UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Trace elements, carbon and sulfur in Devonian black shale cores from Perry County, Kentucky; Jackson and Lincoln Counties, West Virginia; and Cattaraugus County, New York

By

Joel S. Leventhal

Open File Report 78-504

1978

Contents

Tables

Figures

Trace elements, carbon and sulfur in Devonian black shale cores from Perry County, Kentucky; Jackson and Lincoln Counties, West Virginia; and Cattaraugus County, New York

Joel S. Leventhal

U.S. Geological Survey, Denver, CO

Abstract

As part of the Eastern Gas Shales Project (Department of Energy, Morgantown, West Virginia), cored samples from four localities have been analyzed by several analytical techniques. Samples were analyzed by six-step semiquantitative emission spectrography for 8 major and 23 minor and trace elements. Semiquantitative X-ray fluorescence was used to analyze for SiO_2, Al_2O_3, Fe_2O_3, TiO_2, K_2O, CaO, As, Se, Ge, Sb, and Sn.

Quantitative analysis was used for organic carbon and sulfur. Uranium and thorium were analyzed by a delayed-neutron technique. Atomic-absorption spectroscopy was used for Mo, Co, Hg, Cd, Ni, and Zn. V was measured by colorimetry.

The contents of minor and trace elements vary considerably in different samples. The maximum value divided by the minimum value illustrates this: for Ca the maximum divided by minimum is 50; for Mn, 20; for Sb, 21; for As, 35; for organic carbon, 56; for Cd, 18; for Mo, 202; for Zn, 30; and for S, 80.

Regional trends are also evident; Lincoln Co, shows higher values for Hg, Ni, As, B, Cr, Cu, Sc, and Mo than the other localities.

The major elements showed changes reflecting the following lithology-shale sand silt, and carbonate. Minor-element abundances are controlled by carbon and sulfur.

Down-hole plots of the core data and plots of one element vs another element are used to understand the controls of element abundance and environment of deposition.

Introduction

As part of the Eastern Gas Shales project, the U.S. Geological Survey is measuring the uranium and trace elements in Appalachian Devonian black shale. Leventhal and Goldhaber (1977) presented results of U, Th, S, and organic C from the same four cores. As a survey, six step emission spectroscopy or X-ray fluorescence analysis is used. Quantitative analysis of certain elements was also done. One of the main objectives is to understand the possible economic resources: U, V, Co, Ni and Mo, as well as of C and S. A second objective is to document the abundance of certain volatile elements: Hg, As, and Se. Finally, a scientific goal is to understand geochemical principles related to the abundance of trace elements in black shale and relate this to source areas and depositional environments. With the aid of USGS associates, this information will be used to support stratigraphic correlation. The underlying assumption is that careful analytical work coupled with geochemical, microscopic, and isotopic information on fewer, well-documented samples will yield insights that are not possible from survey-type chemical analysis and statistical treatments of large numbers of samples.

The data presented here are in final form. The geochemical interpretations are preliminary and are meant to show the possible treatments that may be made in addition to the usual statistical treatments, such as regression coefficients and factor analysis. As the data for more cores become available, it will be possible to give a basin-wide geochemical treatment to understand the source of sediments, depositional environment, and diagenetic effects.

Samples

Core samples were obtained as follows:

Perry County, Kentucky. Nicholas Combs #7239. Twenty-one samples from 2371 to 2706 ft. The core is described by Bryer and Trumbo (1976).

Jackson County, West Virginia. Columbia Gas Co. well 12041. Five samples representing a depth interval from 3483-366 ft.

Lincoln County, West Virginia. Columbia Gas Well 20402. Nine samples over three shale intervals.

Cattaraugus County, New York. Samples were obtained by the author from Arthur Van Tyne (N.Y. State Geological Survey). In all, 48 samples were taken, all were analyzed for uranium and organic carbon and 25 were analyzed for other elements. The core was taken from the West Valley Nuclear Fuel waste disposal site and is described by de Laguna (1972).

The locations are shown on Figure 1. The core logs and descriptions for Perry County (Provo, Kepferle, Maynard, Potter, Univ. Cincinnati, written communications, 1977) and New York (de Laguna 1972 and Van Tyne, written communication, 1977) are shown in Figures 2 and 3, respectively.

Depths are given in feet (to the nearest foot) rather than meters for two reasons: the drilling depths and measurements were made that way, and other investigators in the Eastern Gas Shales program will all be using feet.

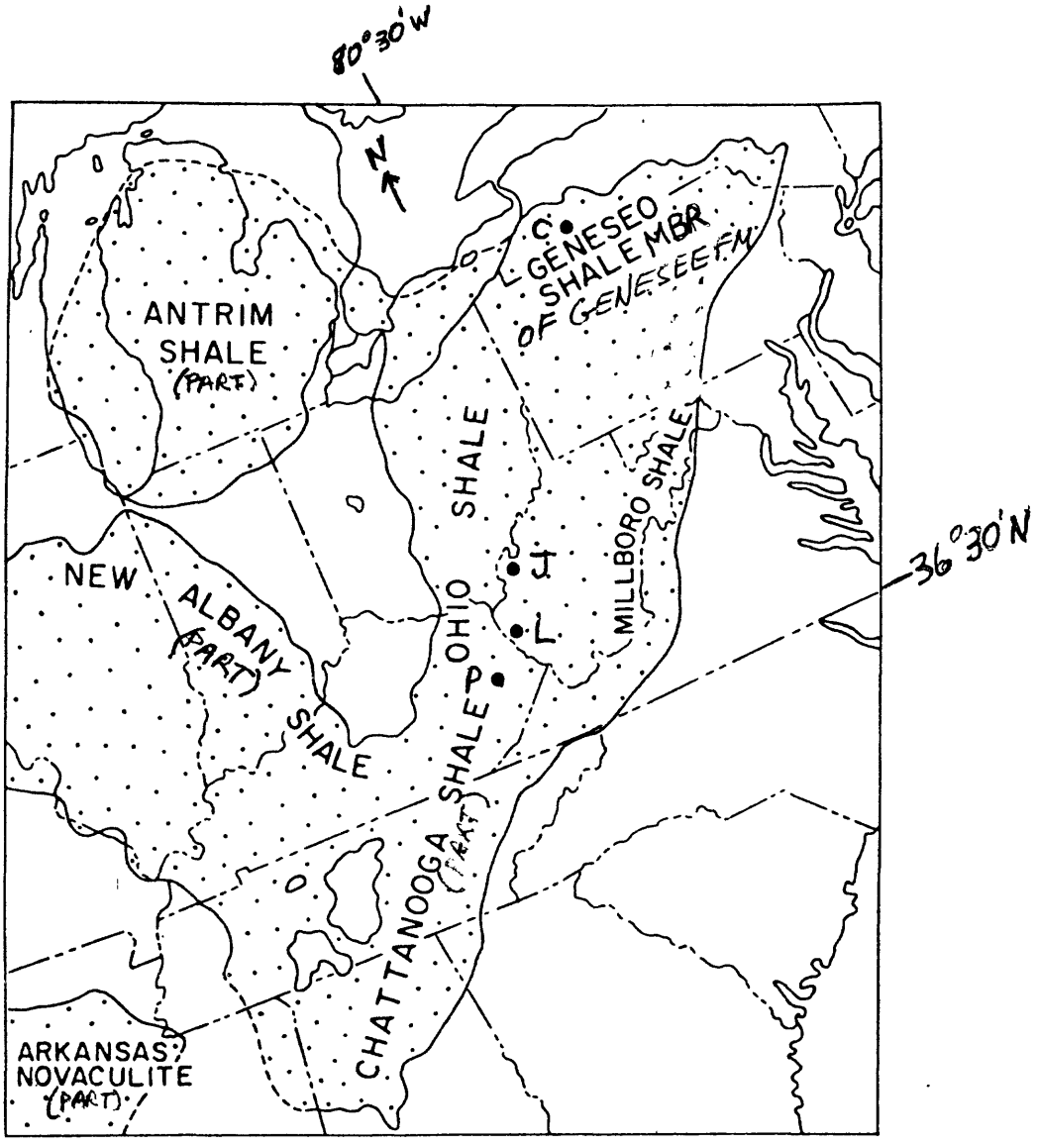

Figure 1. Map showing regional distribution of Devonian black shale (dot pattern) in eastern United States, and location of Perry County, Kentucky (P); Lincoln County, West Virginia (L); Jackson County, West Virginia (J); and Cattaraugus County, New York (C) (from Leventhal and Goldhaber, 1977)

