leventhal

## Abstract

Core samples from Devonian shales from five localities in the Appalachian Basin have been analyzed for major, minor, and trace constituents. The contents of major elements are rather similar; however, the minor constituents, organic C, S, $PO_4$, and $CO_3$, show variations by a factor of 10. Trace elements Mo, Ni, Cu, V, Co, U, Zn, Hg, As, and Mn show variations that can be related graphically and statistically to the minor constituents. Down-hole plots show the relationships most clearly. Mn is associated with $CO_3$ content, the other trace elements are strongly controlled by organic C. Amounts of organic C are generally in the range of 3-6 percent, and S is in the range of 2-5 percent. Trace-element amounts show the following general ranges (ppm, parts per million): Co, 20-40; Cu, 40-70; U, 10-40; As, 20-40, V, 150-300; Ni, 80-150; high values are as much as twice these values. The organic C was probably the concentrating agent, whereas the organic C and sulfide S created an environment for preservation or immobilization of trace elements. Closely spaced samples showing an abrupt transition in color from black to gray and gray to black shale show similar effects of trace-element changes, that is, black shale contains enhanced amounts of organic C and trace elements. Ratios of trace elements to organic C or sulfide S were relatively constant even though deposition rates varied from 10 to 300 meters in 5 million years.

## Introduction

The U. S. Geological Survey in cooperation with Morgantown Energy Technology Center, U.S. Department of Energy, is characterizing the Devonian age black shales of the Appalachian basin as part of the Eastern Gas Shales program under interagency agreement EX-76-C-01-2278.

The chemical data presented in this report can be used for resource assessment of such elements as U and V and can be used to recognize environmental problems caused by such elements as Hg. This chemical data can also be useful in stratigraphic correlations, geochemical assessment of source rocks, and characterization of depositional environment for oil and gas potential or resources.

The chemical data and geochemical controls and affinites of Cd, Co, Hg, Mo, Ni, V, Zn, Mn, Cu, Th, U, and As in black shales are presented in this report. Earlier reports dealt with U, Th, C, and S (Leventhal and Goldhaber, 1978) and major, minor, and trace elements (Leventhal, 1978a) from Perry County, Ky., Jackson and Lincoln Counties, W. Va., and Cattaraugus County, N. Y. This paper does not consider U and organic C relationships (Leventhal, unpublished data, 1979) or organic C and sulfide S relationships (Leventhal, 1979).

## Literature review

A selective review of the literature was made for studies on trace-element geochemistry of organic-rich marine shales. Studies on the geochemistry of recent marine sediments were excluded.

Le Riche (1959) studied trace elements in two cores from Lower Lias (marine) shales in England. Down-hole (core) plots show associations of organic C with Mo, V, Cu, and Ni. However, on the basis of successive chemical-leach methods, he reported that Mo resided in the silicate and pyrite fraction and V in the silicate fraction. Co was not clearly associated with organic material. Although he did not mention it, it is possible that the down-hole associations of the samples reflect original concentration of the metals by organic material, whereas his chemical dissolution data showed the present residence of the elements, after diagenetic processes may have mobilized them from the organic material to a sulfide phase.

H. A. Tourtelot (1964) examined nonmarine, nearshore marine, and offshore marine organic-rich shales of Cretaceous age. Offshore marine shales showed the highest contents of As, Cr, Cu, Mo, Se, V, and Zn, which were associated with the organic C content. Tourtelot stressed the importance of sorption of trace elements from seawater on to organic C and clay as it was being transported from the land to the sea.

Curtis (1964) presented geochemical results from cores of a marine shale, finding that trace elements V, Cr, Mn, Nr, Cu, Co, Mo, and U showed a general association with what he defined as "organic C" content. However, he did not actually determine organic C, but ashed the sample at 375°C so undoubtedly considerable sulfide was also lost. He attributed the association of trace elements to films of organic C on clay particles; these films could have adsorbed or formed complexes with the various trace elements. The statistical correlation of "organic matter" to Cu and U is significant; for other elements, especially Mn and Cr, the correlation may not be true.

Wedepohl (1964) presented an extensive literature review of the geochemistry of metalliferous sediments and compared them to the Permian age Kupferschiefer of Germany. In the Kupferschiefer, the content of V, Cr, Ni, Mo, and Co is related to organic C. He proposed that the seawater contained enhanced amounts of the metals on the basis of his calculations. His data showed covariance between Sr and Mn and carbonate. The affinity of metals and organic C is shown in down-hole (core) plots and metal vs. organic C plots. Although S content was not plotted, he noted affinity of Cu, Zn, Pb, and As with pyrite.

Brongersma-Sanders (1965) proposed that the metals of the Kupferschiefer were supplied by normal seawater. She overcame previous objections (Wedepohl, 1964) to this source by postulating an estuary trapping mechanism which allows for inflow at depth and outflow and evaporation at the surface. She proposed that the increased circulation of the estuary, along with arid conditions, little detrital input, and high organic productivity can give a source and concentration necessary to account for elements in the sediment.

Vine and E. B. Tourtelot (1970) summarized their work (Vine and others, 1969) on the geochemistry of black shales. Using 779 samples from 20 black-shale formations, they applied statistical techniques to find element associations. Their statistical methods included frequency distributions, coefficients of correlation for each pair of constituents and correlation matrices to identify groups. They found the organic fractions of the shale to be enriched in Ag, Mo, Zn, Ni, Cu, Cr, V and sometimes enriched in Co, Pb, La, Se, U, and Tl. They found the $CO_3$ fraction to be enriched in Ca, Mg, Mn, and Sr. The source of the metals was ascribed to seawater containing higher than normal concentrations of these elements (following the suggestion of Wedepohl, 1964). The concentration of the organic matter was hypothesized to be from the accumulation, decay, and burial of living organisms. In general, S data were not available, so they were not able to assess the relative importance of S or its relationship to the organic C.

Tardy (1975) used multiple regression and factor analysis on the data of Vine and E. B. Tourtelot (1970). He found Mo, Y, La, V, Cr, Co, Ni, Cu, Zn, and Ag in the organic fraction; Co, Ni, Mo, Ca, and Zn were found in the sulfide fraction. The $PO_4$ fraction contained V, Sr, Y, La, and Cr, and the $CO_3$ fraction contained Zn and Sr. Be, Ba, Ga, Se, and Zr occur chiefly in the detrital fraction.

Recently, Holland and Tulcanaza (1978) presented data on trace elements in black shales. They showed that several of these shales had metal enrichments for Pb, Cu, Ni and V that were $10^5$ times greater than seawater. Rather than being related to crustal abundance, the abundance of these elements in the shales was related to seawater content. They reported, however, that Zn and Mo were not as enriched as other metals. The $10^5$-times enrichment could be obtained by removing all the elements in a 1-$cm^2$ column which is $10^5$ cm (1000 m) deep. If the basin turnover time is 1,000 years, then 1 cm thickness of sediment deposited in this time will have $10^5$ times the seawater concentration. The Suzak (Eocene) shale of central Asia is enriched in Re, Mo, Cd, Se, V, Br, Sb, Ag, Ni, Cu, Cr, Zn, and Pb. All these elements have highly insoluble sulfides and oxides or are strongly complexed to organic matter, which accounts for their enrichment. However, the 1,000-year turnover time requires that all the metal be removed to the 1-cm-thick newly formed sediment. Actually, much less than 1 cm may have been deposited; if only 1 mm is deposited (this is still 1 m in $10^6$ years), then only 10 percent of the metal needs to be removed in 1000 years, or all the metal could be removed in a 100 year turnover, or the water only needs to be 100 m deep.

Extensive work has been done on the mineralogy and geochemistry of Upper Devonian black shales of the Appalachian basin; the reader is referred to Strahl (1958), Bates and Strahl (1957), and Brown (1975). Specific work on U in the Chattanooga Shale is reported in Breger and Brown (1962, 1963) and Swanson (1960, 1961).

The regional geology of the Appalachian basin was reviewed by Oliver and others (1968).

## Sample localities

The core samples studied are from the following locations (fig. 1):

Martin County, Ky., 19 samples, cored interval 2,479 to 3,379 ft, API (American Petroleum Institute) well no. 16-159-31020.

Carroll County, Ohio, 10 samples, 2,081-2,191 and 3,081-3,180 ft depth, API well no. 34-019-20835.

Washington County, Ohio, 7 samples, 3,491-3,717 ft, API well no. 34-167-23521.

Wise County, Va., 12 samples, 4,887-4,968 ft and 5,241-5,471 ft, API well no. 45-035-21369.

Overton County, Tenn., 14 samples, 181-207 ft, taken at Tennessee coordinates 708,550 N and 2,154,750 E, obtained through R. C. Milici from D. D. Harper of American Smelting and Refining Co., API well no. 41-133-00000.

## Experimental methods and techniques

Analytical work was provided by Van Shaw, Jim Crock, Paul Briggs, Leon Bradley, Jim Thomas, Celeste Ellis, Jim Baker, and others of the U.S. Geological Survey, Denver.

The analytical techniques and precision have been discussed by Leventhal and others (1978). Total C and S were measured by high-temperature combustion, carbonate C by titration, and organic C by difference. U was measured by delayed neutron analysis. $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $TiO_2$, $K_2O$, MnO, and As were measured by X-ray fluorescence. Ni, Cu, Cd, Zn, Co, and V were measured by atomic-absorption spectrophotometry. Hg was measured by flameless atomic-absorption spectrophotometry. Mo was determined colorimetrically. Ash was measured gravimetrically. Data for other elements were by

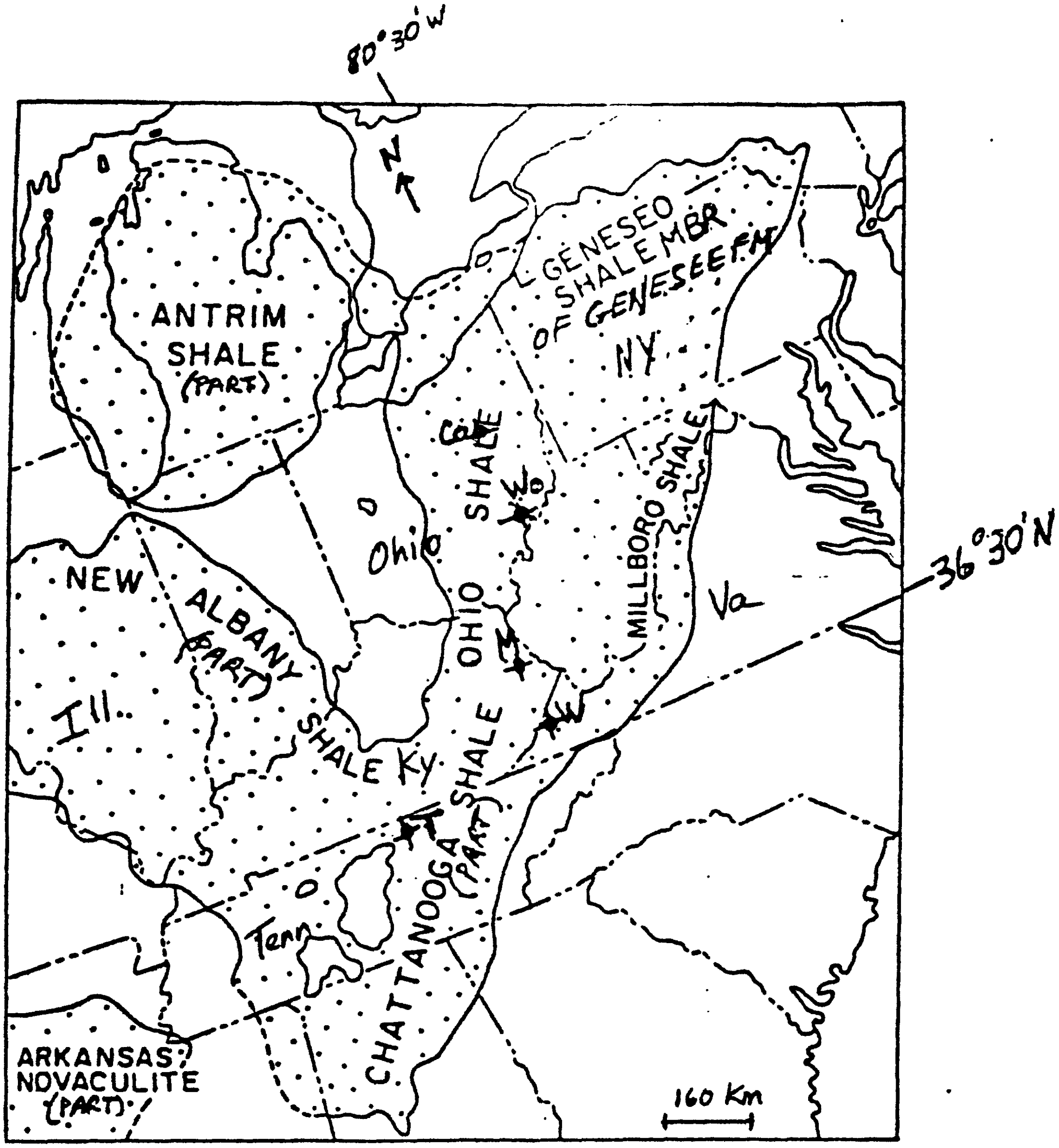


Figure 1. Map showing regional distribution of Upper Devonian black shale (dot pattern) in eastern United States and locations of samples: ✦ Co and Wo, Carroll and Washington Counties, Ohio; T, Overton County, Tenn.; M, Martin County, Ky.; W, Wise County, Va. Solid line or dashed line is approximate limit of Upper Devonian sedimentary rocks.

semiquantitative emission spectroscopy or X-ray fluorescence (sulfide group) and are given only as ranges and mean values because of poorer precision. In general, based on splits and replicates, the results are precise to the following degree (in percent):

| | |
|---|---|
| ±1 | Ash |
| ±2-3 | U, S, C (total), C (organic), $SiO_2$ |
| ±4-7 | Ni, Cu, Cd, Zn, Co, Hg, C (carbonate), V MnO |
| ±10 | Mo, $Al_2O_3$, CaO, $TiO_2$, $Fe_2O_3$, $K_2O$, As. |

## Results of analytical determinations

The results for chemical analysis of samples from Martin County, Ky., are given in table 1; Washington and Carroll Counties, Ohio, in table 2; Wise County, Va., in table 3, and for Overton County, Tenn., in table 4.

The means and ranges of abundance for certain elements or oxides are given in tables 5 and 6. The mean abundances are shown diagramatically on figure 2 (Leventhal, 1978b).

Table 7 lists values of elements determined only by six-step semiquantitative spectrographic analysis and sulfide-group X-ray fluorescence. The results are precise to ±33 percent, so only ranges and average values are listed.

## Covariance between elements

S and C are two minor constituents of black shale that have been shown to be related to variations in trace elements (Leventhal, 1978a; Vine and E. B. Tourtelot, 1970). Knowledge of the relationships between S and C and other elements may help in understanding the occurrence, distribution, and (or) geochemistry of the other elements in the black shales. Some of the expected relationships were found, others were not; all samples did not show the same analytical results. See the section on "Discussion of statistical treatment results of analyses of samples from Martin County, Kentucky.