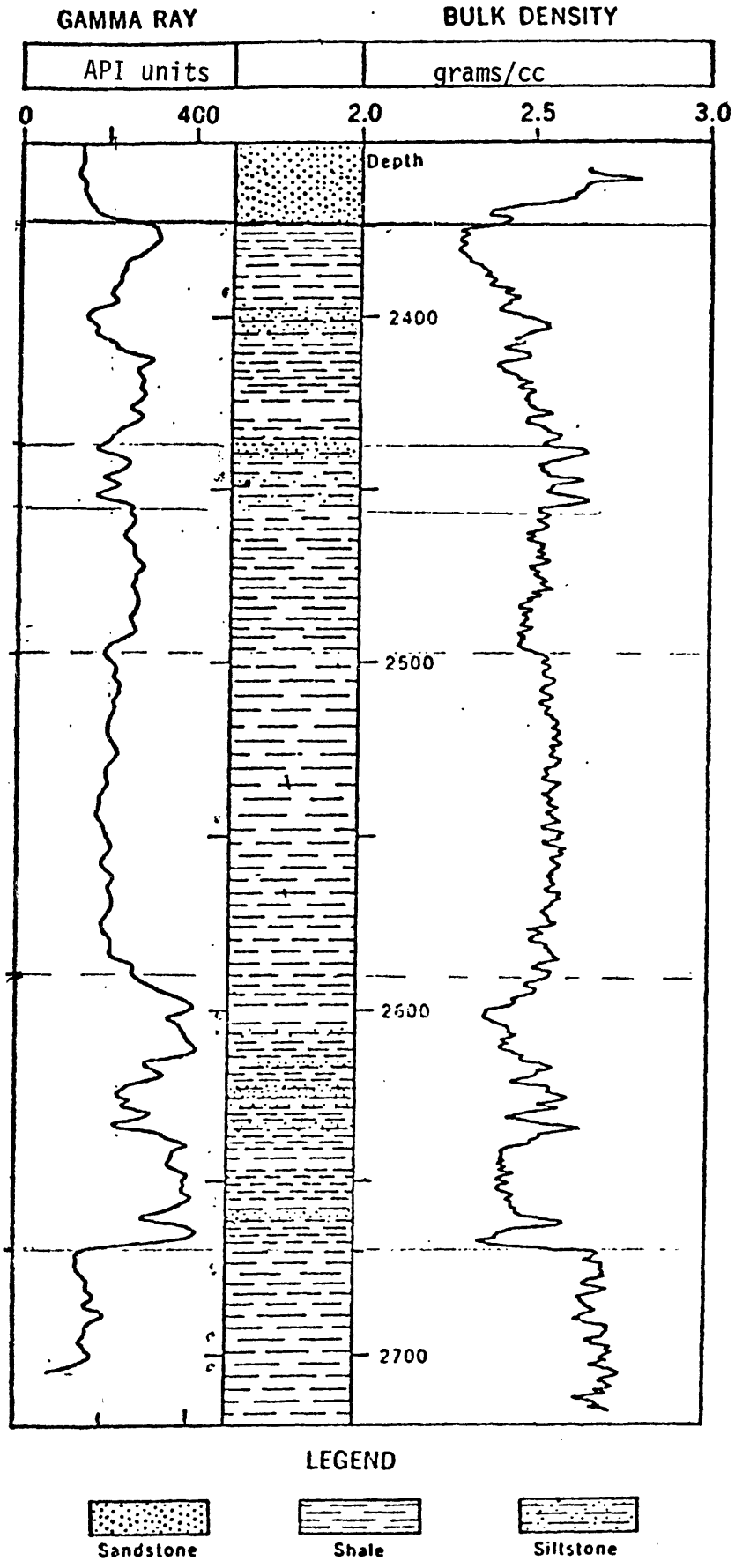

Figure 2. Gamma-ray and bulk-density logs, Perry County, Kentucky

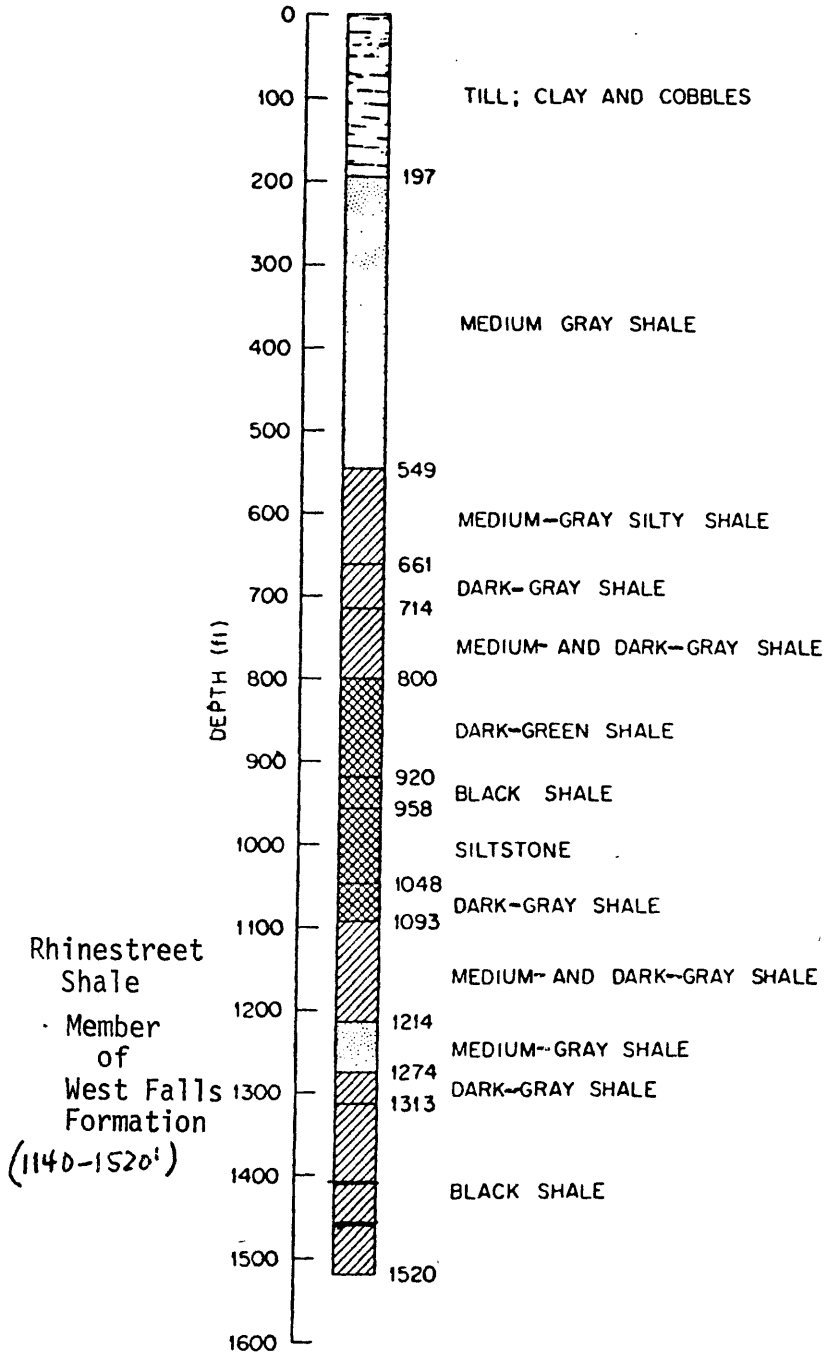

Figure 3. Graphic plot of a somewhat simplified log, Cattaraugus County, New York.

Methods of Analysis

Six-step emission spectroscopy was used to analyze for the following elements: Si, Al, Fe, K, Na, Ca, Ti, Mg, Ag, B, Ba, Be, Cr, Cu, Co, La, Ni, Nb, Pb, Sc, Sr, V, Y, Zn, Zr, Na, Ce, Ga, Li, Yb, Nd, Mo, and Mn.

Semiquantitative X-ray fluorescence was used to analyze for Fe, Ca, Si, Al, K, Ti, Mn, As, Se, Ge, Sn, and Sb. Organic carbon was determined by difference or by wet oxidation.

Quantitative measurements of Mo, Ni, Co, Hg, Cd, and Zn were determined by atomic absorption, and V was determined by spectrophotometry.

Sulfur was analyzed by the induction-furnace combustion-iodimetry method.

Details of C, S, U, and Th determinations are given in Leventhal and Goldhaber (1977). Details of the other analytical procedures and precision are given in Leventhal and others (1978).

Results

Raw data for Perry County, Kentucky, are given in Tables 1 and 2. Raw data for Lincoln and Jackson Counties, West Virginia, are presented in Tables 3a and b and 4a and b. They are presented together to save space, not because they are the same.

Raw data for the Cattaraugus County, New York, core are given on Tables 5 and 6. Table 5 includes additional data for S and C not given in Leventhal and Goldhaber (1977).

Table 1

Data for selected elements from

Perry County, Kentucky

Serial No.	Field No.	ON THE ASH % Ash	Cd (ppm)	Co (ppm)	Mo (ppm)	Ni (ppm)	V (ppm)	Zn (ppm)	Hg[1] (ppm)
D185730	P-1	82.2	28	16	202	213	1800	1310	.07
D185731	P-2	88.0	11	13	91	155	1260	414	.06
D185732	P-3	89.4	25	16	39	170	440	1430	.08
D185733	P-4	89.0	4	16	92	164	850	326	.06
D185734	P-5	95.0	<1	18	5	91	335	61	.05
D185735	P-6	96.1	<1	18	<1	67	145	39	.02
D185736	P-7	90.0	<1	34	75	179	215	150	.06
D185737	P-8	93.3	<1	28	44	134	210	95	.05
D185738	P-9	94.0	<1	21	27	117	220	48	.05
D185739	P-10	92.2	<1	26	47	86	120	135	.04
D185740	P-12	95.4	<1	26	42	75	185	71	.04
D185741	P-13	94.9	<1	24	39	76	140	89	.04
D185742	P-14	92.6	<1	27	42	91	170	78	.05
D185743	P-15	86.8	<1	19	109	82	180	53	.08
D185744	P-16	89.8	<1	39	78	171	240	106	.06
D185745	P-17	96.8	<1	10	<1	45	140	47	.02
D185746	P-18	89.6	<1	32	105	112	195	66	.08
D185747	P-19	97.5	<1	13	<1	62	129	56	.03
D185748	P-20	96.7	<1	13	<1	66	140	69	.01
D185749	P-21	97.3	<1	15	<1	66	175	68	.01

[1]On the raw sample.

Table 2
X-ray fluorescence data for
Perry Co. KY

		on the ash, in percent						on raw sample in ppm				Ash
		SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	Sn	Sb	Ge	As	Se	MnO
1	2371.1	67	17	5.4	4.	0.96	1.0	1.5	6.4	1.7	16	11	*
2	2383.6	70	14	4.3	3.9	1.7	.80	15	5.3	1.6	16	7.1	*
3	2393.1	63	12	9.8	3.4	1.1	.78	20	21.	1.2	52	8.0	*
4	2410.4	68	17	4.6	3.9	1.7	.97	1.7	4.7	1.8	26	3.3	*
5	2431.7	65	18	5.4	4.8	1.1	.96	2.0	2.2	1.5	25	0.6	*
6	2449	64	16	6.6	4.8	1.2	.95	2.3	*	1.7	7.2	.3	*
7	2456	65	18	6.5	4.2	1.3	.99	18	1.9	.9	25	1.1	*
8	2471	62	17	6.5	4.8	1.1	.89	17	1.6	1.1	36	.6	*
9	2491	62	14	7.5	4.3	.87	.87	2.0	2.4	1.0	44	1.3	*
10	2513.2	65	17	6.7	3.8	3.2	.84	1.9	*	1.1	25	.7	*
11	2531.1												
12	2553.2	59	17	8.0	4.8	.93	.62	1.7	*	1.0	25	.4	*
13	2572.2	61	17	8.6	4.4	1.2	.76	2.2	1.1	1.4	35	.9	.054
14	2589.5	60	17	9.0	4.5	1.4	.76	1.6	1.1	.9	41	.8	*
15	2605.4	63	13	14	3.6	1.3	.73	1.0	1.2	.6	55	.9	*
16	2617.2	63	16	8.4	4.4	1.7	.93	1.3	2.3	.9	30	.3	.970
17	2629.8	65	18	4.8	4.9	1.7	.95	3.0	*	1.7	3.1	.2	.060
18	2648	63	17	7.2	4.8	1.1	.78	1.7	1.9	1.2	23	*	*
19	2670	65	18	5.6	4.3	1.2	.93	2.1	*	1.7	3.2	.1	.064
20	2689.9	57	18	6.3	5.0	3.6	.97	2.8	*	1.6	6.1	.2	.089
21	2706.0	60	20	6.2	5.5	1.4	1.0	1.7	*	1.8	1.5	.2	.059

Table 3a. Data for Lincoln County, West Virginia, for selected elements.

(⊛ on the raw (unashed) sample,

Field No.	Organic ⊛ Carbon	% Ash	Cd ppm	Co ppm	Hg ⊛ ppm	Mo ppm	Ni ppm	V ppm	Zn ppm	%S ⊛
L-2733	----	96.6	<1	22	0.03	<1	73	190	108	0.37
L-3020	0.64	96.3	<1	21	.55	3	70	160	104	1.2
L-3312	1.32	93.4	<1	45	.37	12	102	130	163	5.7
L-3398	1.25	95.8	<1	18	.11	15	67	170	136	1.1
L-3551	4.2	92.2	<1	38	.08	55	124	150	116	2.4
L-3914	2.6	95.0	<1	13	.09	6	87	445	49	1.7
L-3951	8.0	88.3	4	28	.13	179	381	800	249	3.3
L-3956	6.4	90.5	1	24	.11	93	225	485	90	2.5
L-3961.6	3.4	95.1	<1	23	.09	70	269	285	55	1.2

Table 3b. Data for Jackson County, West Virginia, for selected elements

(* on the raw (unashed) sample, * below detection limits 1 ppm for Cd and Mo.)

Field No.	Organic ⊛ Carbon	% Ash	Cd ppm	Co ppm	Hg ⊛ ppm	Mo ppm	Ni ppm	V ppm	Zn ppm	%S ⊛
C-3483	0.2	95.2	1	14	0.03	1	53	150	60	0.26
C-3573	3.9	92.2	<1	26	.04	42	90	150	116	2.5
C-3625	3.5	93.9	<1	21	.05	37	80	150	81	1.7
C-3640	5.6	93.3	<1	23	.05	84	131	205	140	1.8
C-3660	0.2	88.4	<1	14	.02	<1	56	185	75	0.1

Table 4a. X-ray fluorescence data for Lincoln County, West Virginia

(* below detection limits, 1.0 for Sb, 0.1 for Se, 0.05 for MnO)

	On the ash in percent						On the raw sample in ppm					on ash %
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	Sn	Sb	Se	As	Se	MnO
L-2733	60	19	6.4	4.7	.62	1.1	4.5	1.3	2.5	27	*	*
L-3020	58	20	7.4	4.7	.87	.99	3.8	*	2.5	30	*	*
L-3312	54	16	14	4.1	1.1	.78	1.9	1.1	1.7	39	*	*
L-3398	60	19	6.3	5.1	.95	1.1	2.9	*	2.1	24	*	.05
L-3551	63	16	7.4	4.2	1.1	.86	.8	*	.8	.4	.4	*
L-3914	63	17	6.1	4.9	.96	.67	.7	1.7	1.4	22	1.2	*
L-3951	53	13	8.2	4.5	7.0	.65	.5	7.0	.9	28	.4	*
L-3956	58	15	7.0	4.8	4.8	.58	.7	4.9	1.0	26	*	*
L-3961.6	61	16	6.1	4.7	2.1	.56	1.5	2.8	1.6	16	*	*

Table 4b. X-ray fluorescence data for Jackson County, West Virginia

(* below detection limits, 1.0 for Sb, 0.1 for Se, 0.05 for MnO)

C-3483	59	17	9.7	4.3	2.7	.92	2.4	*	2.1	11	*	0.14
C-3573	64	16	8.2	4.5	.76	.89	2.3	2.5	1.6	28	*	*
C-3626	65	17	6.7	4.5	.82	.84	3.7	1.8	2.0	18	.1	*
C-3640	64	16	6.7	4.2	.85	.89	3.4	2.7	2.1	26	.2	*
C-3660	64	18	5.6	4.6	2.2	1.0	4.4	*	2.5	2.1	*	*

Table 5. Data for Cattaraugus County, New York, for selected elements.

(Ⓐ on the raw (unashed) sample; other elements on the ash)
(* below detection limits, 1 for Cd, 1 for Mo; ---no data)

Depth Ft.	% S Ⓐ	% Ash	Cd ppm	Co ppm	Hg Ⓐ ppm	Mo ppm	Ni ppm	V ppm	Zn ppm	% Ⓐ C org
562	1.3	97.0	*	25	.02	*	79	185	103	0.43
721	1.1	98.7	*	9	.01	2	36	65	57	.13
962	---	97.2	*	26	.02	1	71	190	107	.24
1047	---	96.1	*	25	.04	22	78	95	112	---
1242	.6	97.2	*	16	.03	*	69	185	68	---
1255	.6	97.2	*	18	.04	*	70	165	68	.34
1256	.3	98.4	*	8	.02	*	48	50	42	.1
1257	---	96.6	*	19	.04	*	78	170	70	.33
1297	1.4	95.1	*	19	.04	33	102	280	63	2.5
1315	2.1	95.9	*	19	.04	12	91	345	56	1.6
1344	.8	96.6	*	15	.03	*	65	235	64	.50
1366	2.0	94.5	*	18	.05	37	101	165	111	3.0
1389	8.7	96.0	*	24	.04	2	98	230	62	1.0
1421	1.4	93.6	16	14	.07	29	105	205	1310	3.8
1439	1.4	92.8	*	19	.06	57	111	245	57	4.3
1442	2.0	96.2	*	20	.05	10	108	295	56	1.4
1450	1.3	94.0	*	15	.05	40	111	235	47	---
1463	1.4	95.8	*	18	.06	1	86	245	98	1.3
1470	---	95.0	*	20	.04	46	106	160	144	2.4
1477	1.9	95.6	*	22	.03	16	117	300	59	1.5
1478	1.4	92.8	9	20	.07	64	129	240	568	3.6
1490	1.4	94.2	*	16	.06	29	112	270	49	3.7
1494	1.3	93.1	*	18	.07	37	100	215	50	---
1498	1.1	93.1	*	16	.05	31	98	220	85	2.2

Table 6. Data for Cattaraugus County, New York, for X-ray fluorescence determination

(* below detection limit 1.0 for Sb, 0.1 for Se, 0.05 for MnO)

	On the ashed sample in percent						On the raw sample in ppm					Ash
Depth Ft.	SiO_2	Ai_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	Sn	Sb	Ge	As	Se	MnO
562	55	19	9.1	5.0	.82	1.0	3.5	*	2.3	2.6	.2	*
721	57	7.1	5.3	1.7	16	.76	2.1	*	1.6	9.3	*	.35
962	60	18	7.7	4.4	1.1	1.1	3.8	*	2.3	19	*	.067
1047	56	13	9.7	3.2	11	.87	2.1	*	1.5	51	*	.071
1242	59	16	6.9	4.1	3.5	.89	2.7	*	2.5	8.7	.3	.067
1255	58	17	6.4	4.3	5.1	.93	2.9	*	2.2	11	*	.081
1256	28	5.2	4.8	1.7	38	.44	1.0	*	.8	2.8	*	.46
1257	57	17	9.9	4.5	3.4	.95	3.1	*	2.4	8.8	*	.100
1297	65	17	6.4	43	.97	.93	1.9	1.1	1.7	17	*	*
1315	61	16	7.4	4.3	.83	.87	2.6	*	2.2	8	.5	.077
1344	60	17	7.0	5.0	1.1	.89	.4	*	.3	22	.4	.069
1366	68	16	6.8	4.0	.85	.97	2.3	1.7	1.8	14	.3	*
1389	62	20	7.5	5.0	1.1	.93	4.1	2.1	2.4	20	.3	*
1421	74	13	4.7	3.4	1.1	.79	1.5	1.4	1.4	9.8	*	*
1439	63	15	6.1	4.2	.87	.89	2.4	1.2	1.6	8.9	.3	*
1442	61	17	7.1	4.3	.96	.79	2.7	5.4	1.9	16	1.2	*
1450	72	15	5.3	3.6	1.0	.87	1.9	1.7	1.8	13	*	*
1463	65	17	7.1	4.6	1.7	.91	2.4	*	2.2	11	*	*
1470	69	17	6.6	4.1	.81	1.0	2.7	1.1	1.9	13	*	*
1477	62	17	6.8	4.6	1.2	.82	1.0	1.7	1.4	25	.2	*
1478	63	17	5.7	4.4	.87	.87	2.6	2.0	1.9	9.1	.5	*
1478	67	18	5.6	4.6	.80	.89	2.9	1.9	2.4	9.8	*	*
1490	64	15	6.0	4.3	.85	.79	2.2	2.0	1.9	16	.7	*
1494	66	15	5.6	4.1	.79	.82	2.5	1.7	1.9	11	.5	*
1498	67	15	5.5	4.1	1.3	.73	3.0	1.9	2.1	10	.3	*

Discussion and Conclusion

The data are summarized on Tables 7, 8, and 9. Table 7 shows the minimum, maximum, and average values for selected elements from the four areas. Also included are the data on C, S, and U from Leventhal and Goldhaber (1977). Certain elements show a very wide range, often owing a few very high or very low values. These elements and the maximum divided by minimum are: organic carbon, 56; Cd, 28; Hg, 18; Mo, 202; Zn, 30; and S, 80 (from data on Table 7).

Table 8 presents a summary of results for elements determined by X-ray fluorescence. Elements sharing a wide range in abundance (and their Max/Min ratio) include CaO, 50; Mn, 20; Sb, 21; As, 35; and Se, 110 (from data on Table 8).

Table 9 gives a summary of the six-step semiquantitative emission spectroscopy results.

Certain elements show higher average values in certain cores: Perry County: organic C, Zn, and U; Lincoln County: Hg, Ni, As, B, Cr, Cu, Sc, and Mo; Cattaraugus County: Mn, Ba, and CaO.

Certain elements show lower average values in certain cores: Jackson County, V; Cattaraugus County, Mo, U, and Cu.

Figures 4 through 21 show plots of one element compared to another. Particularly interesting are a major element (Fe, S, or organic carbon) relative to a minor element or two minor elements that should behave similarly in the igneous or sedimentary environment. Leventhal and Goldhaber (1977) have presented this data for U, S, and C as they relate to each other. Statistical-regression-equation determinations will be presented at a later time.

Table 7

Concentrations of certain elements in black shales (see text for analytical technique) in ppm except as noted

a, represents additional or fewer analyses (Leventhal and Goldhaber, 1977);
b, includes one high value or non-normal distribution;
c, $\frac{x}{2}$ as the value for < x, where x is the analytical lower limit; and
d, average not meaningful (see text)

	Perry, KY (20)		Jackson W.VA (5)		Lincoln W.VA(9)		Cattaraugus,NY (25)	
	min max	(avg)	min max	(avg)	min max	(avg)	min max	(avg)
Organic C%	0.2-12.9	(4.3)	0.1-5.6[a]	(1.9)	0.3 - 6.4[a]	(2.9)	0.1-4.5[a]	(1.5)
% Ash	82.2-97.5	(92.3)	88.4-95.2	(92.6)	88.3-96.6	(93.7	92.8-98.7	(95.4)
Cd	<1-28	d	< 1	d	<1-4[b]	d	<1-16[b]	d
Co	10-34	(21.2)	14-26	(19.6)	13-45	(25.8)	3-26	(18.2)
Hg	.01-.08	(.048)	.02-.05	.038	.03-.55	(0.17)[b]	.01-.07	(.044)
Mo [c]	<1-202	(52)	<1-84	(33)	<1-179	(48.2)[b]	<1-64	(21)
Ni	45-213	(111)	53-131	(82)	67-381	(155)	36-129	(91.4)
V	140-1800	(364)	150-205	(168)	130-800	(313	50-355	(214)
Zn	48-1430	(236)	60-140	(94)	55-249	(119)	42-1310	(145)
S %	.08-6.4	(2.3)	.03-2.6[a]	(1.5)	.37-5.7[a]	(2.3)	.3-8.7[a]	(1.7)[b]
U	3.2-3.8	(16.5)	3.4-21[a]	(9.1)	3.4-36.6[a]	(11.8)	1.5-15.8[a]	(6.7)
Th	12-17	d	12-19[a]	d	9.7-21.2[a]	d	7.2-19.6[a]	d