[--, no data] [<, less than]

| Sample | Depth feet | On the ash in percent | | | | | | | On the raw sample in ppm- | | | | | | | | On the raw sample -in percent | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | K$_2$O | CaO | TiO$_2$ | MnO | Co | Mo | Ni | V | Zn | Hg | As | U | S | C Organic | C CO$_3$ |
| M-1 | 2479 | 58 | 12 | 5.7 | 2.8 | .50 | .78 | <.050 | 12 | 6 | 72 | 250 | 155 | .07 | 63 | 7.1 | 3.16 | 3.38 | .07 |
| 2 | 2529 | 54 | 18 | 5.2 | 4.1 | .16 | .93 | <.050 | 21 | < 2 | 63 | 170 | 91 | .04 | 35 | 3.8 | 1.15 | .98 | .06 |
| 3 | 2579 | 55 | 19 | 4.1 | 4.1 | .13 | .96 | <.050 | 14 | < 2 | 50 | 170 | 60 | .03 | 14 | 4.0 | .20 | .23 | .07 |
| 4 | 2629 | 31 | 9.9 | 23 | 2.4 | 3.1 | .46 | .27 | 15 | < 2 | 38 | 100 | 39 | .03 | 2.9 | 2.7 | .09 | .63 | 4.69 |
| 5 | 2679 | 56 | 13 | 5.0 | 3.0 | .41 | .78 | <.050 | 26 | 34 | 100 | 160 | 133 | .07 | 29 | 18.2 | 2.28 | 3.47 | .07 |
| 6 | 2739 | 55 | 14 | 6.3 | 3.5 | .27 | .80 | <.050 | 21 | 13 | 67 | 120 | 86 | .04 | 45 | 7.1 | 3.16 | 1.24 | .07 |
| 7 | 2779 | 51 | 17 | 8.2 | 4.5 | 1.5 | .84 | .091 | 14 | < 2 | 47 | 120 | 69 | .03 | 2.8 | 3.3 | .14 | .24 | .87 |
| 8 | 2829 | 48 | 17 | 9.5 | 4.2 | .68 | .80 | .091 | 11 | 4 | 44 | 130 | 77 | .02 | -- | 4.3 | .17 | .54 | .98 |
| 9 | 2879 | 53 | 16 | 6.5 | 3.9 | .47 | .77 | <.050 | 23 | 27 | 66 | 120 | 110 | .04 | 30 | 9.2 | 2.35 | 2.49 | .11 |
| 10 | 2979 | 55 | 13 | 5.2 | 3.4 | .46 | .72 | <.050 | 32 | 57 | 91 | 140 | 136 | .05 | 36 | 22.5 | 2.44 | 4.25 | .07 |
| 11 | 3029 | 52 | 14 | 6.1 | 3.4 | 1.1 | .78 | <.050 | 31 | 57 | 103 | 190 | 152 | .05 | 27 | 18.6 | 2.40 | 5.28 | .26 |
| 12 | 3079 | 51 | 15 | 6.4 | 3.6 | .48 | .75 | <.050 | 31 | 145 | 87 | 150 | 176 | .06 | -- | 37.7 | 2.40 | 7.19 | .07 |
| 13 | 3129 | 54 | 16 | 5.8 | 4.0 | .43 | .88 | <.050 | 22 | 10 | 64 | 120 | 68 | .04 | 19 | 5.8 | 1.10 | .42 | .13 |
| 14a | 3179 | 39 | 13 | 17. | 3.6 | 2.3 | .60 | .27 | 12 | < 2 | 47 | 110 | 64 | .02 | 2.4 | 2.1 | .08 | .21 | 3.02 |
| 14b | 3179 | 50 | 16 | 9. | 4.4 | .87 | .84 | .092 | 14 | < 2 | 55 | 130 | 72 | .02 | 2.1 | 2.9 | .06 | .18 | .96 |
| 15 | 3229 | 55 | 16 | 6.3 | 3.6 | .27 | .83 | <.050 | 24 | 24 | 66 | 140 | 116 | .04 | 39 | 11.0 | 2.58 | 2.57 | .14 |
| 16 | 3279 | 54 | 16 | 6.2 | 4.3 | .36 | .82 | <.050 | 24 | 6 | 88 | 140 | 74 | .07 | 29 | 12.2 | 4.07 | 1.37 | .07 |
| 17 | 3329 | 43 | 12 | 16. | 3.6 | .41 | .62 | <.050 | 25 | 140 | 404 | 230 | 4360 | .11 | 180 | 20.8 | 9.89 | 3.28 | .07 |
| 18 | 3379 | 56 | 15 | 4.7 | 4.4 | .41 | .65 | <.050 | 17 | 40 | 107 | 350 | 63 | .09 | 19 | 12.1 | 1.92 | 3.45 | .07 |

Table 2. Quantitative results of analyses of samples from Washington, and Carroll Counties, Ohio. [--, not analyzed]

| | | On the ash in percent | | | | | | | On the ash in ppm | | | | | | | On the raw sample | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | | | in ppm | | | | in percent | | |
| Sample | Depth ft | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $K_2O$ | CaO | $TiO_2$ | Ash | Cd | Co | Mo | Ni | Zn | Mn | Cu | V | Hg | As | U | S | C Organ | C $CO_3$ |
| Washington County, Ohio | | | | | | | | | | | | | | | | | | | | | | |
| Wa-1 | 3491 | 55. | 20. | 6.0 | 3.6 | .36 | .83 | 95.6 | <1 | 23 | 3 | 75 | 77 | 600 | 42 | 202 | .03 | 23 | 4.0 | .97 | .34 | .35 |
| 2 | 3525 | 54. | 17. | 8.1 | 3.4 | .41 | .76 | 95.2 | <1 | 25 | 5 | 80 | 122 | 290 | 55 | 109 | .04 | 42 | 4.9 | 4.77 | .73 | .14 |
| 3 | 3556 | 57. | 17. | 4.9 | 3.3 | .22 | .79 | 94.3 | <1 | 27 | 12 | 90 | 60 | 260 | 47 | 174 | .05 | 26 | 7.5 | 2.05 | 2.62 | <.01 |
| 4 | 3592 | 57. | 16. | 4.3 | 3.1 | .27 | .69 | 95.4 | <1 | 24 | 23 | 85 | 113 | 230 | 53 | 163 | .05 | 30 | 12.2 | 1.74 | 1.98 | <.01 |
| 5 | 3630 | 57. | 18. | 5.4 | 3.4 | .70 | .82 | 96.4 | <1 | 22 | <2 | 70 | 132 | 360 | 39 | 168 | .02 | 20 | 5.1 | 1.46 | .35 | .21 |
| 6 | 3679.6 | 51. | 16. | 4.7 | 3.4 | .22 | .71 | 94.4 | <1 | 30 | 39 | 90 | 122 | 265 | 52 | 156 | .05 | 25 | 8.4 | 2.10 | 2.59 | <.01 |
| 7 | 3713 | 61. | 17. | 4.2 | 3.0 | 1.5 | .82 | 96.6 | <1 | 18 | 4 | 60 | 62 | 570 | 34 | 127 | .03 | 20 | 4.1 | .67 | .03 | .49 |
| Carroll County, Ohio | | | | | | | | | | | | | | | | | | | | | | |
| C-1 | 2081 | 59. | 17. | 5.3 | 3.0 | .31 | .78 | 96.9 | <1 | 19 | <2 | 75 | 116 | 740 | 51 | 85 | .03 | 8.8 | 3.6 | .74 | .23 | .14 |
| 2 | 2109 | 54. | 18. | 6.8 | 3.7 | .15 | .92 | 96.7 | <1 | 28 | 5 | 105 | 52 | 330 | 51 | 145 | .04 | 27 | 4.1 | 2.20 | .41 | <.01 |
| 3 | 2191 | 59. | 19. | 5.2 | 3.8 | .17 | .81 | 96.8 | <1 | 18 | <2 | 70 | 148 | 315 | 39 | 179 | .03 | 17 | 4.3 | .71 | .27 | .07 |
| 4 | 3081 | 62. | 15. | 4.0 | 3.2 | .19 | .66 | 93.0 | <1 | 17 | 73 | 130 | 52 | 180 | 60 | 325 | .11 | -- | 18.2 | 1.51 | 4.36 | <.01 |
| 5 | 3101 | 67. | 11. | 2.8 | 2.3 | .42 | .48 | 89.9 | 2 | 15 | 144 | 150 | 326 | 130 | 71 | 302 | .13 | 13 | 29.1 | 1.42 | 7.06 | .14 |
| 6 | 3121 | 70. | 13. | 3.9 | 2.8 | .81 | .44 | 96.7 | <1 | 17 | 13 | 70 | 36 | 160 | 54 | 202 | .14 | 8.7 | 14.2 | 2.32 | 1.19 | .14 |
| 7 | 3122 | 67. | 10. | 4.9 | 2.4 | .31 | .44 | 94.1 | <1 | 21 | 17 | 135 | 98 | 115 | 109 | 348 | .16 | 6.1 | 18.5 | 3.26 | 3.41 | .07 |
| 8 | 3151 | 53. | 15. | 8.4 | 3.3 | .35 | .75 | 91.0 | <1 | 37 | 29 | 125 | 61 | 235 | 117 | 127 | .13 | 17 | 6.2 | 5.52 | 5.42 | .07 |
| 9 | 3152 | 58. | 16. | 5.3 | 3.3 | 1.6 | .84 | 96.0 | <1 | 28 | <2 | 80 | 61 | 300 | 89 | 139 | .09 | 22 | 4.5 | 2.33 | 1.47 | .49 |
| 9x | 3152 | 58. | 16. | 5.7 | 3.4 | 1.7 | .86 | 95.8 | <1 | 28 | <2 | 80 | 61 | 300 | 86 | 139 | .09 | 27 | 4.5 | 2.60 | 1.60 | .48 |
| 10 | 3180 | 56 | 19.. | 5.2 | 4.0 | .99 | .70 | 96.5 | <1 | 24 | <2 | 95 | 84 | 285 | 27 | 185 | .05 | 8.2 | 3.4 | .97 | .73 | .21 |

Table 3. Quantitative results of analyses of samples from Wise County, Va.

| | | On the ash | | | | | | | | | | | On the raw sample | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | in percent | | | | | | | | in ppm | | | in ppm | | | | in percent | | |
| Sample | Depth feet | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $K_2O$ | CaO | $TiO_2$ | MnO | Ash | Cu | Mo | Ni | V | Hg | As | U | S | C Organ | C $CO_3$ |
| W-1 | 4887.3 | 64 | 14 | 3.9 | 3.2 | .72 | .82 | <.05 | 90.5 | 95 | 41 | 150 | 1000 | .04 | 17 | 20.6 | 1.18 | 6.46 | .20 |
| 2 | 4906.3 | 65 | 12 | 7.4 | 2.6 | .89 | .77 | <.05 | 93.0 | 66 | 9 | 120 | 360 | .07 | 89 | 6.8 | 3.96 | 3.02 | .21 |
| 3 | 4934.4 | 76 | 11 | 3.1 | 2.1 | .2 | .89 | <.05 | 95.2 | 44 | 14 | 90 | 460 | .03 | 18 | 13.4 | 1.17 | 2.77 | <.01 |
| 4 | 4968.9 | 48 | 19 | 12. | 4.4 | 1.6 | .87 | .158 | 92.2 | 49 | <2 | 100 | 150 | .01 | 12 | 2.2 | .09 | .52 | 1.63 |
| 5 | 5241.0 | 57 | 19 | 7.3 | 4.6 | <.1 | .94 | <.05 | 95.5 | 40 | 9 | 90 | 160 | .03 | 33 | 5.8 | 2.49 | .92 | <.01 |
| 6 | 5252.2 | 56 | 20 | 7.2 | 4.6 | <.1 | .93 | <.05 | 95.5 | 39 | 10 | 100 | 150 | .02 | 41 | 5.7 | 2.52 | .94 | <.01 |
| 7 | 5282.0 | 58 | 16 | 8.3 | 3.8 | .2 | .91 | <.05 | 94.1 | 43 | 20 | 90 | 140 | .04 | 12 | 9.9 | 2.98 | 1.93 | .20 |
| 8 | 5312.0 | 59 | 17 | 7.0 | 4.2 | .3 | .81 | .057 | 94.4 | 42 | 20 | 95 | 150 | .05 | 33 | 9.1 | 2.66 | 2.27 | .07 |
| 9 | 5341.6 | 58 | 18 | 7.9 | 4.3 | .2 | .87 | <.05 | 93.8 | 49 | 25 | 120 | 160 | .06 | 31 | 14.5 | 3.06 | 2.53 | .07 |
| 10 | 5372.0 | 63 | 13 | 6.5 | 3.1 | .68 | .75 | <.05 | 91.9 | 61 | 57 | 100 | 150 | .07 | 27 | 25.7 | 3.14 | 4.30 | .21 |
| 11 | 5401.0 | 63 | 16 | 5.6 | 3.8 | .2 | .82 | <.05 | 93.1 | 64 | 42 | 135 | 230 | .05 | 37 | 24.4 | 2.17 | 3.53 | .07 |
| 12 | 5471.0 | 60 | 16 | 6.2 | 3.9 | .55 | .76 | <.05 | 92.1 | 43 | 62 | 115 | 190 | .05 | 29 | 22.3 | 2.49 | 4.30 | .19 |

Table 4. Quantitative results of analyses of samples from Overton County, Tenn.

| | | On the ash in percent | | | | | | | On the ash in ppm | | | | | | | On the raw sample in ppm | | | | On the raw sample in percent | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Depth ft | SiO2 | Al2O3 | Fe2O3 | K2O | CaO | TiO2 | Ash | Cd | Co | Mo | Ni | Zn | Mn | Cu | V | Hg | As | U | S | C Organ | C CO3 |
| T-1 | 181.4 | 67 | 15 | 2.7 | 4.2 | .34 | .76 | 97.1 | <1 | 107 | 2 | 595 | 83 | 110 | 90 | 455 | .04 | 18 | 5.9 | 1.07 | .20 | <.01 |
| 2 | 182.7 | 33 | 8.7 | 3.9 | 2.0 | 17.0 | .32 | 90.5 | 4 | 143 | 18 | 550 | 1292 | 185 | 185 | 637 | .13 | 30 | 25.4 | 3.33 | 6.51 | .50 |
| 3 | 184.2 | 48 | 10 | 4.4 | 2.7 | 7.3 | .63 | 88.2 | 2 | 11 | 47 | 155 | 428 | 115 | 137 | 428 | .10 | 86 | 29.4 | 4.00 | 7.74 | .07 |
| 4 | 186.7 | 54 | 13 | 4.4 | 3.6 | .62 | .67 | 82.1 | 4 | 17 | 86 | 220 | 736 | 165 | 183 | 696 | .12 | 73 | 42.2 | 3.53 | 12.45 | <.01 |
| 5 | 189.7 | 49 | 11 | 7.4 | 3.0 | 2.2 | .55 | 81.8 | <1 | 79 | 181 | 215 | 388 | 210 | 107 | 359 | .18 | 110 | 80.9 | 6.61 | 11.13 | .49 |
| 6 | 192.2 | 48 | 11 | 8.1 | 3.1 | .64 | .57 | 79.2 | <1 | 89 | 207 | 155 | 390 | 200 | 108 | 235 | .16 | 98 | 91.4 | 7.02 | 13.54 | <.01 |
| 7 | 194.7 | 53 | 11 | 6.8 | 3.2 | .84 | .66 | 83.3 | <1 | 78 | 141 | 185 | 262 | 215 | 96 | 235 | .16 | 79 | 76.6 | 2.77 | 10.77 | .27 |
| 8 | 197.2 | 61 | 14 | 4.5 | 3.9 | .72 | .77 | 92.1 | <1 | 39 | 59 | 130 | 195 | 200 | 79 | 257 | .10 | 57 | 40.6 | 6.03 | 4.76 | .21 |
| 9 | 199.2 | 54 | 12 | 6.5 | 3.3 | .48 | .71 | 84.3 | <1 | 61 | 101 | 175 | 267 | 200 | 126 | 235 | .13 | 56 | 56.4 | 5.50 | 10.22 | .07 |
| 10 | 199.7 | 57 | 15 | 5.2 | 3.9 | .26 | .71 | 88.7 | <1 | 48 | 75 | 115 | 253 | 185 | 101 | 207 | .13 | 60 | 53.5 | 3.41 | 7.09 | <.01 |
| 11 | 200.5 | 53 | 14 | 4.3 | 3.8 | .29 | .66 | 89.1 | <1 | 37 | 55 | 130 | 173 | 205 | 149 | 207 | .11 | 42 | 43.0 | 3.96 | 6.83 | <.01 |
| 12 | 202.5 | 61 | 18 | 3.4 | 4.6 | .70 | .81 | 96.6 | <1 | 19 | 4 | 75 | 168 | 330 | 56 | 219 | .06 | 24 | 20.1 | 1.25 | .68 | .28 |
| 13 | 205.3 | 52 | 14 | 5.3 | 3.6 | 1.4 | .61 | 87.4 | <1 | 32 | 108 | 195 | 309 | 560 | 183 | 348 | .13 | 48 | 33.7 | 3.46 | 8.76 | <.01 |
| 14 | 207.7 | 19 | 4.8 | 2.4 | 1.0 | 21.0 | .19 | 97.1 | <1 | 5 | 3 | 45 | 72 | 4090 | 17 | <50 | .04 | 9.2 | 14.3 | 1.68 | .45 | 8.51 |

Table 5.--Range in abundance and mean abundance of major constituents in Devonian shales