Table - 8

Range in concentration (of the ash) for elements and oxides, for X-ray fluorescence analyses

		Perry Co, Ky.		Jackson Co, W.Va.		Lincoln Co, W.Va.		Cattaraugus Co, N.Y.	
		Min Max	(Avg)	Min Max	(Avg)	Min Max	(Avg)	Min Max	(Avg)
SiO_2	%	57-70	(63.4)	59-65	(63.2)	53-63	(58.9)	28-74	(61.6)
Al_2O_3	%	12-20	(16.6)	16-18	(16.8)	13-20	(16.8)	5.2-20	(15.6)
Fe_2O_3	%	4.3-14	(7.1)	5.6-9.7	(7.4)	6.1-14	(7.7)	4.8-9.7	(6.6)
K_2O	%	3.4-5.5	(4.4)	4.2-6.6	(4.4)	4.1-5.1	(4.6)	1.7-5.0	(4.1)
CaO	%	.87-3.6	(1.5)	0.76-2.7	(1.5)	0.62-7.0	(2.2)	0.79-38	(3.8)
TiO_2	%	.62-1.0	(0.87)	0.84-1.0	(0.91)	0.56-1.1	(0.81)	.73-1.1	(0.87)
Mn*	%	.015-.050		.020-.085		.015-.030		.015-.300	
MnO	%	<.05-.089	d	<.05-.14	d	<.05-.05	d	<.05-.46	d
Sn	ppm	1.0-3.0	(1.9)	2.3-4.4	(3.2)	0.5-4.5	(1.9)	0.4-4.1	(2.4)
Sb[c]	ppm	<1.0-21[b]	(2.8)	<1.0-2.7	(1.7)	1.1-7.0	(2.3)	<1.0-5.4	(1.3)
Ge	ppm	.6-1.8	(1.3)	1.6-2.5	(2.1)	0.8-2.5	(1.6)	0.3-2.5	(1.9)
As	ppm	1.5-52	(2.62)	2.1-28	(17.0)	14-39	(25.1)	2.8-51	(14.8)
Se[c]	ppm	<1-11	(1.9)	<1-.2	(<1)	<.1-1.2	(0.3)	<.1-1.2	(0.25)

b. 1 high value or non normal distribution

c. using $\frac{<x}{2}$ as the value for <x, where x is the lower analytical limit.

* by 6 step spec, see table Multiply Mn x 1.29 to get MnO

d. average not meaningful (see text)

Table 9

Range in concentration for trace elements determined by six-step semiquantitative emission spectroscopy (on the ash)

(all values in ppm, except Mg and Na in %
(N, not detected; L, detected; --, average not meaningful)

	Perry, KY		Jackson, W.VA		Lincoln, W.VA		Cattaraugus, NY	
	Min Max	(Avg)	Min Max	(Avg)	Min Max	(Avg)	Min Max	(Avg)
%Mg	0.7 - 2	(1.3)	1.5 - 1.5	(1.5)	1.0 - 1.5	(1.3)	1.5 - 3.0	(1.6)
Mn	150 - 500	(213)	200 - 850	(390)	150 - 300	(190)	150 - 3000	(540)
Ag	N - 3	---	N	---	N - 2	---	N - .7	---
B	70 - 150	(144)	150	(150)	150 - 300	(217)	30 - 150	(139)
Ba	500 - 1000	(650)	500 - 600	(520)	300 - 700	(500)	300 - 3000	(840)
Be	3 - 3	(3)	3 - 3	(3)	3 - 7	(3.9)	N - 5	(29)
Cr	30 - 150	(77)	70 - 110	(84)	100 - 150	(139)	30 - 150	(109)
Cu	30 - 200	(106)	70 - 150	(108)	30 - 300	(138)	15 - 150	(81)
La	70 - 70	(70)	70 - 70	(70)	70 - 70	(70)	N - 70	(67)
Nb	15 - 30	(24)	20 - 30	(26)	15 - 30	(22)	10 - 30	(24)
Pb	10 - 70	(29)	10 - 70	(34)	15 - 70	(37)	10 - 70	(30)
Sc	15 - 30	(17)	75 - 30	(19)	30 - 30	(30)	15 - 30	(18)
Sr	150 - 200	(160)	150 - 300	(220)	100 - 300	(167)	150 - 300	(160)
Y	50 - 70	(64)	70 - 70	(70)	50 - 70	(68)	30 - 150	(68)
Zr	100 - 500	(160)	150 - 175	(155)	100 - 200	(139)	150 - 300	(168)
%Na	0.5 - 1.5	(0.73)	.7 - 1.1	(0.84)	0.1 - 1.5	(0.82)	.7 - 1.5	(.73)
Ce	L - 150	(100)	100 - 100	(100)	100 - 150	(106)	N - 100	(96)
Ga	15 - 30	(28)	30 - 30	(30)	30 - 30	(30)	15 - 30	(27)
Li	N - 100	---	N - L	---	N - 100	---	N - 150	---
Yb	7 - 10	(7.3)	7 - 7	(7.0)	7 - 10	(7.3)	3 - 7	(6.7)
Nd	70 - 150	(93)	70 - 70	(70)	70 - 100	(80)	N - 100	(70)
Mo	N - 150	(52)	N - 100	(49)	N - 150	(60)	N - 150	(37)

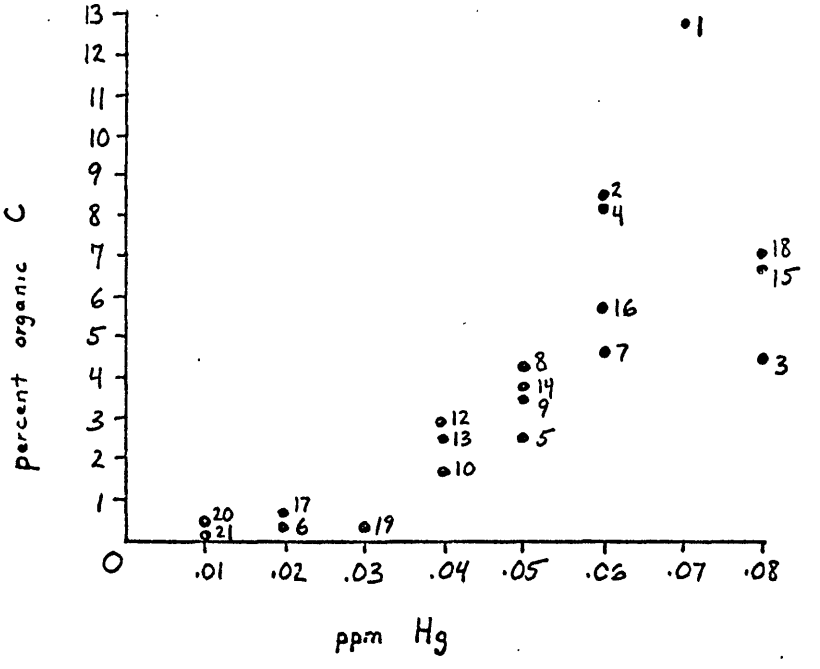

Figure 4. Perry County, Kentucky percent organic C plotted against ppm Hg

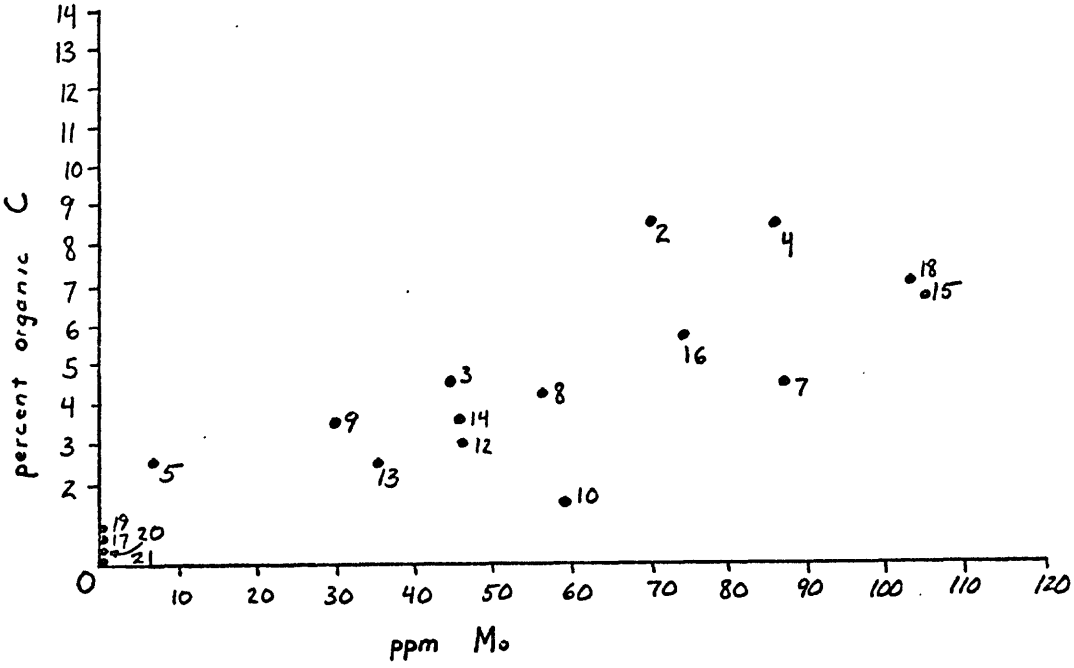

Figure 5. Perry County, Kentucky percent organic C plotted against ppm Mo

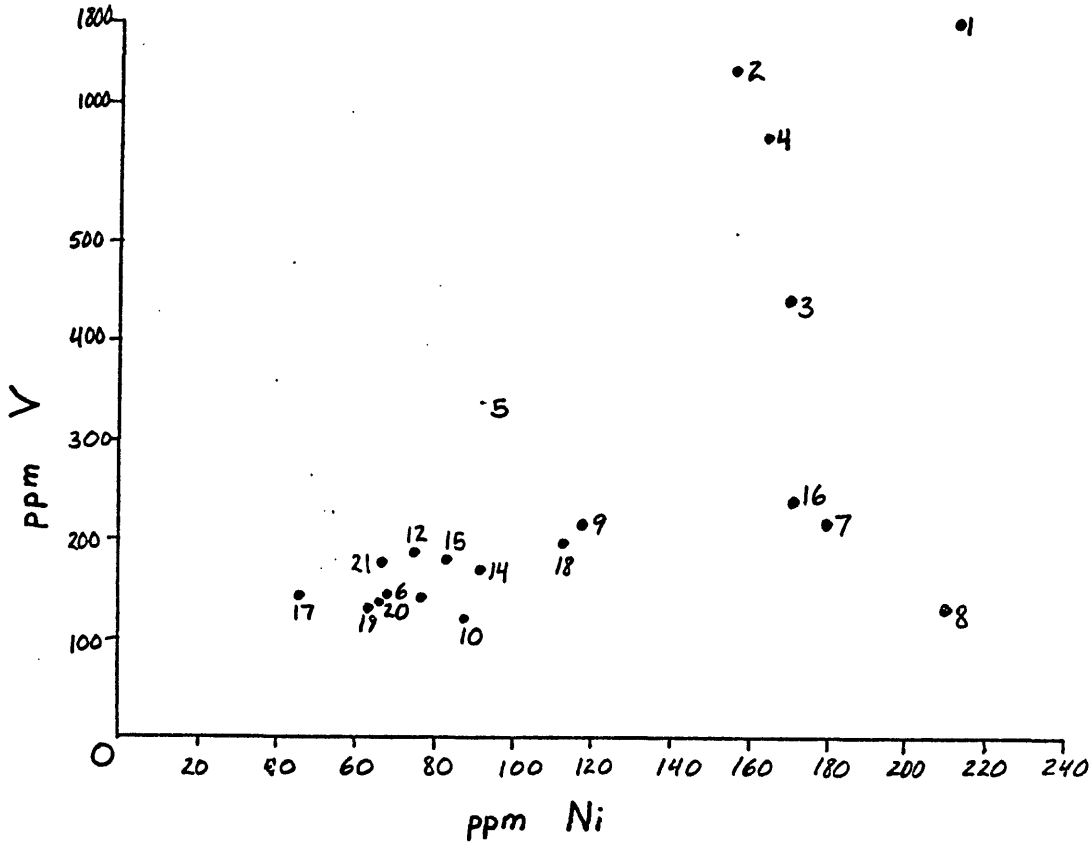

Figure 6. Perry County, Kentucky ppm V plotted against ppm Ni

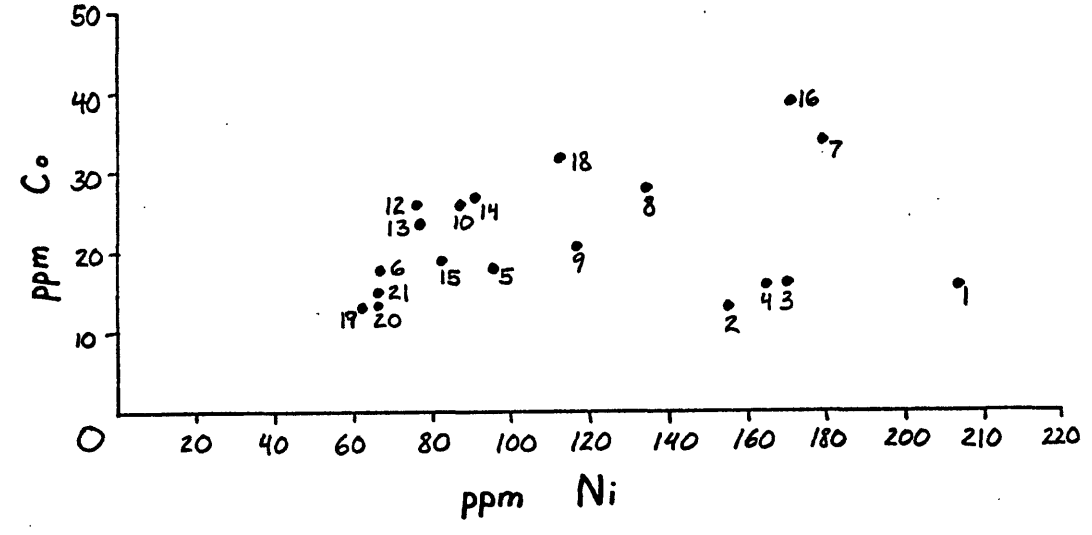

Figure 7. Perry County, Kentucky ppm Co plotted against ppm Ni

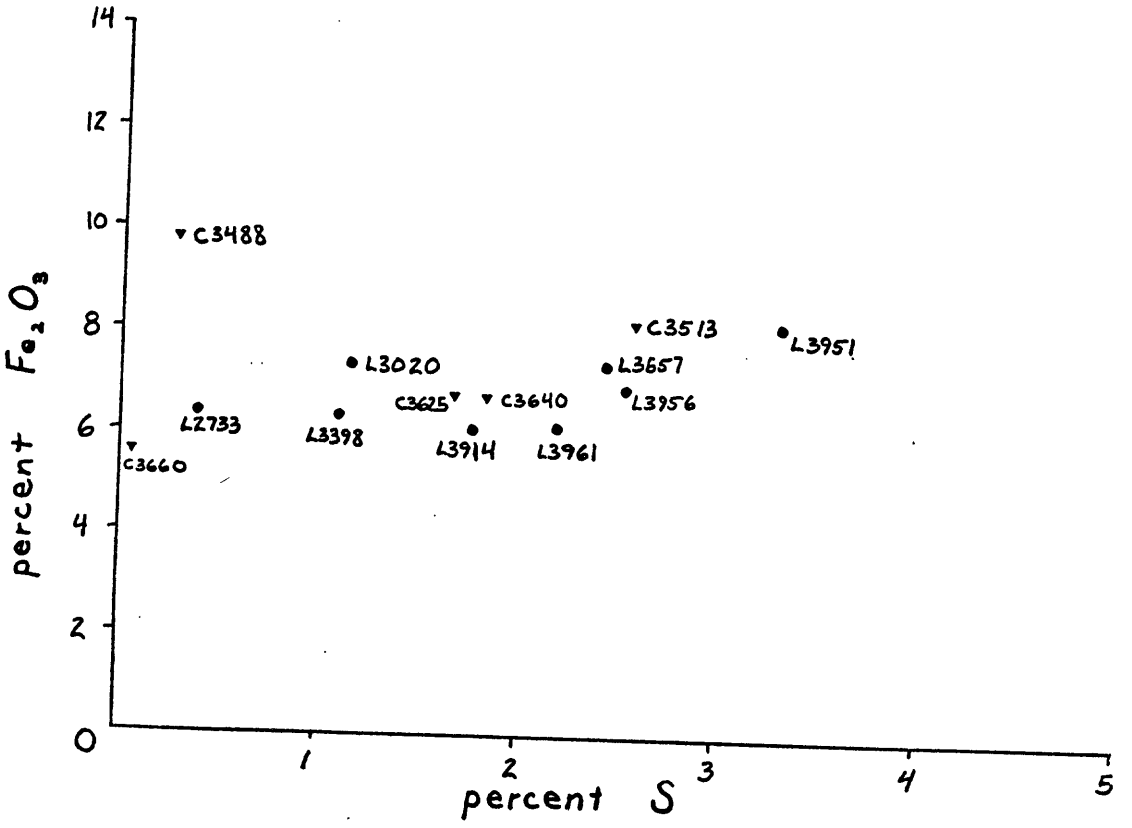

Figure 9. Jackson & Lincoln County, West Virginia percent Fe_2O_3 plotted against percent S

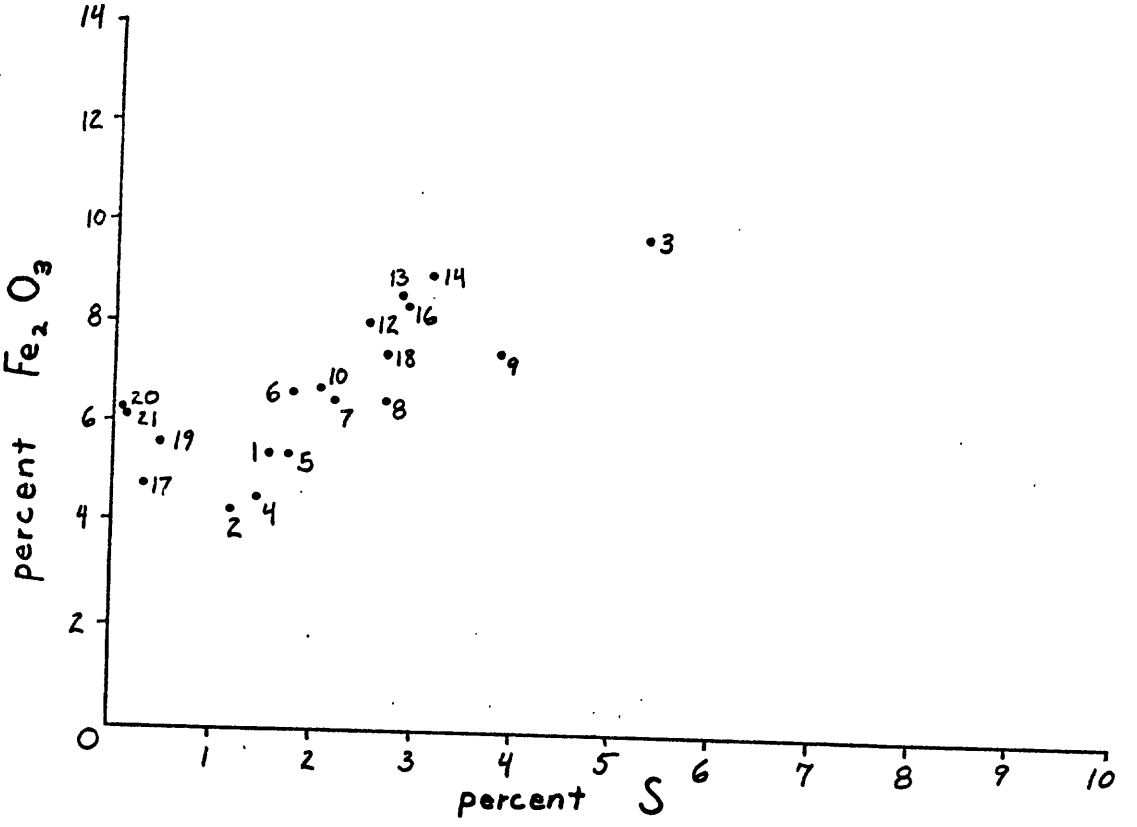

Figure 8. Perry County, Kentucky percent Fe_2O_3 plotted against percent S

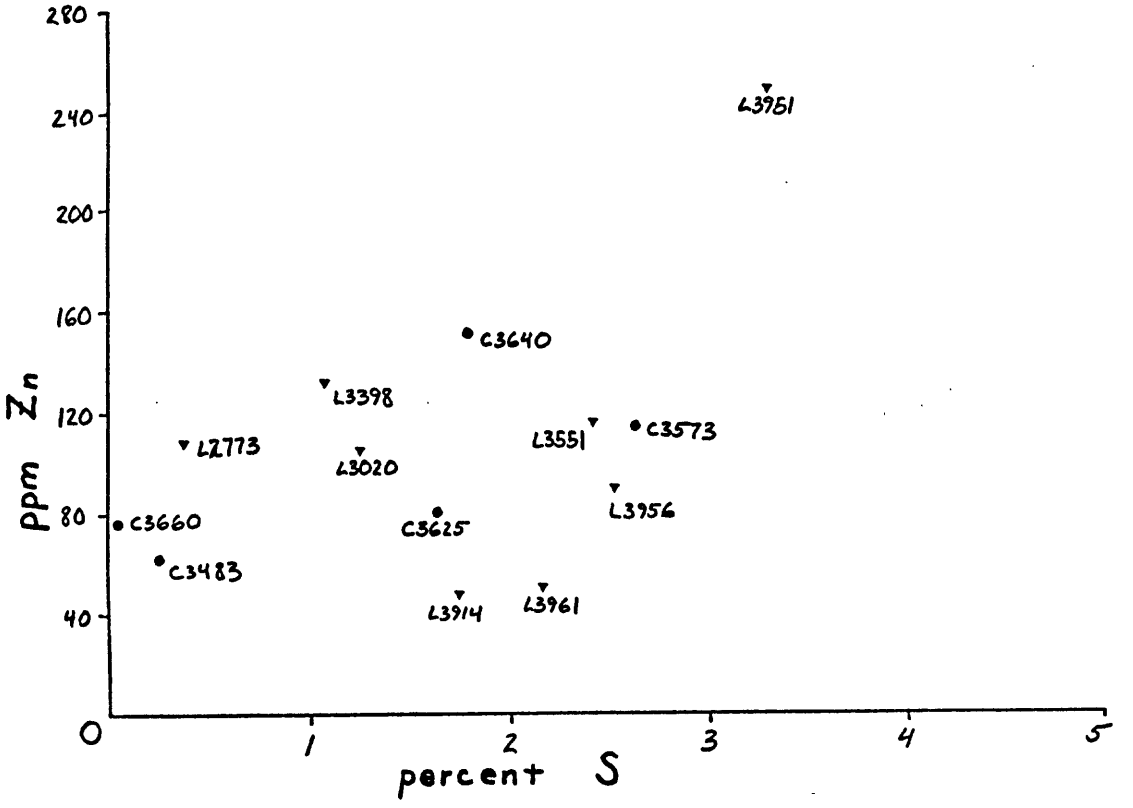

Figure 10. Jackson & Lincoln County, West Virginia ppm Zn plotted against percent S