[min, minimum; max, maximum; <, less than]

| Constituent in percent | Washington Co., Ohio | | | Carroll Co., Ohio | | | Wise Co., Va. | | | Martin Co., Ky. | | | Overton Co., Tenn. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | min. | max. | mean | min. | max. | mean | min. | max. | mean | min. | max. | mean | min. | max. | mean |
| $SiO_2$ | 51 | 61 | 56 | 53 | 70 | 60.5 | 57 | 88 | 71.6 | 31 | 58 | 51 | 19 | 67 | 51 |
| $Al_2O_3$ | 16 | 20 | 17.3 | 10 | 19 | 15.3 | 12 | 20 | 16.3 | 9.9 | 19 | 14.8 | 4.8 | 18 | 12.3 |
| $Fe_2O_3$ | 4.2 | 8.1 | 5.4 | 2.8 | 8.4 | 5.2 | 2.6 | 11 | 6.2 | 4.1 | 23 | 8.2 | 2.4 | 8.1 | 5.0 |
| $K_2O$ | 3.0 | 3.6 | 3.3 | 2.3 | 4.0 | 3.2 | 1.8 | 4.2 | 3.4 | 2.4 | 4.5 | 3.7 | 1.0 | 4.6 | 3.3 |
| CaO | .22 | 1.5 | .53 | .15 | 1.65 | .56 | .09 | 1.4 | .44 | .13 | 3.1 | .75 | .26 | 21 | 3.8 |
| $TiO_2$ | .69 | .83 | .7 | .44 | .92 | .68 | .84 | 1.0 | .92 | .46 | .96 | .77 | .19 | .81 | .62 |
| Ash | 94.3 | 96.6 | 95.4 | 89.9 | 96.9 | 94.8 | 90.5 | 95.5 | 93.4 | Not determined | | | 81.8 | 97.1 | 88.4 |
| $Co_3$ as C | <.01 | .49 | .17 | <.01 | .49 | .13 | <.01 | 1.63 | .24 | .06 | 4.69 | .62 | <.01 | 8.5 | .75 |
| Organic C as C | .03 | 2.6 | 1.2 | .23 | 7.1 | 2.4 | .52 | 6.47 | 2.8 | .18 | 7.19 | 2.2 | 0.2 | 13.5 | 7.2 |
| Total S | .67 | 4.77 | 2.0 | .71 | 5.5 | 2.1 | .09 | 3.96 | 2.3 | .06 | 9.89 | 2.1 | 1.1 | 7.0 | 3.8 |

Table 6.--Range in abundance and mean abundance of trace elements in Devonian shales

[N.d., not determined; *, not meaningful; <, less than; min, minimum; max, maximum]

| Element | Washington Co., Ohio | | | Carroll Co., Ohio | | | Wise Co., Va. | | | Martin Co., Ky. | | | Overton Co., Tenn. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | min | max | mean | min | max. | mean | min | max | mean | min | max | mean | min | max | mean |
| Cd | <1 | | * | <1 | 2 | * | N.d. | N.d. | N.d. | N.d. | N.d. | N.d. | <1 | 4 | * |
| Co | 18 | 30 | 24 | 15 | 37 | 22 | N.d. | N.d. | N.d. | 11 | 32 | 21 | 5 | 143 | 55 |
| Mg | .02 | .05 | .04 | .03 | .16 | .09 | 0.01 | 0.07 | 0.04 | .02 | .11 | 0.05 | .04 | .18 | .11 |
| Mo | 1 | 39 | 12 | <2 | 144 | 29 | <2 | 62 | 26 | <2 | 145 | 30 | 2 | 207 | 78 |
| Ni | 60 | 90 | 79 | 70 | 150 | 103 | 90 | 150 | 109 | 38 | 404 | 87 | 45 | 595 | 210 |
| V | 109 | 202 | 157 | 85 | 348 | 204 | 140 | 1000 | 275 | 100 | 350 | 160 | <50 | 696 | 325 |
| Zn | 60 | 132 | 98 | 36 | 326 | 100 | N.d. | N.d. | N.d. | N.d. | N.d. | N.d. | 72 | 1292 | 358 |
| Mn | 230 | 600 | 368 | 115 | 740 | 279 | <500 | 1399 | * | <500 | 2000 | * | 110 | 4090 | 498 |
| Cu | 34 | 55 | 46 | 27 | 117 | 67 | 39 | 95 | 53 | * | * | * | 17 | 185 | 116 |
| Th | 12.4 | 16.7 | 14.3 | 13.6 | 15.6 | 14.7 | 11.5 | 15.0 | 13.2 | 6.8 | 16.6 | 13.4 | * | * | * |
| U | 4.0 | 12.2 | 6.6 | 3.4 | 29.1 | 10.0 | 2.2 | 25.7 | 13.4 | 2.1 | 37.7 | 10.8 | 5.9 | 91 | 43.8 |
| As | 20 | 42 | 26.6 | 6.1 | 27. | 15.5 | 12 | 89 | 32.4 | 2.1 | 180 | 33.8 | 9.2 | 110 | 56.4 |

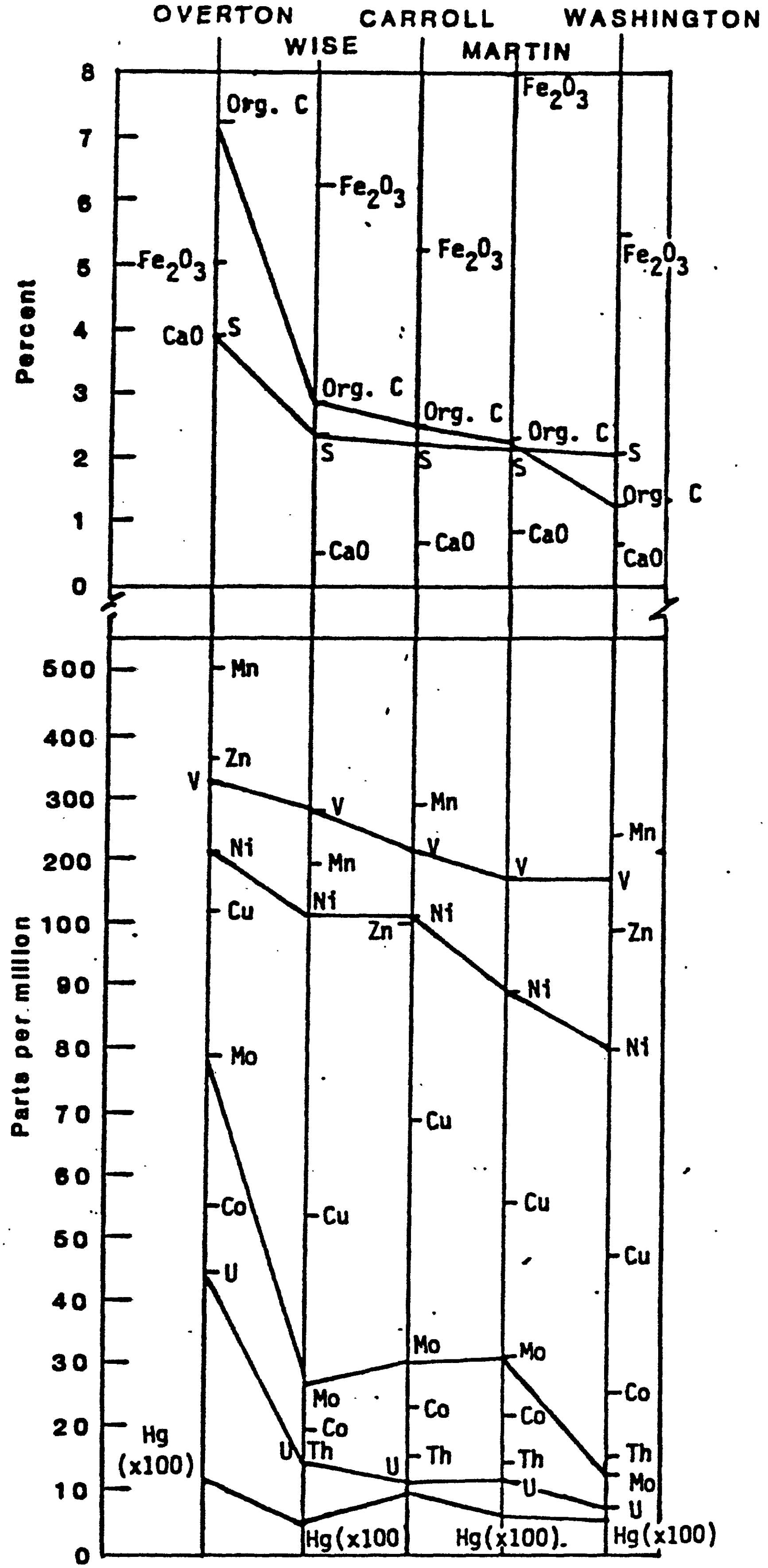


Figure 2. Mean abundances of selected constituents of Devonian black shales.

Table 7.--Semiquantitative determination of 28 elements from samples of Devonian shales

[+, one high value; N, not detected; L, detected; *, not meaningful, <, less than; --, see table 6 for these elements; min, minimum; max, maximum; in parts per million, except Mg and Na, in percent]

| | Washington Co., Ohio | | | Carroll Co., Ohio | | | Wise Co., Va. | | | Martin Co., Ky. | | | Overton Co., Tenn. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Element | min. | max. | mean | min. | max. | mean | min. | max. | mean | min. | max. | mean | min. | max. | mean |
| Mg | 0.7 | 0.7 | 0.7 | 0.5 | 1.5 | 1.0 | 0.5 | 1.0 | 0.85 | 0.5 | 1.0 | 0.8 | 0.7 | 5.0 | 1.29 |
| Mn | 150 | 500 | 260 | 70 | 500 | 220 | 70 | 700+ | 190 | 100 | 1500 | 400 | 70 | 3000 | 380 |
| Ag | N | 7 | * | N | 0.7 | * | N | 1 | .13 | N | N | -- | N | 1.5 | * |
| B | 100 | 150 | 140 | 70 | 200 | 150 | 70 | 150 | 110 | L | 100 | 110 | 20 | 150 | 110 |
| Ba | 300 | 1500 | 500 | 200 | 1000 | 410 | 200 | 300 | 580 | 100 | 500 | 340 | 70 | 3000 | 480 |
| Be | 2 | 3 | 2.4 | 1.5 | 3 | 2.0 | 1.5 | 3 | 2.0 | N | 2 | 1.7 | N | 3 | 2.4 |
| Cr | 70 | 70 | 70 | 30 | 100 | 67 | 50 | 100 | 69 | 20 | 70 | 60 | 15 | 100 | 64 |
| Cu | 30 | 70 | 64 | 30 | 150 | 95 | 50 | 100 | 64 | 20 | 150 | 60 | 15 | 200 | 120 |
| La | 50 | 70 | 67 | L | 70 | 33 | L | 70 | 56 | N | L | * | L | 150 | 70 |
| Nb | 15 | 20 | 16 | L | 20 | 14 | 15 | 15 | 15 | N | L | * | N | 20 | 13 |
| Pb | 10 | 30 | 22 | 15 | 30 | 22 | 10 | 30 | 24 | N | 30 | 15 | 20 | 300+ | 49 |
| Sc | 20 | 30 | 24 | 10 | 30 | 17 | 10 | 10 | 20 | 10 | 20 | 15 | 5 | 30 | 15 |
| Sr | 150 | 300 | 180 | 70 | 300 | 160 | 70 | 150 | 130 | 70 | 200 | 120 | 150 | 300 | 170 |
| Y | 30 | 50 | 36 | 20 | 30 | 28 | 20 | 70 | 34 | 10 | 20 | 17 | 30 | 200 | 70 |
| Zr | 100 | 150 | 140 | 70 | 150 | 120 | 70 | 300+ | 140 | 30 | 150 | 120 | 50 | 200 | 150 |
| Na | .7 | .7 | .7 | .5 | .7 | .65 | .7 | .7 | .7 | .5 | .7 | .7 | .5 | .7 | .66 |
| Ce | L | L | L | N | L | L | L | L | L | N | N | * | N | 300+ | * |
| Ga | 30 | 50 | 33 | 15 | 30 | 26 | 15 | 30 | 26 | 7 | 30 | 20 | 7 | 30 | 19 |
| Li | L | L | L | L | 100 | 9.0 | N | 150 | 12 | N | N | * | N | L | * |
| Yb | 3 | 5 | 3.3 | 3 | 5 | 3.4 | 3 | 7 | 4 | 2 | 3 | 2.5 | 1.5 | 7 | 3.8 |
| Nd | L | 100 | 64 | N | 70 | 45 | 70 | 100 | 72 | N | N | * | L | 150 | 68 |
| Mo | N | 30 | 9.7 | N | 70 | 16 | N | 50 | 25 | N | 50 | -- | N | 100 | 48 |
| Co | -- | -- | -- | -- | -- | -- | 10 | 30 | 19 | -- | -- | -- | -- | -- | -- |
| Cu | -- | -- | -- | -- | -- | -- | -- | -- | -- | 20 | 150+ | 56 | -- | -- | -- |
| Ge | 2.2 | 2.5 | 2.3 | .6 | 5.6 | 2.2 | .4 | 2.5 | 1.8 | .3 | 3.9 | 2.1 | .5 | 2.2 | 1.7 |
| Sb | 0.9 | 1.2 | 1.8 | <.2 | 4.9 | 1.9 | <.6 | 5.3 | 2.4 | <.2 | 11 | 1.6 | 2.8 | 8.1 | 4.9 |
| Se | 0.5 | 1.2 | 0.8 | <.2 | <9.6 | 1.9 | <.2 | 5.1 | 2.2 | <.2 | 2.8 | .6 | .6 | 5.0 | 2.0 |
| Sn | 2.3 | 4.2 | 3.0 | .4 | 3.6 | 2.2 | 0.7 | 3.6 | 2.1 | .6 | 3.5 | 2.2 | .2 | 2.7 | 1.6 |

Corrected p 16 on O.F. 79-1503

J.S. Leventhal 2/5/

and misleading results." for the reason for omission of some samples in the following paragraphs.

### Sulfur and other trace elements

Fe and S make up pyrite; however, Fe can also reside in clays and (or) carbonates. In the samples studied the Fe (plotted as $Fe_2O_3$) and S show a statistically significant correlation for Overton County (fig. 3, r=0.77, significant at the 99 percent level), for Washington County (r=0.79, significant at the 99 percent level), and for Wise County (one sample omitted, r=0.85, significant at the 99 percent level). Data from Wise County (all samples included, fig. 4), Carroll County, and Martin County do not show a statistically significant correlation between Fe and S.

The Fe/S ratio can be related to pyrite. On figure 3 (Overton County) the slope of the dotted line for Fe and S present as pyrite (slope=0.80) is very close to the statistically determined slope of the solid line for all the samples from Overton County. Some sample values are very close to the pyrite line (samples 14, 2, 4, 11, 3 13, 10, 9, 5, and 6, Overton County), other samples show an excess of S (sample 8) or an excess of Fe (samples 7, 12, and 1). The samples whose values are near the pyrite line may not necessarily have pyrite; they may just contain the same stoichiometric amounts of Fe and S. However, observations of hand specimens and thin sections do show the presence of abundant pyrite. Samples from the other localities show excess Fe, and all sample values are below the pyrite line, as shown in figure 4 (Wise County). The excess Fe could be present in clays, amorphous coatings, or as carbonate containing Fe.

Zn and S are correlated in the Martin County samples (sample 17 omitted, r=0.59, significant at the 99 percent level) (fig. 5). No correlation of these elements was found in samples from Carroll, Overton, or Washington Counties.

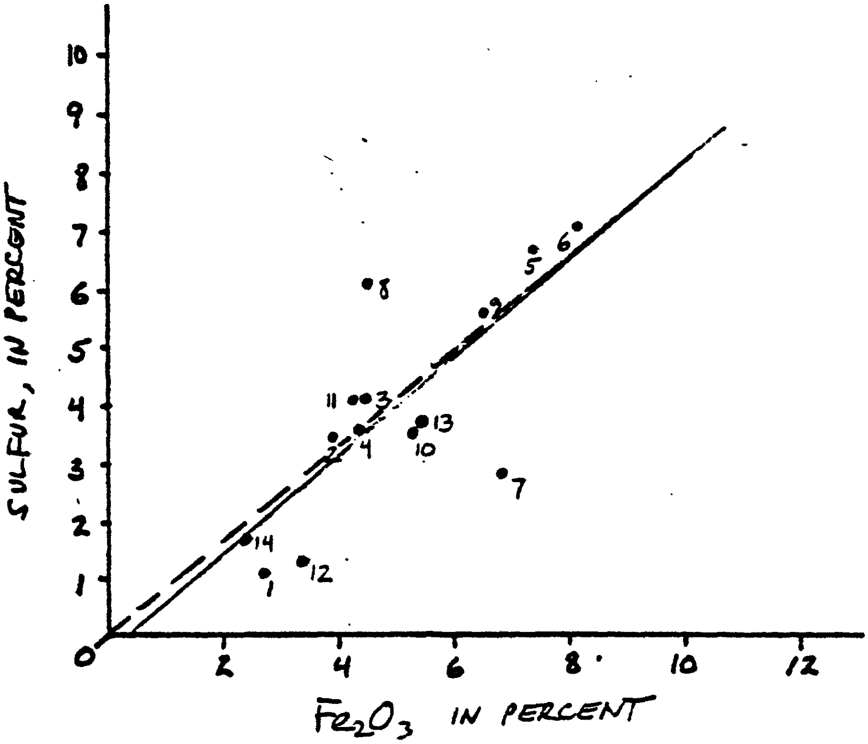


Figure 3. Diagram showing plot of $Fe_2O_3$ vs. S. Solid line is the linear-least-squares-fit of the data. The dashed line is the stoichiometry for $FeS_2$ (pyrite).