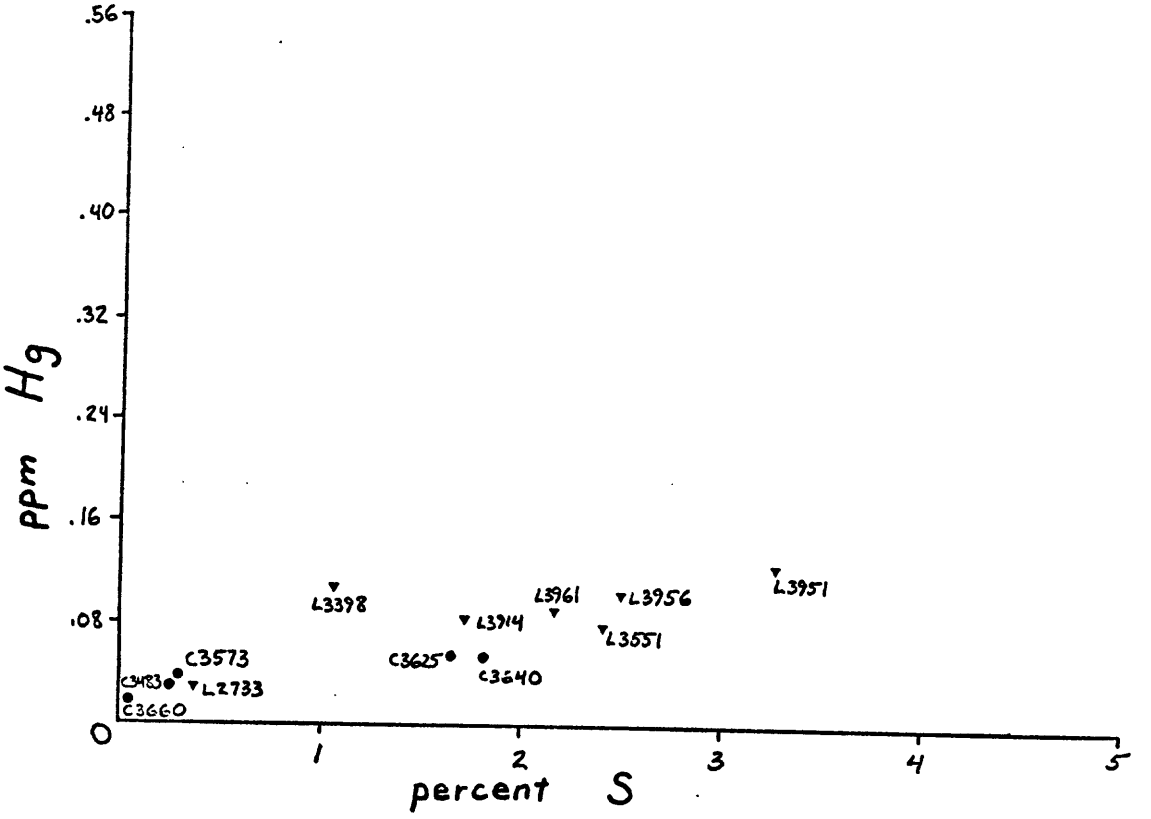

Figure 11. Jackson & Lincoln County, West Virginia ppm Hg plotted against percent S