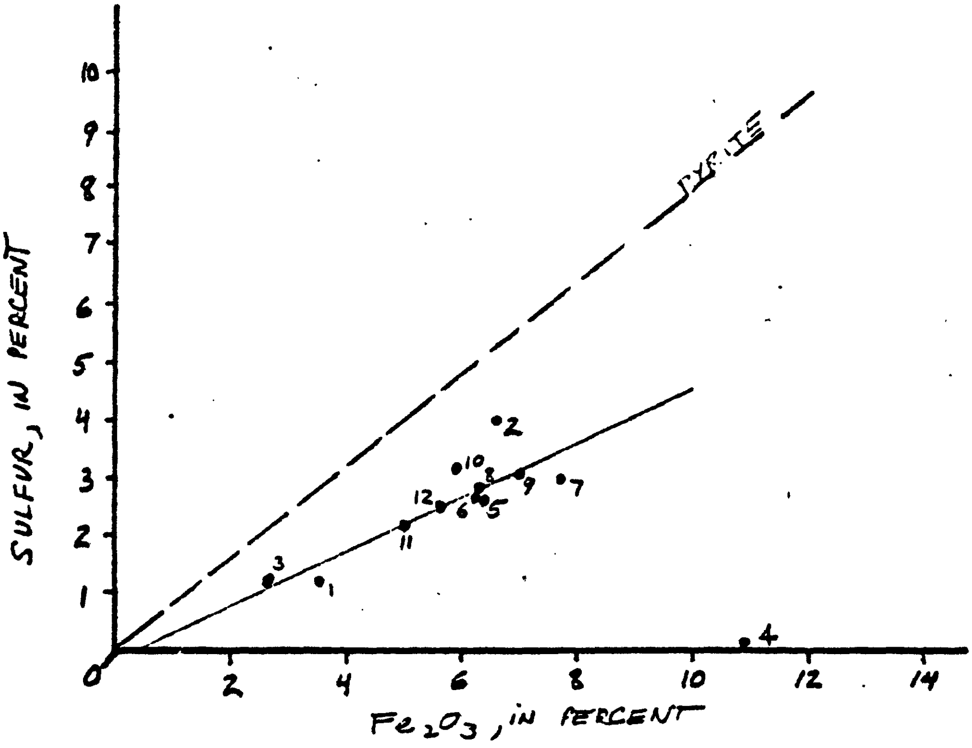


Figure 4. Diagram showing plot of Wise County, Va., see fig. 3 caption.

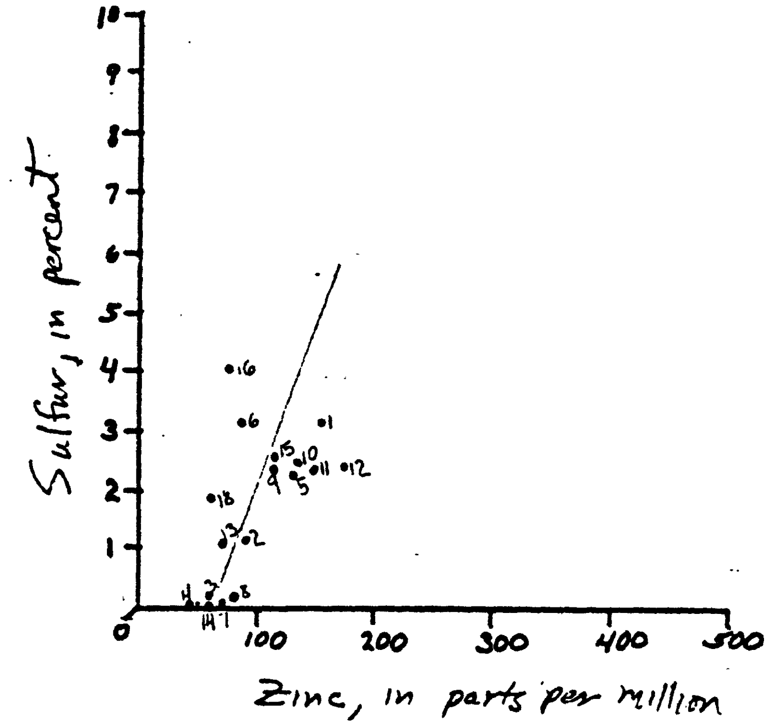


Figure 5. Diagram showing plot of S vs. Zn for samples from Martin County, Ky. The line is the linear-least-square fit of the data.

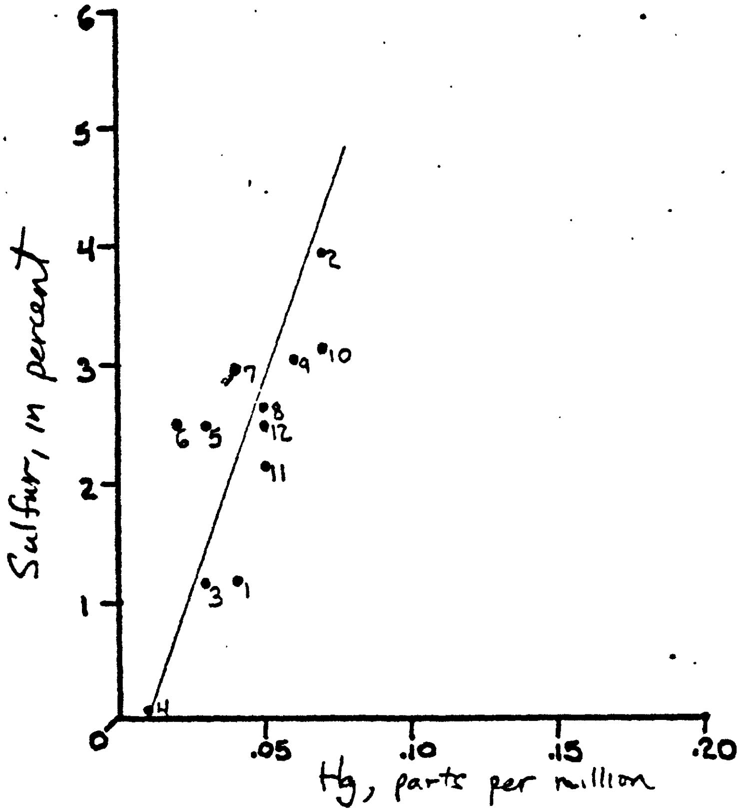


Figure 6. Diagram showing plot of S vs. Hg for samples from Wise County, Va. The line is the linear-least-square fit of the data..

S and Hg are correlated in the samples from Wise County (r=0.76, significant at the 99 percent level, fig. 6), Overton County (r=0.71, significant at the 99 percent level), and Martin County (sample 17 omitted, r=0.72, significant at the 99 percent level). In samples from Carroll County Hg and S are correlated (r=0.60, significant at the 95 percent level), whereas samples from Washington County do not show a significant relationship between Hg and S.

S and Mo show a significant relationship only in the samples from Overton County (r=0.75, significant at the 99 percent level, fig. 7).

S and As (fig. 8) show a significant relationship only in the samples from Overton County (r=0.75, significant at 99 percent level).

### Organic C and trace elements

The relationship between organic C and V is not statistically significant for any samples from the studied areas except for Wise County (r=0.63, significant at the 95 percent level, fig. 9). However, if the one high value (sample 1, 1,000 ppm V) is excluded, this relationship is not statistically significant (r=0.26) either. Clearly, the one high value gives misleading results on the basis of the statistical techniques used in this study (the r values for samples from other localities are not statistically significant: Carroll County, r=0.57; Martin County, r=0.39; Overton County, r=0.28; and Washington County, r=0.17). Owing to possibly misleading statistical results and in addition to determining the correlation coefficients, the data are plotted on graph paper.

Organic C and Mo show highly significant correlations (at the 99 percent level) from all sample localities except Washington County (in which the correlation is at the 95 percent level). The samples from Wise County have a spread of values (fig. 10), whereas Carroll County and Martin County (fig. 11)

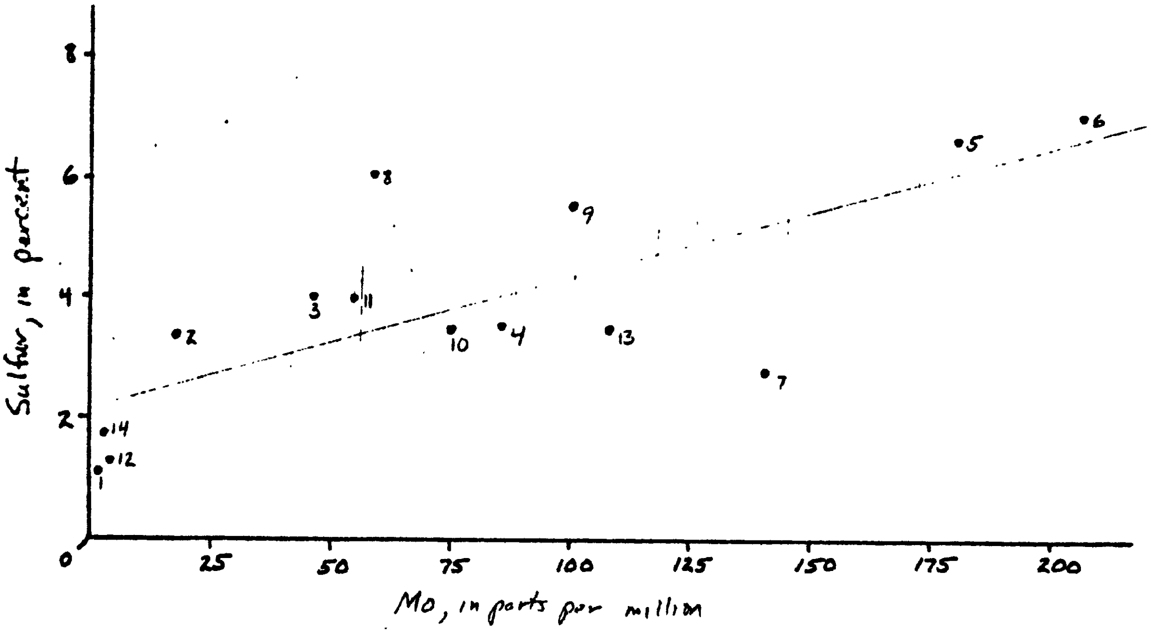
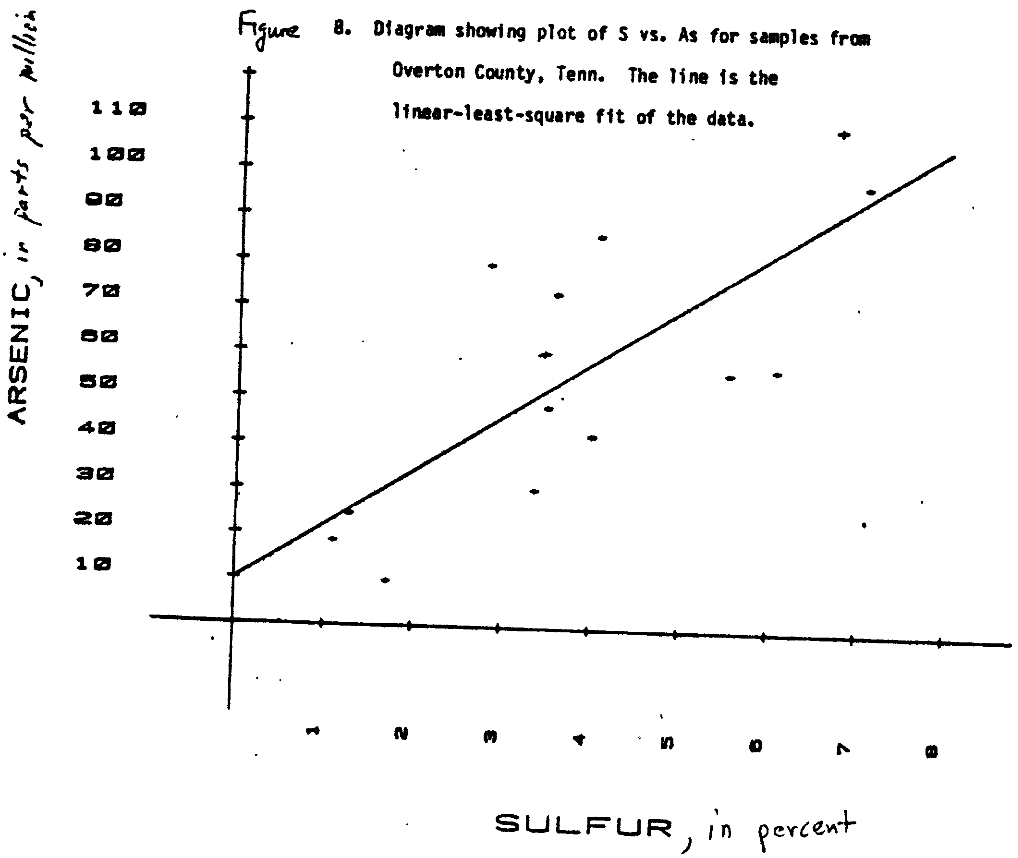


Figure 7. Diagram showing plot of S vs. Mo for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.

Figure 8. Diagram showing plot of S vs. As for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.



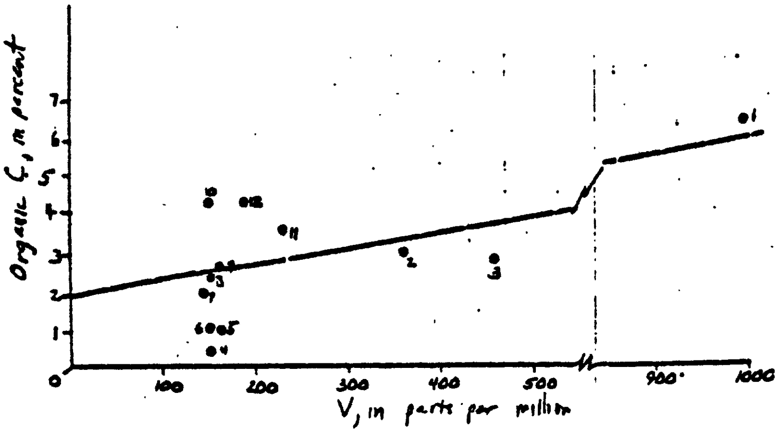


Figure 9. Diagram showing plot of organic C vs. V for samples from Wise County, Va. The line is the linear-least-square fit of the data.

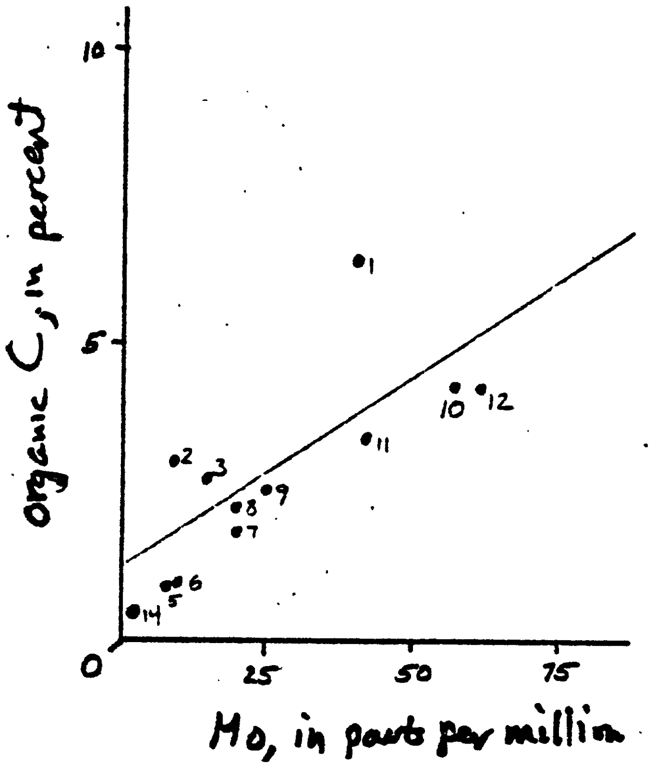


Figure 10. Diagram showing plot of organic C vs. Mo for samples from Wise County, Va. The line is the linear-least-square fit of the data.

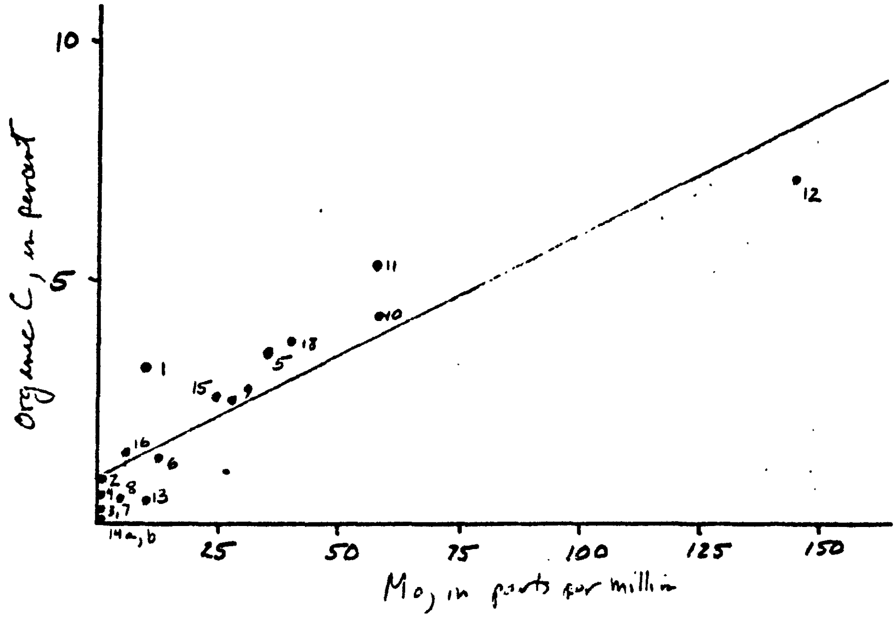


Figure 11. Diagram showing plot of organic C vs. Mo for samples from Martin County, Ky. The line is the linear-least-square fit of the data.

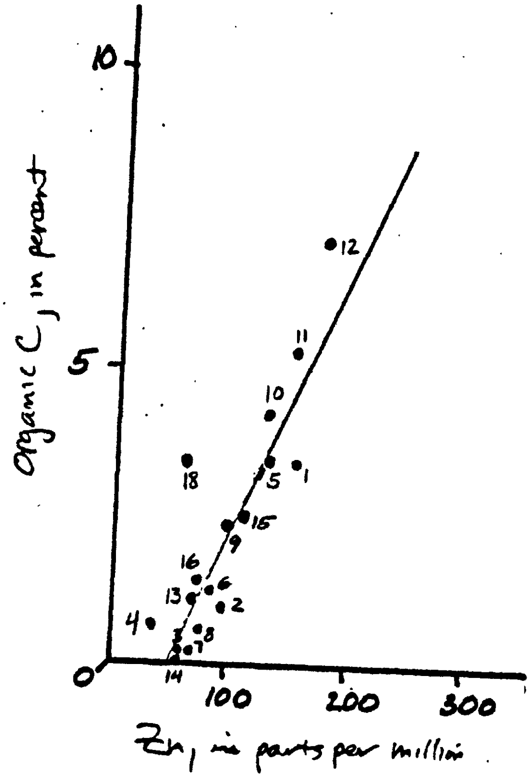


Figure 12. Diagram showing plot of organic C vs. Zn for samples from Martin County, Ky. The line is the linear-least square fit of the data.

values cluster at very low amounts.

Organic C and Zn show a significant correlation (r=0.87, significant at the 99 percent level, fig. 12) in samples from Martin County if sample 17 is omitted. By omitting Overton County sample 2, r=0.76, which is significant at the 99 percent level. Organic C and Zn in samples from Carroll and Washington Counties do not show a significant correlation, and the samples from Wise County were not analyzed for Zn.

Hg and organic C show a highly significant correlation (at the 99 percent level) in samples from Overton County, Washington County, and Martin County (when sample 17 is omitted). Figure 13 shows the plot for Overton County where the highest Hg values occur. Hg and organic C in samples from Wise County do not show a significant correlation unless sample 1 is omitted (fig. 14); the correlation is then r=0.79, which is significant at the 99 percent level. Hg and organic C in Carroll County samples show a positive correlation (r=0.71, significant at the 95 percent level).

As and organic C (fig. 15) show a statistically significant correlation (r=0.84, significant at the 99 percent level) only for Overton County.

Ni and organic C from the Martin County samples (fig. 16) show a significant correlation (r=0.77, significant at the 99 percent level). Two other localities show correlations; samples from Wise County (r=0.72) and Carroll County (r=0.87) are both significant at the 99 percent level. Samples from Washington County show no relationship, whereas samples from Overton County (fig. 17) make up a mixed group. If Overton samples 1 and 2 are omitted, r=0.88, which is significant at the 99 percent level. Ni and organic C in samples from Perry County, Ky., and Cattaraugus County, N.Y., are shown on figure 18; they were not given in the previous report (Leventhal, 1978a).

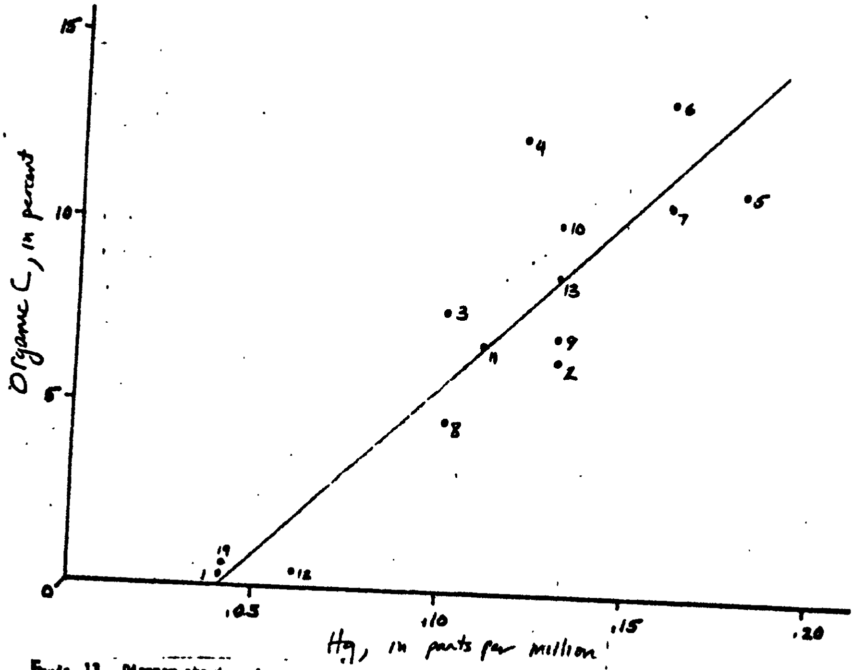


Figure 13. Diagram showing plot of organic C vs. Hg for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.

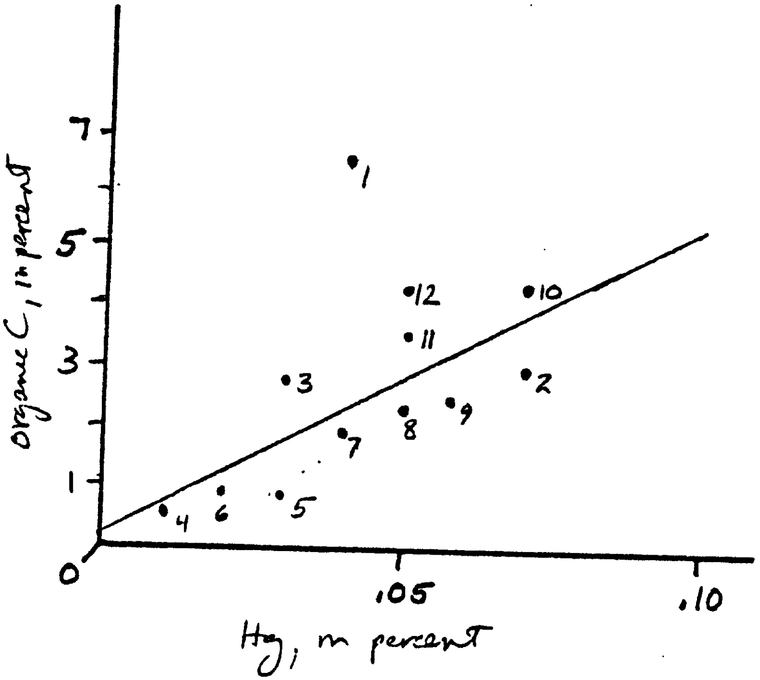


Figure 14. Diagram showing plot of organic C vs. Hg for samples from Wise County, Va. The line is the linear-least square fit of the data.

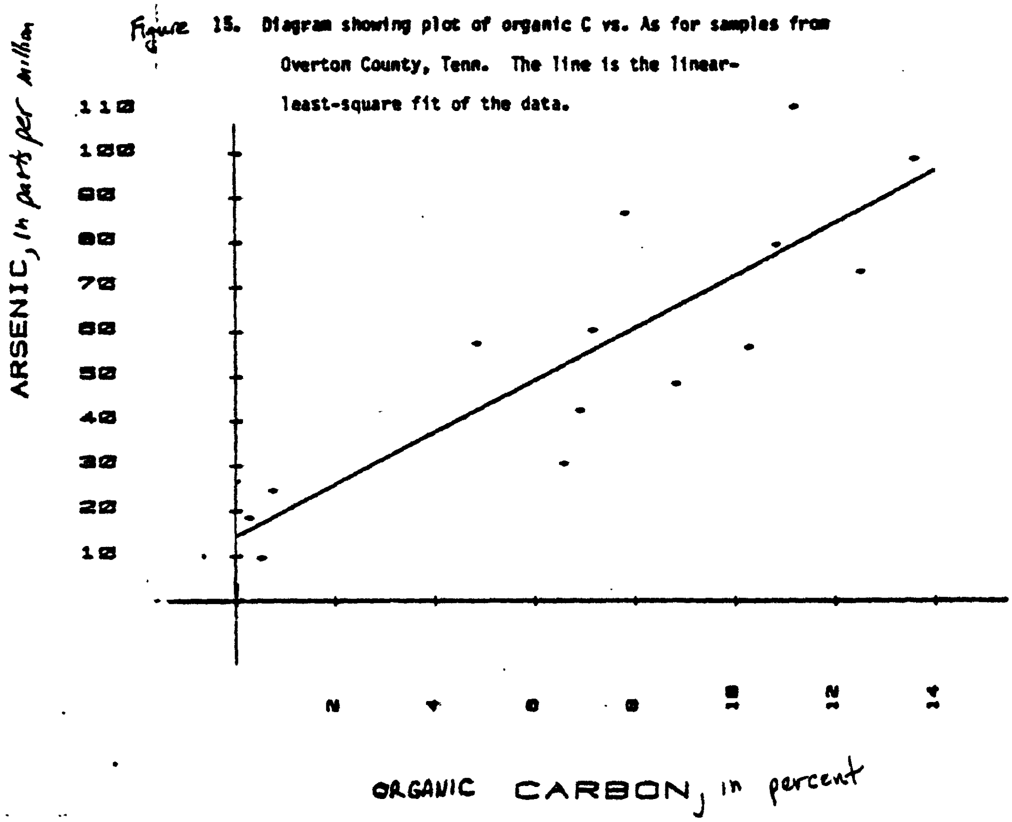


Figure 15. Diagram showing plot of organic C vs. As for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.

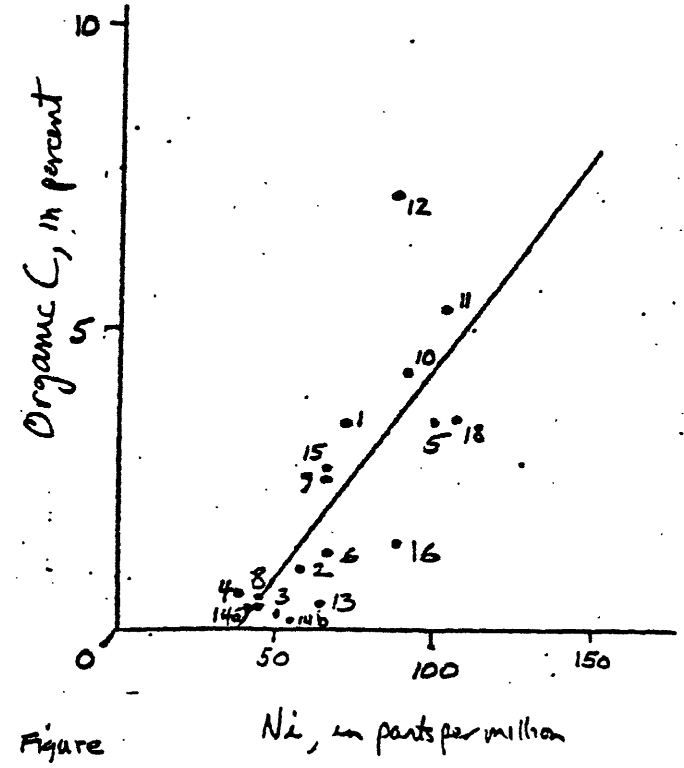


Figure 16. Diagram showing plot of organic C vs. Ni for samples from Martin County Ky. The line is the linear-least-square fit of the data.

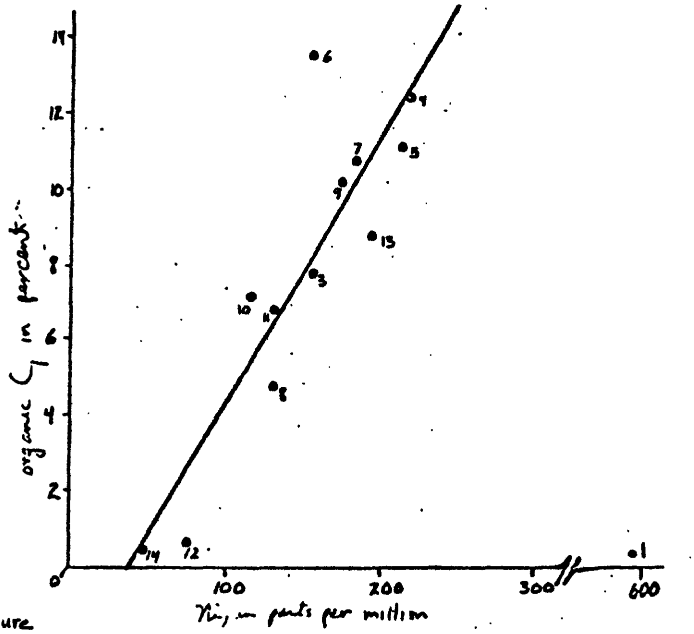


Figure 17. Diagram showing plot of organic C vs. Ni for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.

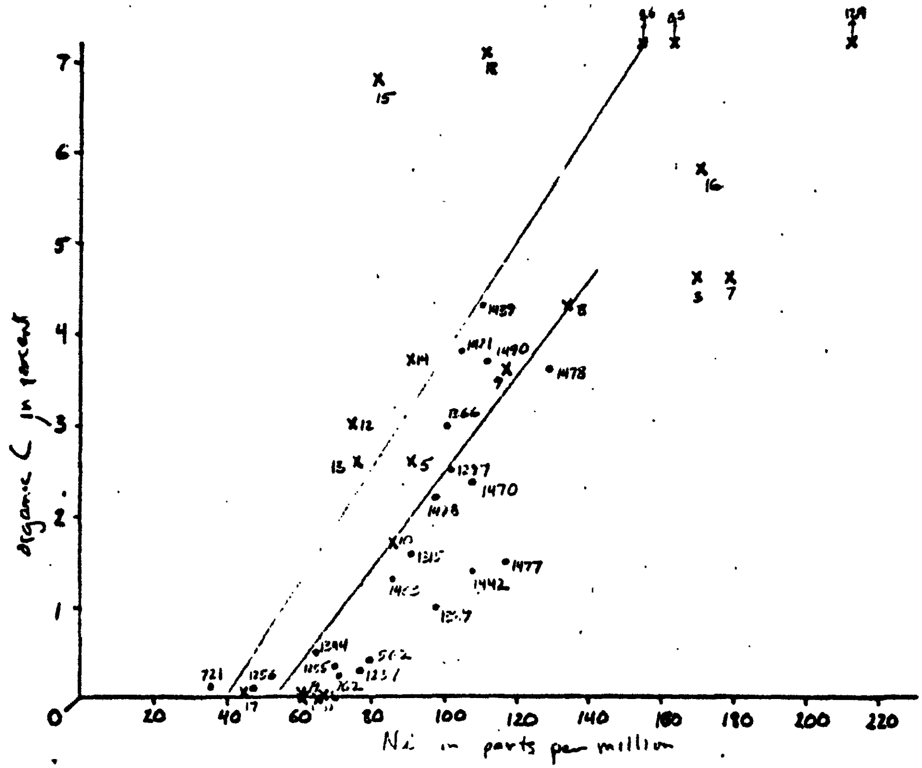


Figure 18. Diagram showing plot of organic C vs. Ni for samples from (X)Perry County, Ky. and Cattaraugus, County, N.Y.(•). The line is the linear-least-square fit of the data.

### Other element pairs

In general, no meaningful relationships were found between Fe and Ni; however, if samples 1 and 2 are omitted from the Overton County data, r=0.66, which is significant at the 98 percent level (fig. 19). Statistics of $SiO_2$ and $TiO_2$ for Overton County (fig. 20) show a strong correlation (r=0.97, significant at the 99 percent level), which suggests that the Ti occurs as a silicate or at least in a resistate or detrital fraction.

The MnO and carbonate C are strongly related when the MnO is greater than 0.05 percent or the carbonate is greater than 0.7 percent. The samples from Martin, Overton, and Wise Counties are plotted together on figure 21 (r=0.98, significant at the 99 percent level).