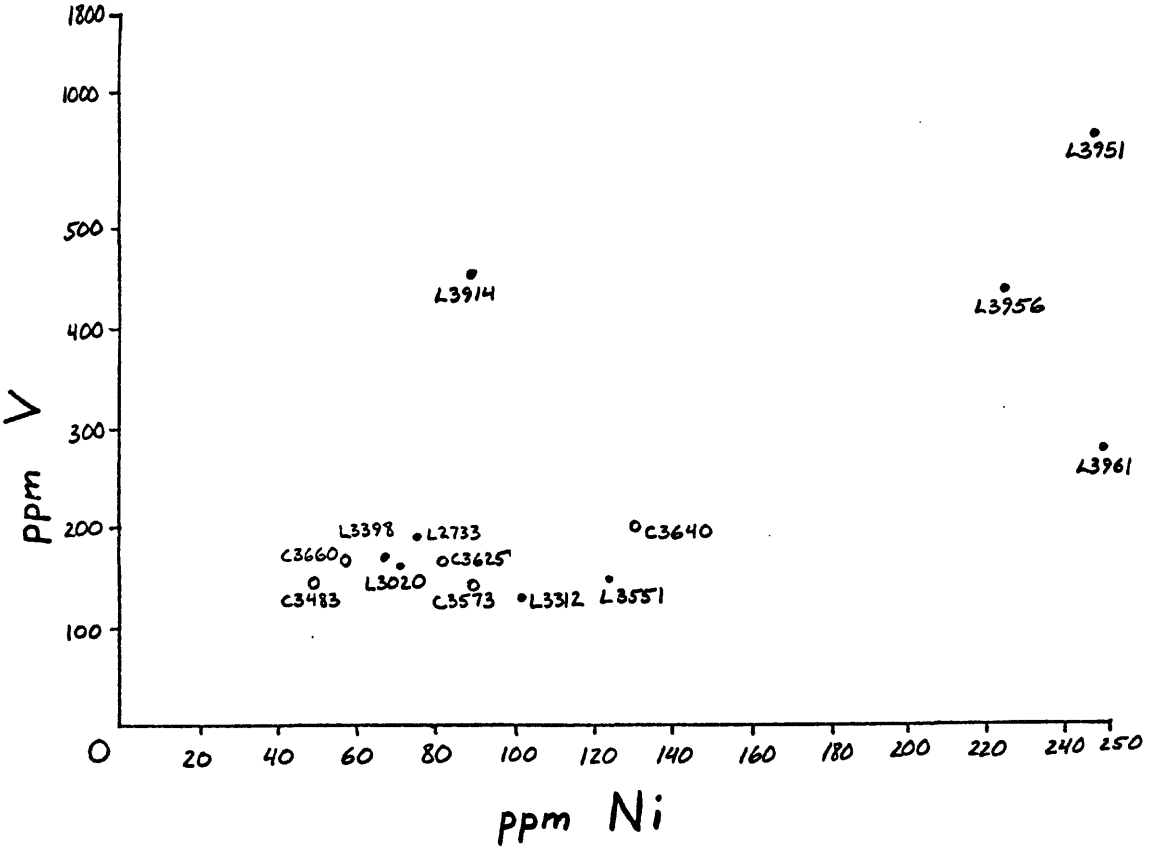

Figure 12. Jackson & Lincoln County, West Virginia ppm V plotted against ppm Ni

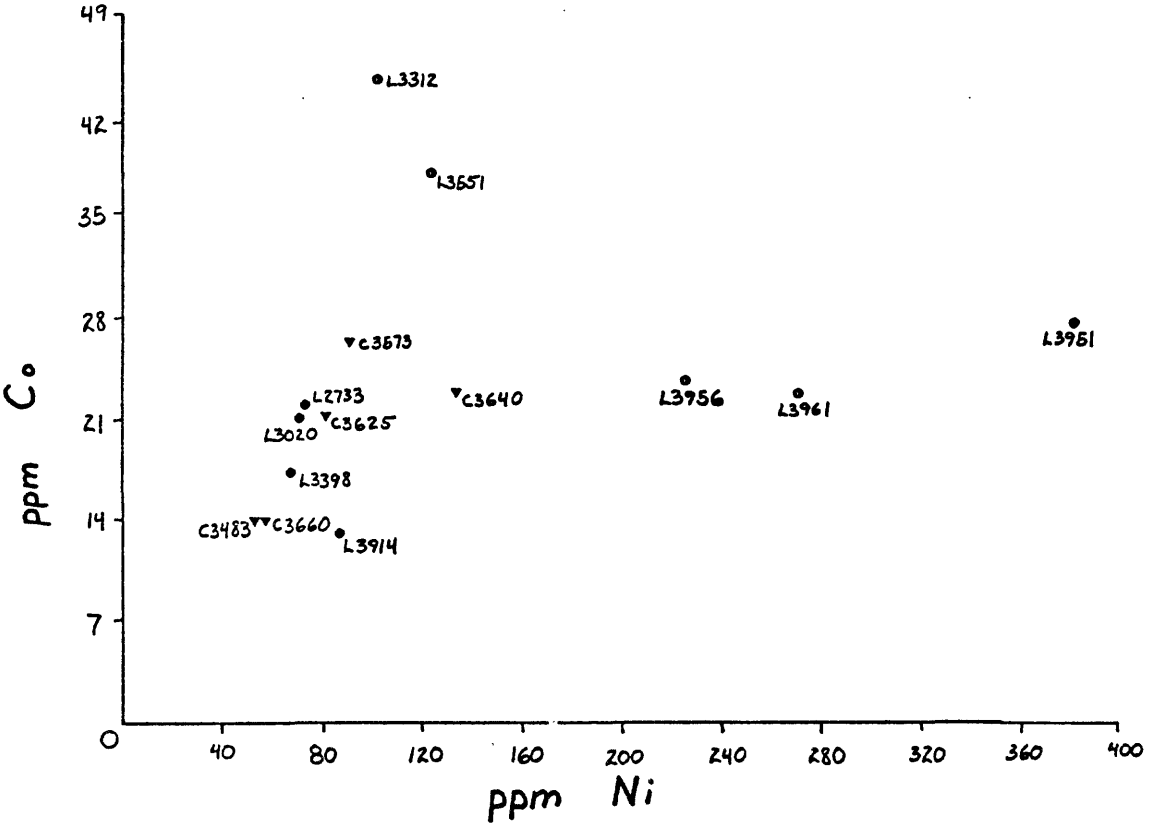

Figure 13. Jackson & Lincoln County, West Virginia ppm Ni plotted against ppm Co

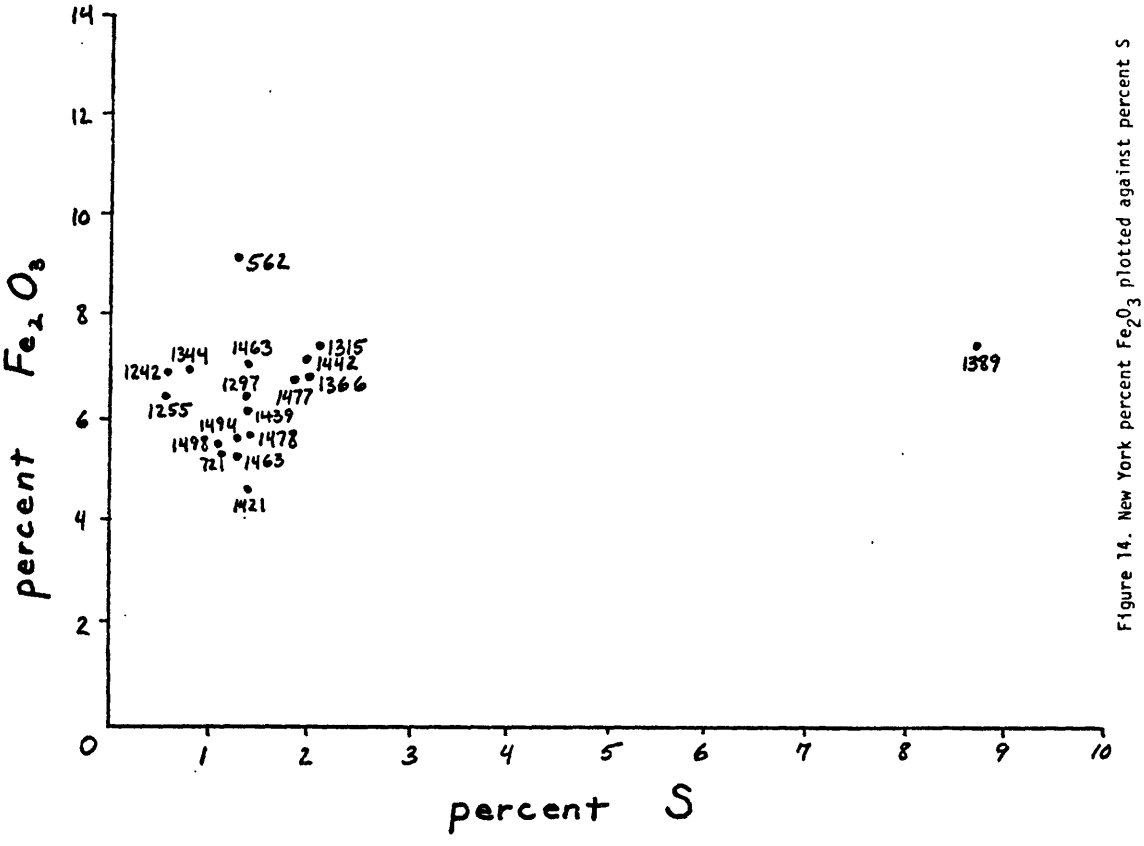

Figure 14. New York percent Fe_2O_3 plotted against percent S

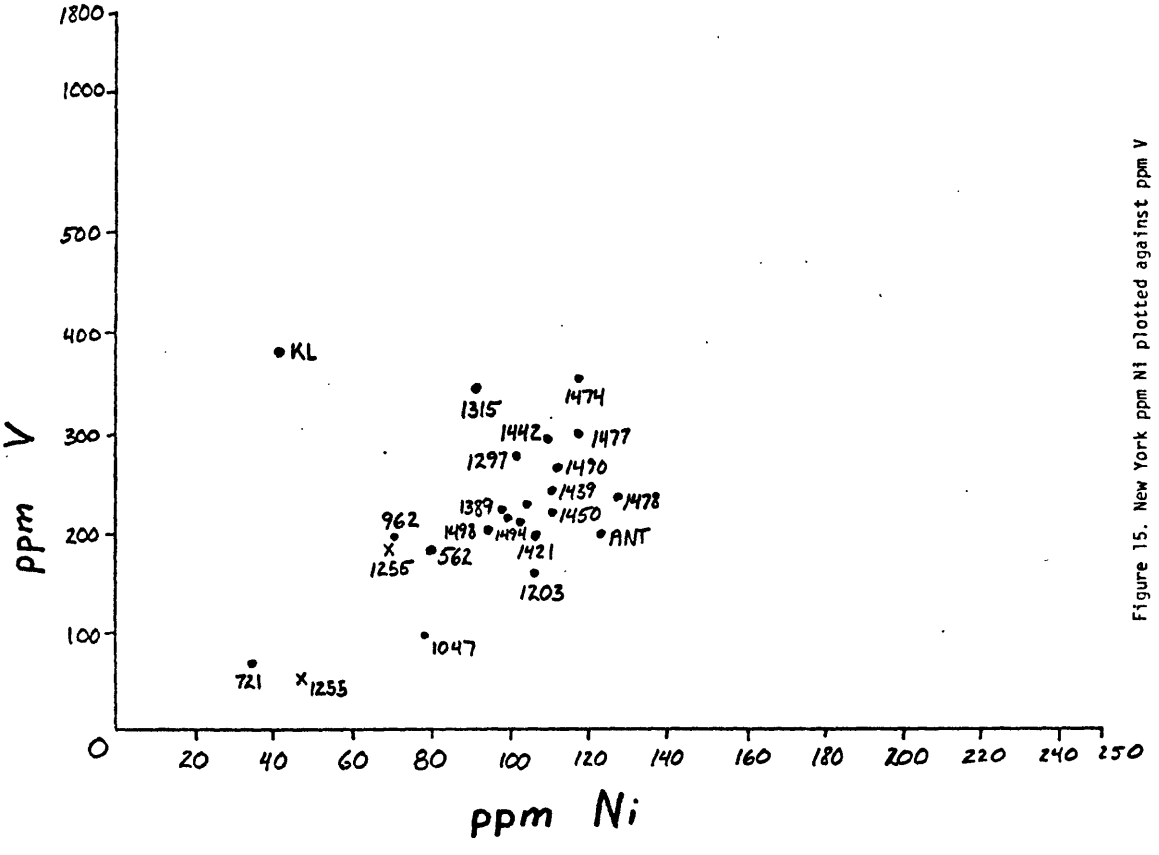

Figure 15. New York ppm Ni plotted against ppm V

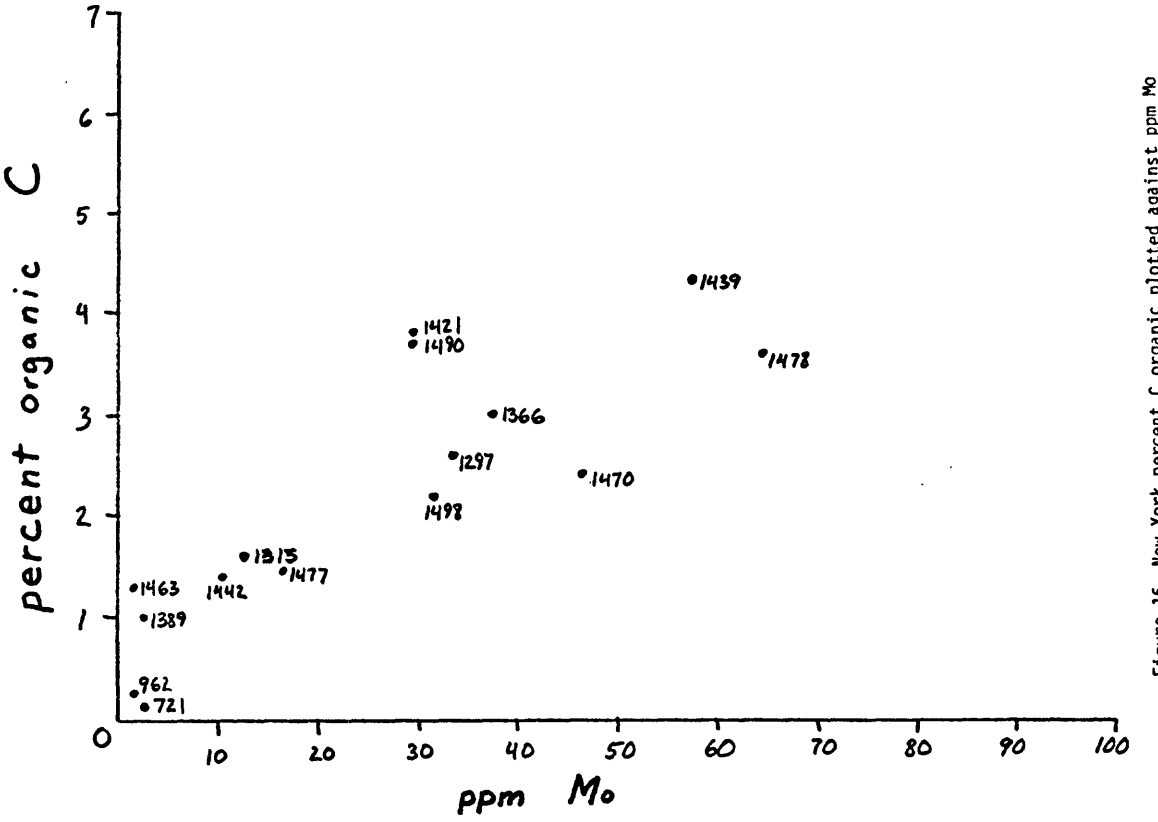