## Associations of trace elements with C and S

### Down-hole plots

The results of this study show wide variations in the trace-element abundance in Devonian shales. The black shales that are organic and sulfide rich contain greater amounts of the transition elements, Hg and As than do the gray shales. Although C and S are related (Leventhal, 1979) to each other, many trace elements seem more closely related to either C or S. Down-hole plots have been used (Leventhal and Goldhaber 1978, Leventhal, 1978a, 1978b) to show element affinities (figs. 22-26).

Elements that always follow organic C or S in the down-hole plots are: U, Mo, Zn, Ni, V (except in samples from Martin, Overton, and Washington Counties), Fe (except in samples from Martin, Overton, and Wise Counties that contain high $CO_3$ and CaO), Co (in samples from Washington, Carroll, and Overton Counties), Hg and Cu (in samples from Martin County only). In samples from certain cores (Martin County, Ky., Perry County, Ky., Leventhal, 1978a) the C and S do not correlate with each other. U, Mo, V, Zn, Ni, Co, show a

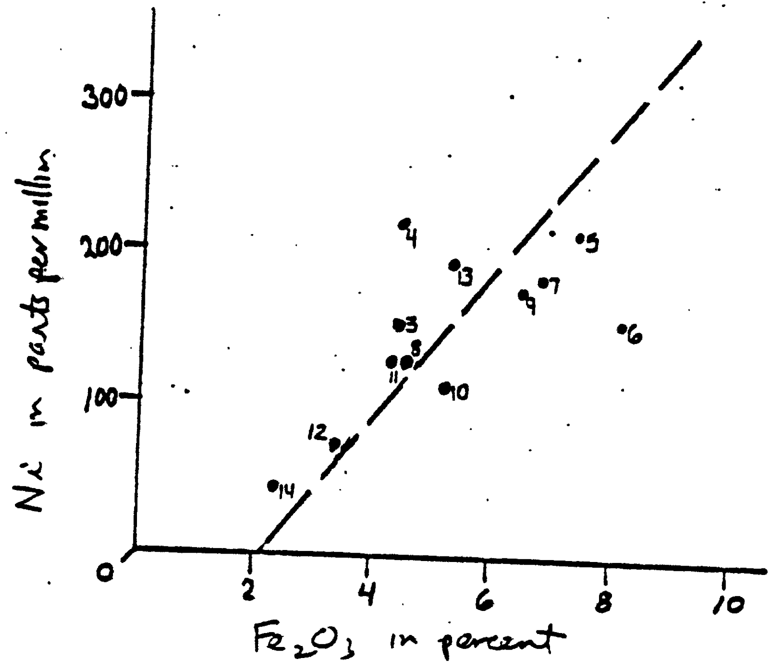


Figure 19. Diagram showing plot of Ni vs. $Fe_2O_3$ for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.

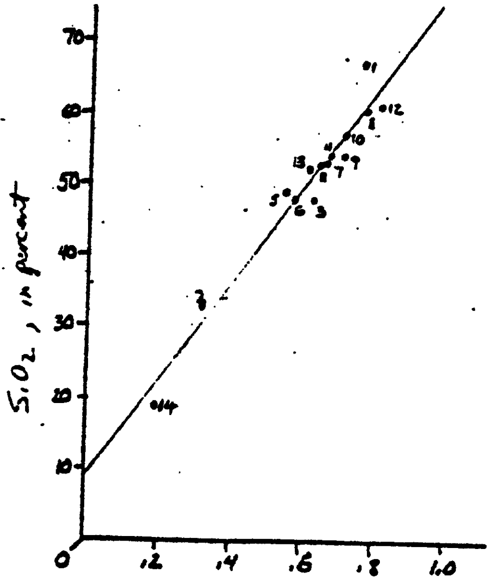


Figure 20. Diagram showing plot of $SiO_2$ vs. $TiO_2$ for samples from Overton County, Tenn. The line is the linear-least-square fit of the data.

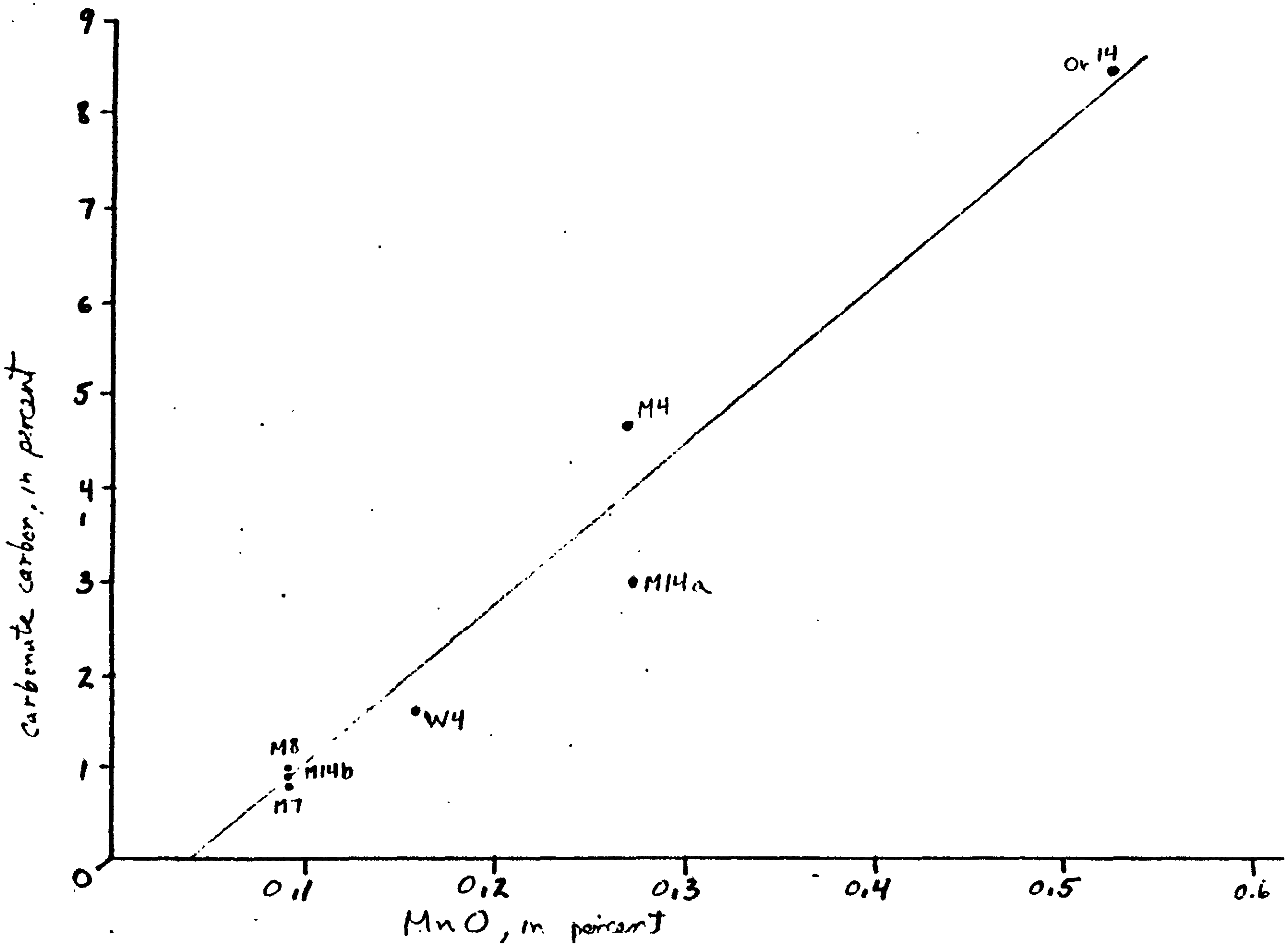


Figure 21. Diagram showing plot of carbonate C vs. MnO for samples from Martin, Wise and Overton Counties. The line is the linear-least-square fit of the data.

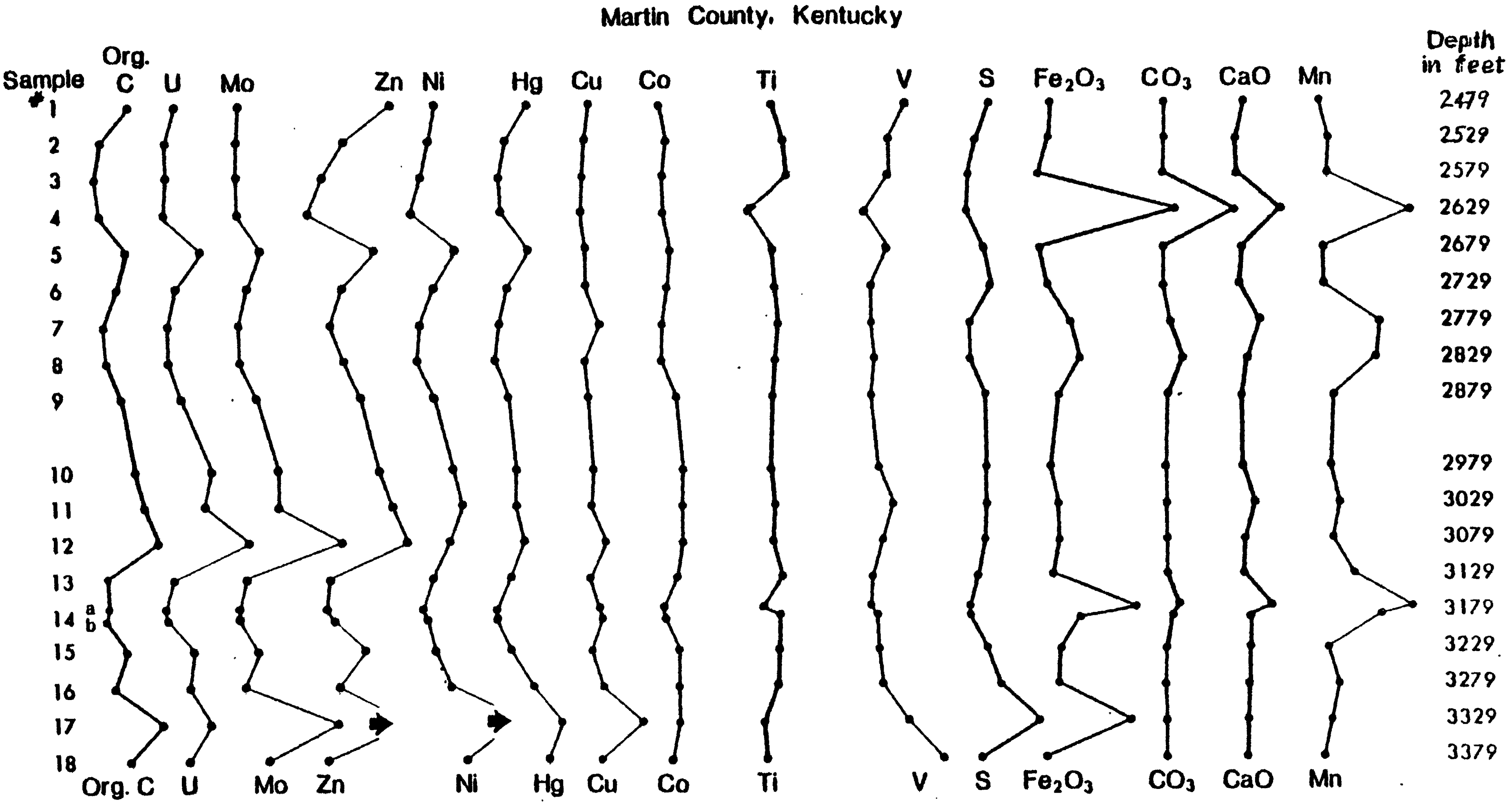


Figure 22. Down hole plots of variations in certain elements from Martin County, Kentucky. Increasing abundance is to the right, in relative amounts. Elements with similar down hole variations are "nested" together. Heavy lines show elements with >0.5% concentration, others are in the ppm range. Arrows indicate high values that are not plotted.

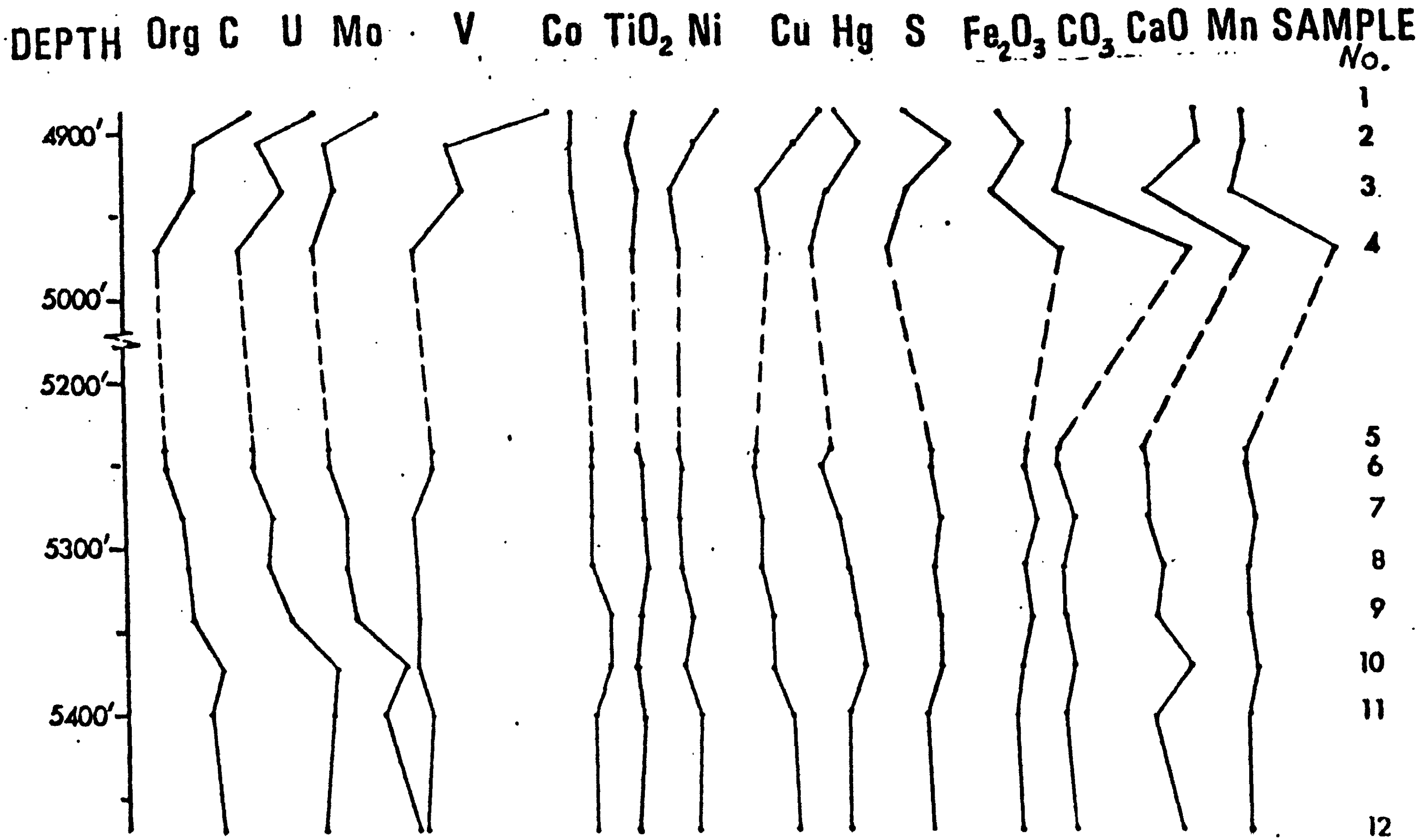


Figure 23. Down-hole plot of selected elements from Wise County, Va. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration. Dashed lines indicate unsampled interval.

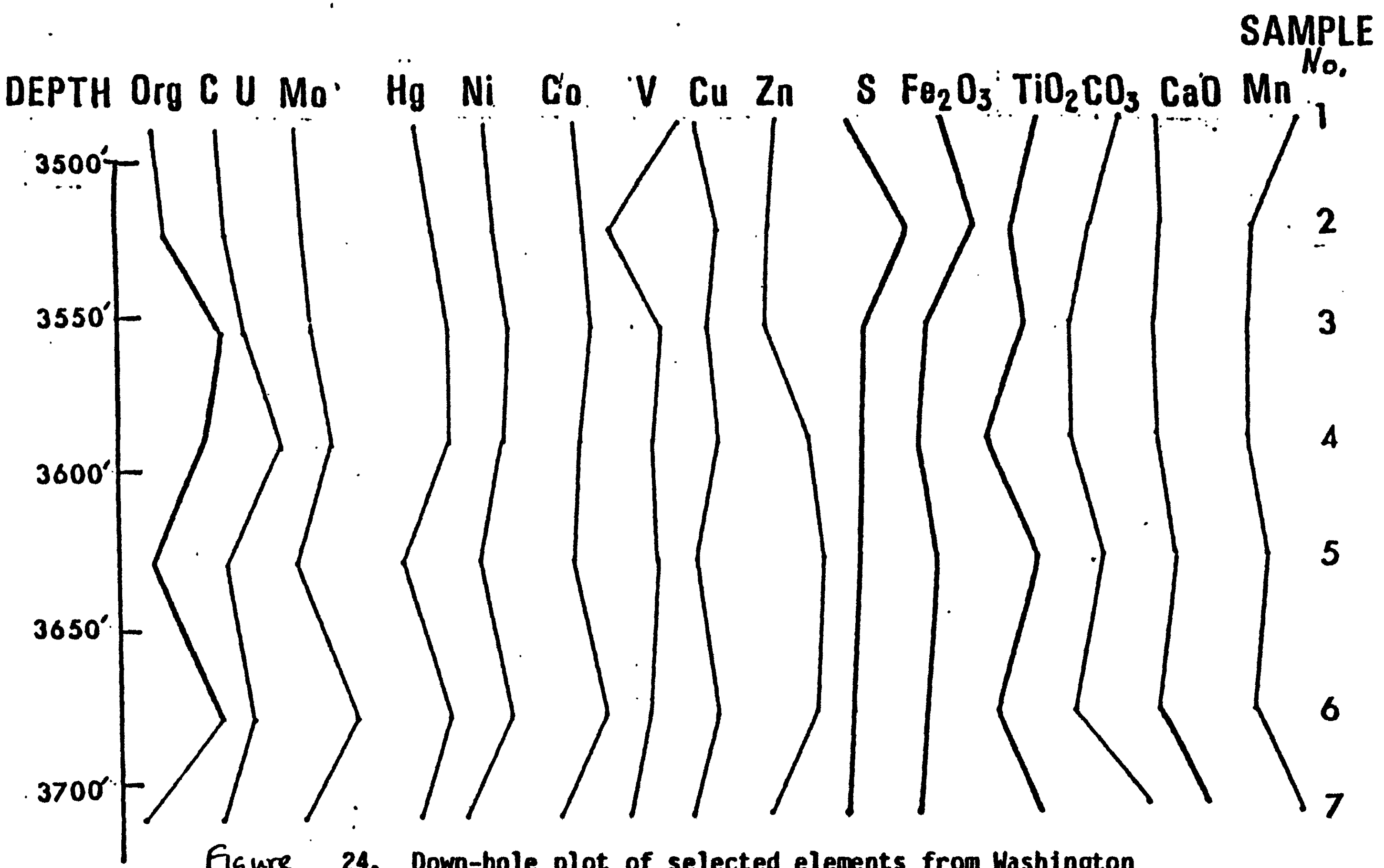
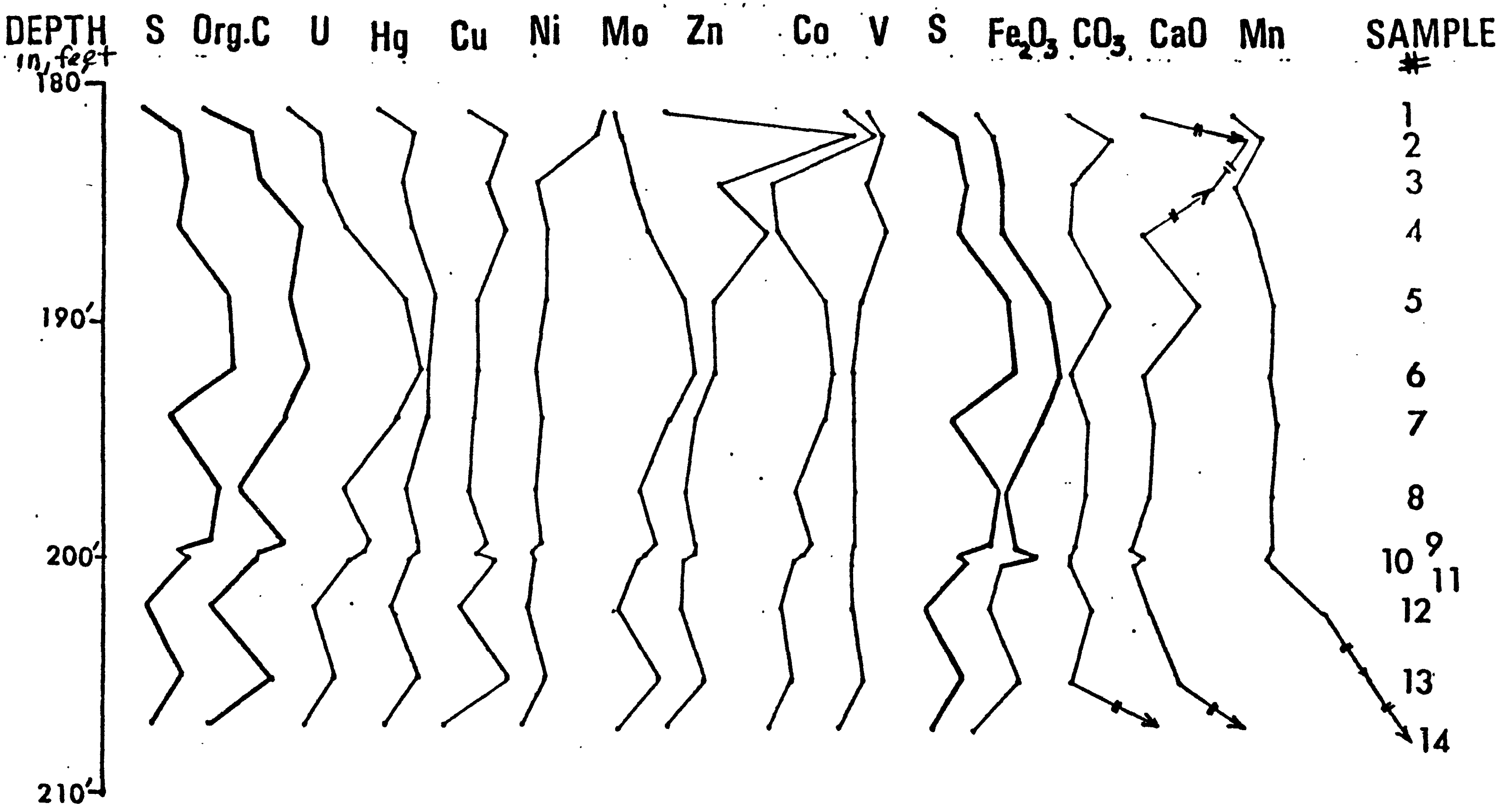
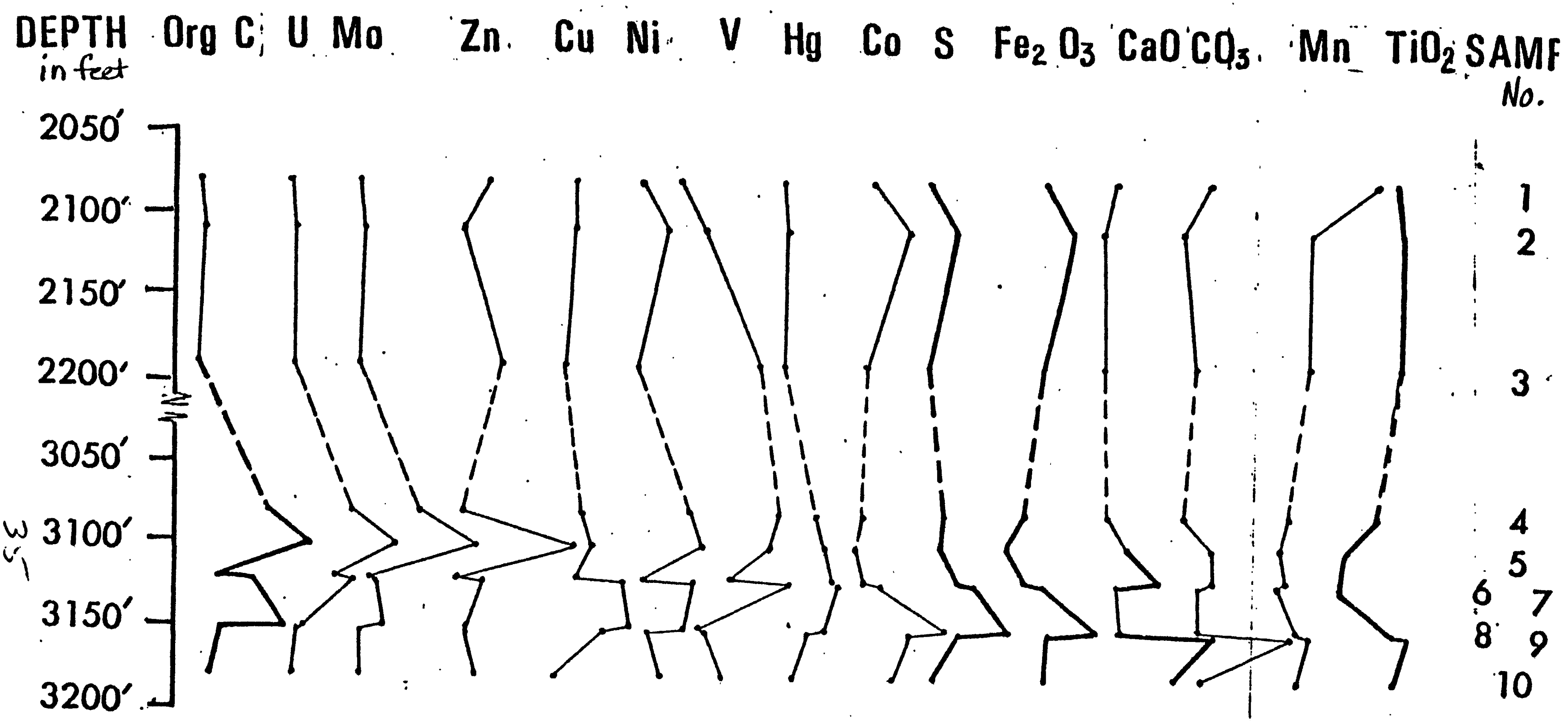


Figure 24. Down-hole plot of selected elements from Washington County, Ohio. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration.

Figure 25. Down-hole plot of selected elements from Overton County, Tenn. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration. Arrows indicate high values, not plotted.





26. Down-hole plot of selected elements from Carroll County, Ohio. Increasing relative abundance is to the right. Elements having similar down-hole variations are nested together. Heavy lines show elements having >0.5 percent concentration Dashed lines indicate unsampled interval.

closer affinity to organic C than to S. Conversely, certain elements, Fe, As, Pb, Sb, Hg, Ag, Cd, and Zn, (also Co in Carroll County only) show a closer affinity to S than to organic C.

CaO and $CO_3$ also seem to control Mn and often $Fe_2O_3$; Mg (not analyzed for chemically) also can occur with $CO_3$, according to preliminary electron-microprobe analysis.

Certain relationships between elements were observed in samples from some cores but not in samples from other cores. For example, the Martin County samples show a statistically significant relationship between Zn and S. This relationship does not imply that Zn is not present in the sulfide fraction in other cores but does mean that the total sulfide content is not related to total Zn present. It is significant that sample 8 from Overton County, which has excess sulfur relative to Fe (fig. 3), does not have the highest amount of Zn; therefore it is possible that the excess S may be present as either elemental S or as a sulfate.

### Calcium carbonate and phosphate

It is also notable that sample 2 from Overton County, containing 1,300 ppm Zn, does not have the highest amount of S or Fe but does have the highest amounts of Cd, Co, and Ag, and relatively high amounts of Cu, V, and Ni. This sample has 17 percent CaO but only 0.5 percent $CO_3$. These amounts can be explained by the fact that the sample contains 14 percent $P_2O_5$, and presumably the Ca and P formed apatite ($CaPO_4$). Sample 2 also has the highest amounts of the rare-earth elements La, Y, Nd, and Ce.

Some unusual samples (too few for statistical treatment) gave important geochemical information. For example, several Overton County samples showed high amounts of trace elements (U, Cu, V, Mn, Ni, etc.). Table 8 gives data for samples T-2, T-3, and T-14 and the mean values for the other Overton

Table 8--Chemical analysis for certain elements of interest in samples from Overton County, Tenn.

[Zn, in ppm by atomic absorption analysis; $CO_3$ in percent by titration; underlined values are discussed in text]

| Sample No. | $^+SiO_2$ | *Ce | *Nd | $^+P_2O_5$ | $^+CaO$ | $CO_3$ | *Mg | Mn | *Ba | *Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| T-2 | 33 | 300 | 150 | 14 | 17 | 0.50 | 1 | 185 | 200 | 300 | 1292 |
| T-3 | 48 | N | 100 | 5.8 | 7.3 | .07 | 1 | 115 | 3000 | 70 | 428 |
| T-14 | 19 | -- | -- | 2.6 | 21 | 8.5 | 5 | 4090 | 70 | 30 | 72 |
| Mean value of other samples | | | | | | | | | | | |
| | 55 | -- | 70 | 1 | .77 | .12 | 1 | 235 | 300 | 25 | 293 |

* Six-step semiquantitative spectrometry, in ppm (except Mg, in percent).
\+ X-ray fluorescence, in percent.

County samples. All these samples have close to average amounts of organic C and S. Samples T-2, T-3, and T-14 have considerably less $SiO_2$ and more of the other tabulated elements than the average of the remaining samples. Samples T-2 and T-3 have high amounts of $P_2O_5$ and CaO, presumably present as apatite ($CaPO_4$). Sample T-2 also has high amounts of Ce and Nd, which are rare-earth elements and are known to associate with phosphates. These samples do not contain very much U (less than 25 ppm) compared to T-5 and T-6 (about 100 ppm), which is surprising as both phosphate and organic matter usually are accompanied by U. This result can be explained by examining the type of organic matter, which is different for T-2 and T-3 and T-5 and T-6 (Leventhal, 1978c).

Sample T-14 shows high amounts of $CO_3$, Mg, and CaO, suggesting a Mg-rich calcite (not quite dolomite). Black shales and other sediments with large $CO_3$ contents often contain Mn; this is true of sample T-14. Samples T-2 and T-3 show enhanced values of Ba, Pb, and Zn, the occurrence of Pb and Zn seems to be related to the apatite, but sample T-3, containing less apatite than T-2, shows the most Ba.

Petrographic work using optical microscopy and electron microprobe will be done to confirm the suggested associations.

### Closely spaced samples showing black to gray transitions

The down-hole plot for Carroll County, Ohio, figure 26, shows two pairs of closely spaced samples at 3,121, 3,122 and 3,151, 3,152 ft depth. These two pairs of samples consist of a sample from each side of the gray shale-black shale boundary. During sedimentation a gray shale was first deposited (at 3,152 ft), then a black shale was deposited at 3,151 ft (table 9). Organic C, S, and Fe increase by large amounts from bottom to top of this gray and black interval. Conversely, the $CO_3$, CaO and $SiO_2$ amounts decrease

Table 9.--Element values and ratios of elements in samples from each side of two black shale-gray shale boundaries, Carroll County, Ohio

[$Fe_2O_3$, S, C organic, and C carbonate in percent, others in parts per million. <, less than; >, greater than]

| Sample No. | Shale color | $Fe_2O_3$ | Co | Mo | Ni | U | Zn | Cu | V | Hg | S | C organic | C carbonate | Mn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3121 | Gray | 3.9 | 17 | 13 | 70 | 14.2 | 36 | 54 | 202 | 0.14 | 2.3 | 1.2 | 0.14 | 160 |
| 3122 | Black | 4.9 | 21 | 17 | 135 | 18.5 | 98 | 109 | 348 | .16 | 3.3 | 3.4 | .07 | 115 |
| Ratio, black/gray | | 1.26 | 1.24 | 1.31 | 1.93 | 1.30 | 2.72 | 2.02 | 1.72 | 1.15 | 1.44 | 2.83 | 0.5 | 7 |
| 3151 | Black | 8.4 | 37 | 29 | 125 | 6.1 | 61 | 117 | 127 | 0.13 | 5.5 | 5.4 | 0.07 | 235 |
| 3152 | Gray | 5.5 | 28 | <2 | 80 | 4.5 | 61 | 89 | 139 | .09 | 2.4 | 1.4 | .49 | 300 |
| Ratio, black/gray | | 1.53 | 1.32 | 15 | 1.56 | 1.36 | 1.0 | 1.31 | .91 | 1.44 | 2.3 | 0.9 | 0.1 | 0.7 |

(table 2). The trace-element content increased in the more organic-rich environment (black shale): Ni, Co, and Cu increased proportionally to organic C and S, Mo, Hg, and U increased less; and Zn had no change; however, V decreased. Mn decreased, probably in affinity with the $CO_3$ which decreased.

The black shale at 3,122 ft changes into a gray shale at 3,121 ft. These two pairs of samples, showing the abrupt transition from gray to black and black to gray, offer an opportunity to consider questions about depositional and geochemical processes. The samples from 3,121- and 3122-ft depth are in the West Falls Formation or Olentangy Shale and those at 3,151-3,152-ft depth are from the Hamilton Group (Marcellus Shale) (assignments by F. Majchszak, in Kepferle and Potter, written commun., 1978). In this interval, the organic C, S, and Fe decrease, and the $CO_3$, $SiO_2$, and $Al_2O_3$ increase (table 2). The trace elements decrease: Cu, Ni, and V showed marked decreases, Zn, Co, and U showed a lesser decrease, and Mo and Hg showed small changes.

The color change in these two intervals is mainly due to the organic and fine-grained sulfide content. The black samples contain 5.4 and 3.4 percent organic C, and the gray samples contain 1.5 and 1.2 percent organic C. The substantial C content indicates that conditions in the sediment were nonoxidizing in both the black and gray sediments. The S contents are 5.5 and 3.3 percent in the black shales and 2.4 and 2.3 percent in the gray shales. This large amount of S (accompanied by iron as pyrite) indicates that the sediments were not only anoxic, but but also that $H_2S$ was present and thus conditions were chemically reducing. The presence of $H_2S$ in the overlying seawater has been suggested by Leventhal (1979).

The mineral ($SiO_2$, $CO_3$) content varies by 5 percent between the samples at 3,151 ft and 3,152 ft (91 percent and 96 percent ash, respectively) and by 3 percent between 3,121 ft and 3,122 ft (97 percent and 94 percent ash, respectively). The ash content is the mineral matter after removal of organic material and most sulfides. The trace elements, on the other hand, generally vary by 30 to 50 percent or more between the black-gray pairs; therefore, the trace element variation is not due to dilution by clastic (mineral) material. That is, addition of 3-5 percent more clastic material to the organic C-rich sample does not decrease the trace-element content comparably. The trace element changes are more likely to be due to a change in the amount of organic C and S, which vary by 30 to 50 percent. It appears that the organic material (and sulfide content, if an $H_2S$ layer was present in the water during deposition) concentrated the trace elements. This concentration could result as the dead organic matter settled through the water column. If an $H_2S$ layer was present, the interface of the $H_2S$ zone would act as a sink for metals that could form insoluble sulfides or be scavenged by FeS.

The above discussion on trace-element variation by dilution or concentration also holds for other black shales. The major-element change in the sample (amount of $SiO_2$ and $Al_2O_3$) was not enough to account for dilution or enrichment of trace elements. The enrichment in trace elements was due to concentration of organic matter as it passed from a terrestrial environment (or top layer of the water) to the floor of the marine body of water (the sediment-water interface). The enrichment could also be due to the presence of sulfide in the water ($H_2S$ layer), which precipitated trace elements with FeS at the sediment-water interface. The organic mode of concentration of trace elements is more powerful than the sulfide mode of concentration because the organic material must traverse the entire water column (allowing necessary time and exposure to the flux of trace elements). The organic mode also eliminates the necessity of an $H_2S$ layer.

If the overlying water is oxygenated, the sulfide produced by sulfate-reducing microorganisms which oxidize organic matter can only be present in the sediment where no oxygen is present. In general, these sediments have already trapped their water and trace elements, and enrichment of metals is no longer possible.

### Sediment deposition rate relative to trace-element contents

Another way to examine the metal concentration in shales is to consider deposition rates within the basin. If ten times as much sediment was deposited and the trace-element content was ten times lower, a dilution effect is clear. However, there is not 10 times (or 40 times) as much metal (average), or organic C, or sulfide in Tennessee samples (representing a 10-m thickness of sediment) relative to Ohio samples (400 m thickness of sediment) (Kepferle and Potter, written commun., 1978). So dilution does not explain the amount of metals, organic C, or sulfide; they are not as enriched in Tennessee (or as diluted in Ohio) relative to difference in deposition rate.

The results of the analyses may be considered on the basis of the metal/organic or metal/sulfide ratio by normalizing the metals to their concentrating agents. The data on table 10 show that the U/organic C ratio is about 20 percent higher for Overton County relative to other areas, whereas the ratios (metal/organic C) for the other metals are the same. The ratios for some of the other metals are actually lower for samples from Overton County, but the metal/organic C plots (figs. 12 and 16 for Zn and Ni, for example), show substantial metal contents at zero organic content, so these contents were subtracted before calculating this metal/organic C or metal/sulfide ratio.

The U/S ratio is much higher for Tennessee samples than for samples from the other areas, as is Zn/S, Mo/S is also higher, and Co/S and Ni/S are

Table 10.--Ratios of trace element/organic C and trace element/S in Devonian shale samples from five cores

[Trace elements in parts per million, organic C and S in percent. N.a., not applicable; --, not determined]

| | Washington Co., Ohio | | Carroll Co., Ohio | | Wise Co., Va. | | Martin Co., Ky. | | Overton Co., Ky. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Organic C | S | Organic C | S | Organic C | S | Organic C | S | Organic C | S |
| Co | 20 | 12 | 9.2 | 10.5 | 6.8 | 8.3 | 7.5 | 10 | 7.6 | 14.5 |
| Hg | .033 | .02 | .038 | .043 | .014 | .017 | .023 | .024 | .014 | .029 |
| Mo | 10 | 6 | 12.1 | 13.8 | 9.3 | 11.3 | 13.6 | 14.3 | 11 | 21 |
| Ni | *24 | 39 | *22 | 49 | *21 | 47 | *17 | 41 | *22 | 55 |
| V | 131 | 78 | 85 | 97 | 98 | 120 | 73 | 76 | 45 | 86 |
| Zn | *40 | 49 | *21 | 48 | -- | -- | -- | -- | *43 | 94 |
| Cu | 38 | 23 | 28 | 32 | 19 | 23 | -- | -- | 16 | 31 |
| U | 5.5 | 3.3 | 4.4 | 5.0 | 4.8 | 5.8 | 4.9 | 5.1 | 6.1 | 11.5 |

*Ni and Zn data were first normalized to zero organic C (figs. 11, 14, 15, and text).

slightly higher. These higher ratios may reflect the nearly complete sulfidation of iron to pyrite (fig. 3), resulting in the concentration of the other metals as sulfides by excess sulfide after all available Fe had been reacted.

## Discussion of statistical treatment and misleading results

Data were plotted and visually examined, notes were checked, and hand specimens or polished sections were reviewed before taking the liberty of eliminating samples which could give statistically misleading results. In determining statistical correlation coefficients a number of misrepresentations can occur if one does not apply geochemical principles.

Two good examples of statistically misleading results presented. As discussed earlier, one sample (fig. 9) from Wise County, Va., containing high values of V and organic C, makes the r value much higher and makes the line statistically significant; however, when excluding that one sample, the line is similar but not statistically significant. The statistics were calculated using the equation $y=mx+b$, where m is the slope and b is the value of y at $x=0$ (intercept). In the statistical treatment, x is specified as the independent variable and y (the dependent variable) is controlled by x. If x and y are interchanged, the equation becomes $x=my+b$, and the r is the same but the slope of the line is different. Figure 9 is reproduced as figure 27 showing the lines for $y=mx+b$ (with and without sample 1) and for $x=my+b$ (with and without sample 1). The lines without sample 1 are not statistically significant and are very different. The intercepts are quite different for $y=mx+b$; the intercept value implies that a sample with about 2 percent organic matter would not have V, which makes no sense. For $x=my+b$ the intercept indicates that a shale containing no organic matter would have about 170 ppm V, which seems reasonable because V is present in the clay fraction. This example

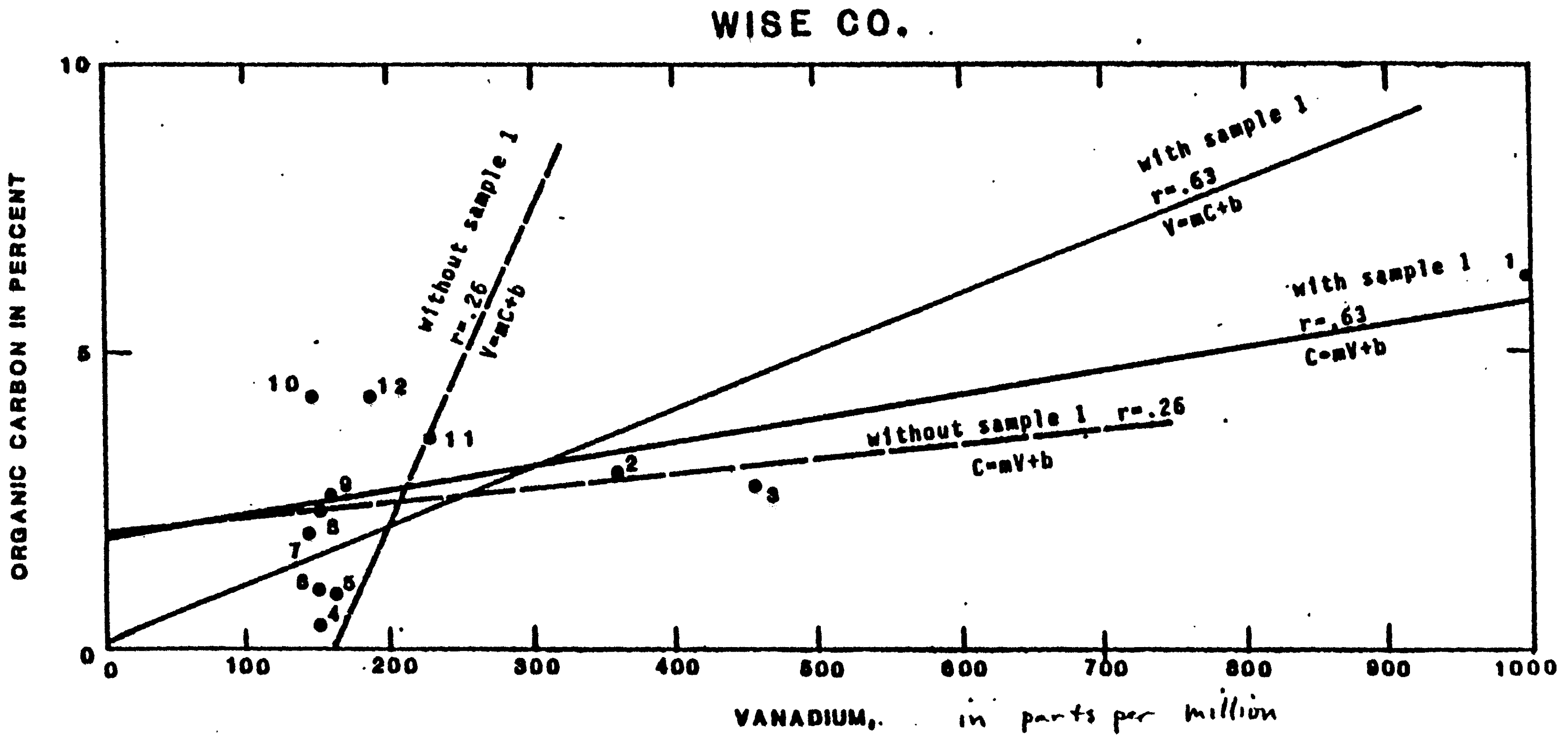


Figure 27. Diagram showing several statistical results in samples from Wise County, Va., for organic C vs. V.

is an extreme case but illustrates the misleading results that can be obtained when statistics are used without plotting and inspecting the data and applying geochemical principles.

The second example of misleading results concerns data which give a poor statistical fit (fig. 12), but if one alue is removed (sample 17, Martin County, Ky.), the fit becomes very good. Sample 17 is pyrite rich (about 10 percent S) and contains a large pyrite nodule; the sample is different enough to easily justify removing it from the data set. The same situation occurs for Martin County, Ky., shown on figure 16 where the Ni vs. organic C correlation is significant if sample 17 is omitted. On figure 17 two samples from Overton County, Tenn., were omitted from the data, resulting in a significant Ni vs. organic C correlation.

From the data from Overton County, Tenn., highly significant correlations were observed between $SiO_2$ and $K_2O$, $Al_2O_3$ and $K_2O$, and $SiO_2$ and $Al_2O_3$. These correlations are perfectly reasonable as these elements (oxides) can form illite which is a major component (Hosterman and Loferski, 1978).

A third instance of misleading results can arise in looking for the site of Ti ($TiO_2$). Is it associated with the Fe, S, organic C, or Si fraction? Many Ti minerals contain Fe, but because much of the Fe is in pyrite we see no clear relationship. It is also possible that we are not seeing geochemical affinities at all, but merely the association of samples with high contents of silicates and Ti and low contents of $CO_3$, organic C, and pyrite. This association, of course, could suggest that those samples containing high Ti and $SiO_2$ were deposited nearest to shore. $SiO_2$ and $TiO_2$ showed a highly significant correlation which could indicate the occurence of Ti in a silicate. However, $TiO_2$ also showed a correlation with $K_2O$, which has no relation to $TiO_2$ in most minerals. The $K_2O$ is, of course, related to part of

Table 11.--Statistical relationship for certain elements in Devonian shales

[S, highly significant; N, not significant]

| Element associations | r | Significance | Comment |
|---|---|---|---|
| $SiO_2$ vs. $Al_2O_3$ | 0.90 | S | Forms clay minerals. |
| $SiO_2$ vs. $K_2O$ | .96 | S | Do. |
| $Al_2O_3$ vs. $K_2O$ | .98 | S | Do. |
| $TiO_2$ vs. $SiO_2$ | .97 | S | $K_2O$, $SiO_2$, and $Al_2O$ in clays, $TiO_2$ not in clay but with $SiO_2$. |
| $TiO_2$ vs. $K_2O$ | .94 | S | |
| $TiO_2$ vs. $Al_2O_3$ | .89 | S | |
| $TiO_2$ vs. $Fe_2O_3$ | .14 | N | |
| $TiO_2$ vs. S | .05 | N | |
| $TiO_2$ vs. organic C | .05 | N | |

Table 12.--Statistical data for elements in shale from Leventhal (1978a)

[N.s., not significant]

| Leventhal (1978a) |  | Element pair | r | Significant at percent level | Location |
|---|---|---|---|---|---|
| Figure | Page |  |  |  |  |
| 4 | 17 | Organic C-Hg | 0.80 | 99 | Perry County, Ky. |
| 5 | 17 | Organic C-Mo | .95 | 99 | Do. |
| 6 | 18 | V-Ni | .69 | 99 | Do. |
| 7 | 18 | Co-Ni | .30 | N.s. | Do. |
| 8 | 19 | $Fe_2O_3$-S | .86 | 99 | Do. |
| 10 | 20 | Zn-S | .59 | 95 | Jackson and Lincoln Counties, W. Va. |
| 11 | 20 | Hg-S | .06 | N.s. | Do. |
| 15 | 22 | V-Ni | .68 | 99 | New York. |
| 16 | 23 | Organic C-Mo | .85 | 99 | Do. |
| 17 | 23 | Organic C-Hg | .99 | 99 | Do. |
| 18 | 24 | Hg-S | .35 | N.s. | Do. |
| 19 | 24 | Organic C-Ni | .79 | 99 | Do. |
| 21 | 25 | Cd-Zn | .93 | 99 | New York, Perry Co., Ky., and Lincoln Co., W. Va. |
| Figure 18 this report |  | Organic C-Ni | .81 | 99 | Perry County, Ky. |

Table 13.--Correlation coefficients (r) for pairs of elements from the samples studied from five locations

[Unless noted, values are statistically significant at the 99-percent level. Values of r < 0.50 not listed. N.s., not statistically significant; --, not tested; n, number of pairs]

| Element pair | Overton Co., Tenn. (n=14) | Wise Co., Va. (n=12) | Martin Co., Ky. (n=18) | Washington Co., Ohio (n=7) | Carroll Co., Ohio (n=10) |
|---|---|---|---|---|---|
| Fe-S | 0.77 | +0.85 | N.s. | N.s. | N.s. |
| Zn-S | N.s. | N.s. | 0.59 | N.s. | N.s. |
| V-S | N.s. | N.s. | N.s. | N.s. | N.s. |
| Hg-S | .71 | .76 | .72 | N.s. | *0.60 |
| As-S | .75 | *.65 | .95 | 0.64 N.s. | N.s. |
| Mo-S | .75 | N.s. | N.s. | N.s. | N.s. |
| Zn-C | +.76 | -- | +.87 | N.s. | N.s. |
| V-C | N.s. | *.63 | N.s. | N.s. | .57 N.s. |
| Hg-C | .90 | +.79 | .63 | .89 | *.71 |
| As-C | .84 | N.s. | N.s. | *.77 | N.s. |
| Mo-C | .86 | .77 | .90 | *.81 | .85 |
| Ni-C | +.88 | .72 | .77 | N.s. | .87 |
| Fe-Ni | *+.66 | -- | -- | -- | -- |

*Only 95 or 98 percent significance level.

___ One high sample included.

+ One high sample omitted.

the $SiO_2$. The relative order of the r values may show the primary relationship, or it may not; geochemical and mineralogical principles are essential. The $SiO_2$ vs. $TiO_2$ gave a larger r (table 11) value than the other relationships, which makes geochemical sense. Table 12 gives the statistical relationships for elements from Leventhal (1978a) and table 13 gives the statistical relationships for data from this study.

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