Figure 16. New York percent C organic plotted against ppm Mo

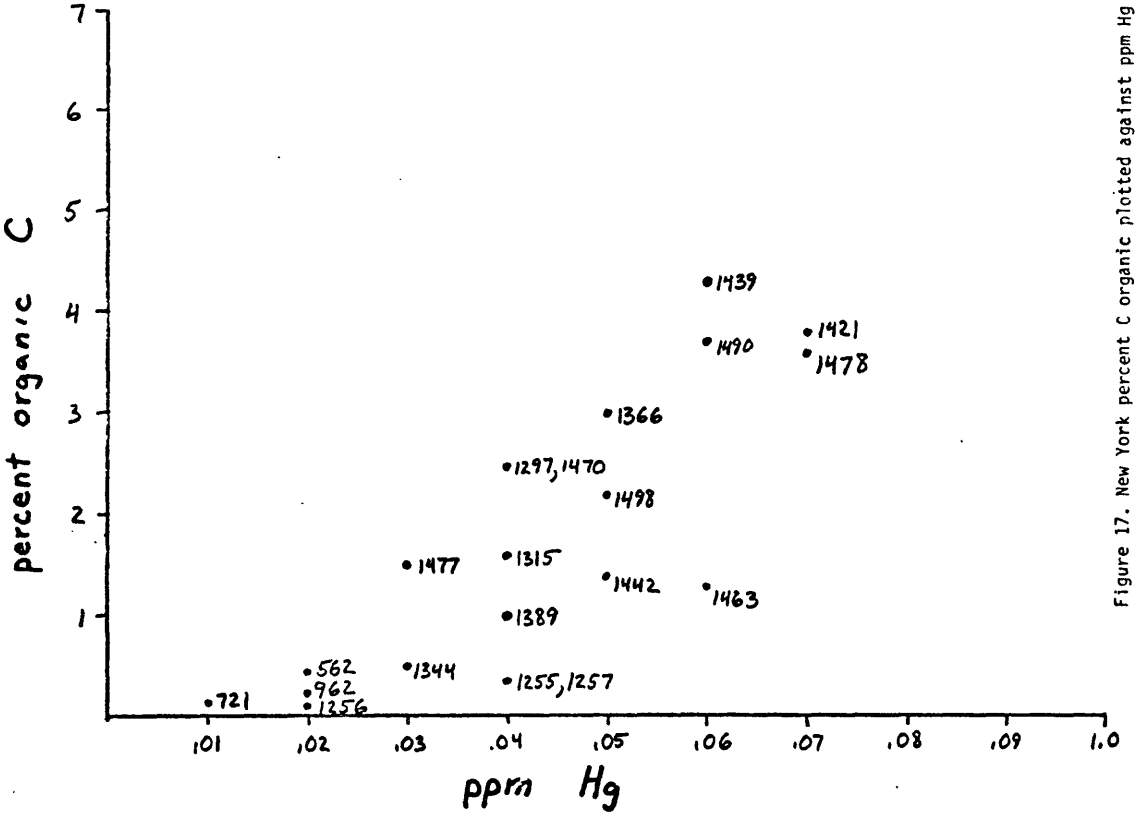

Figure 17. New York percent C organic plotted against ppm Hg

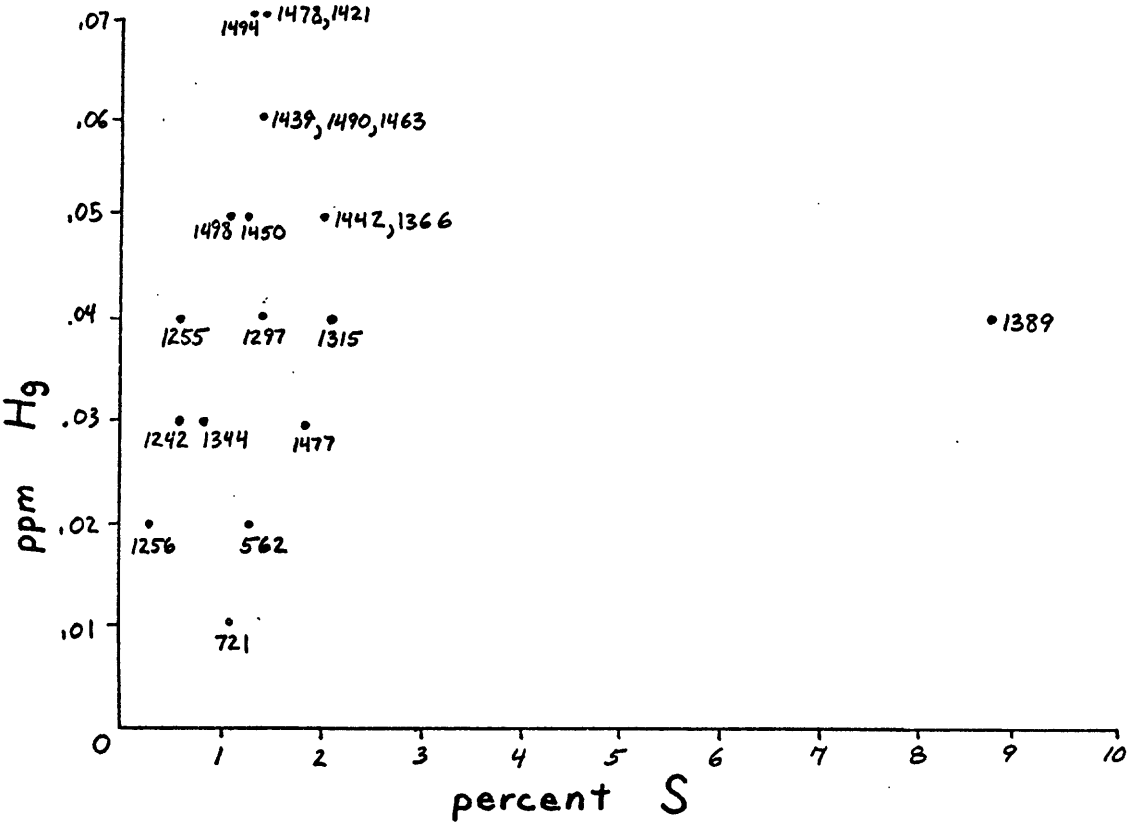

Figure 18. New York ppm Hg plotted against percent S

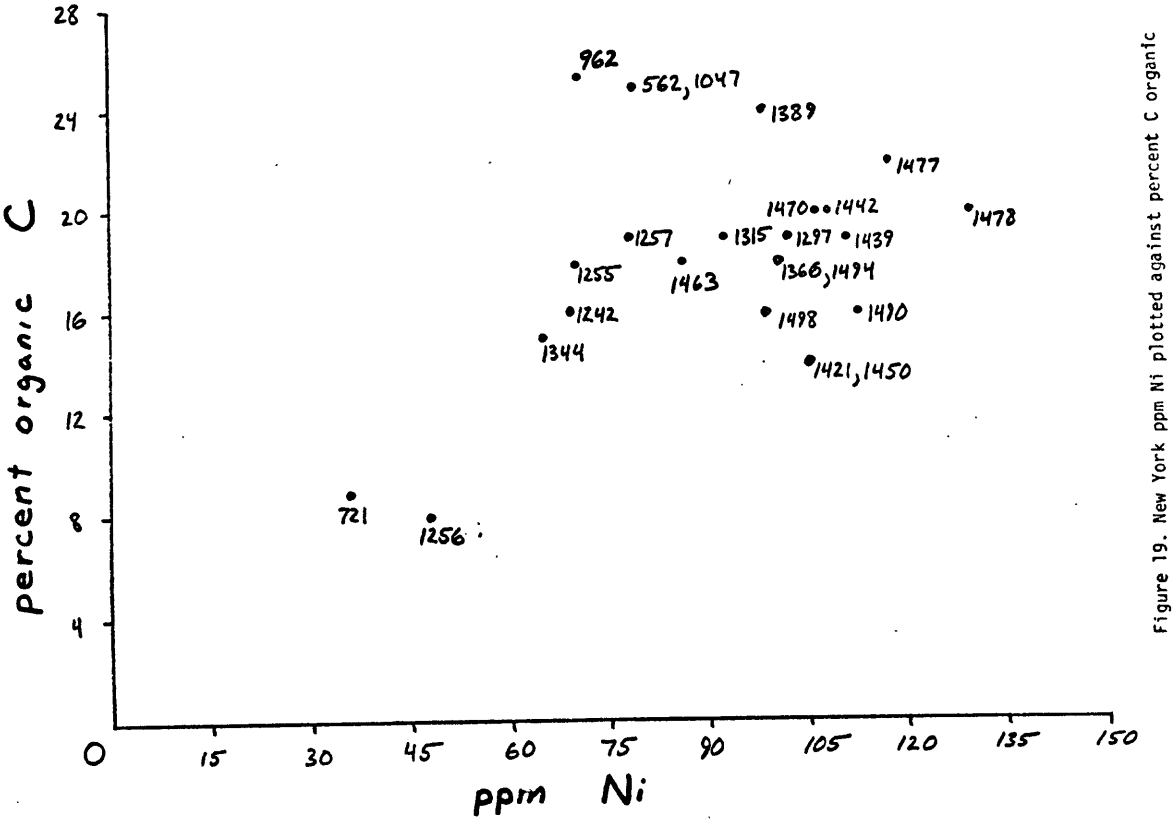

Figure 19. New York ppm Ni plotted against percent C organic

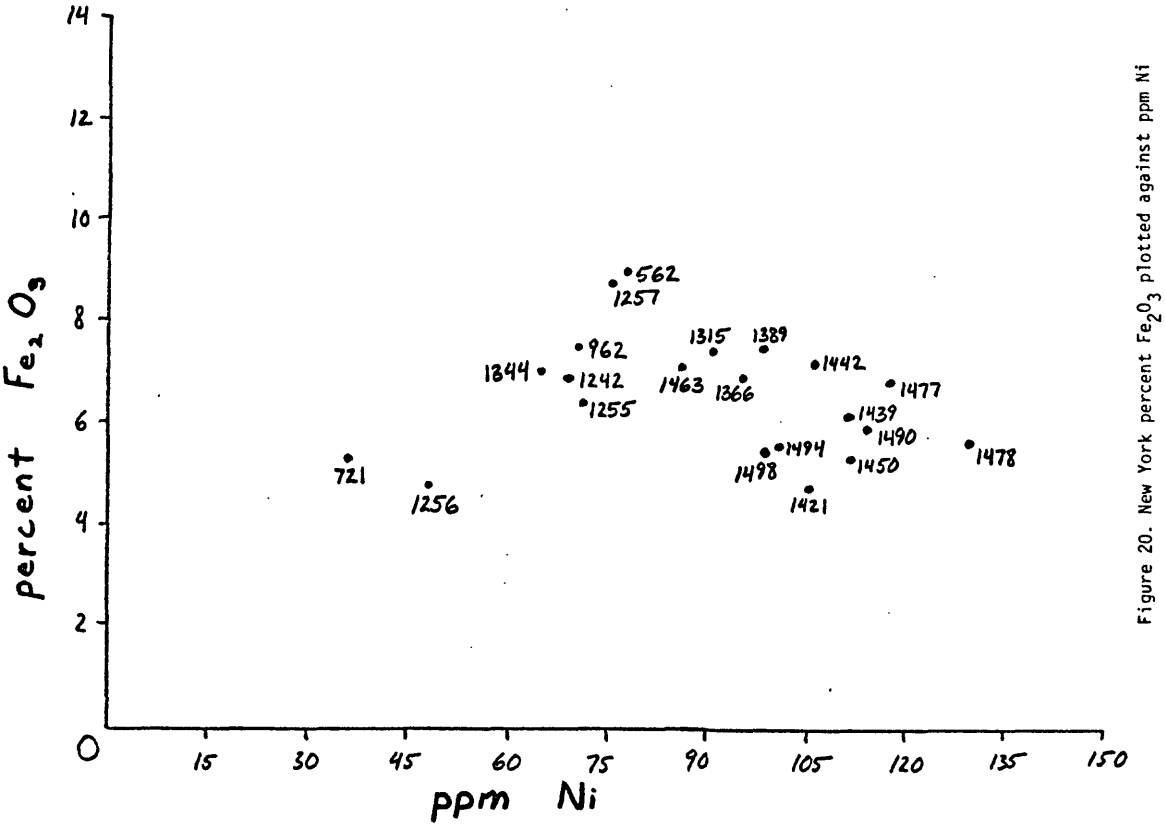

Figure 20. New York percent Fe_2O_3 plotted against ppm Ni

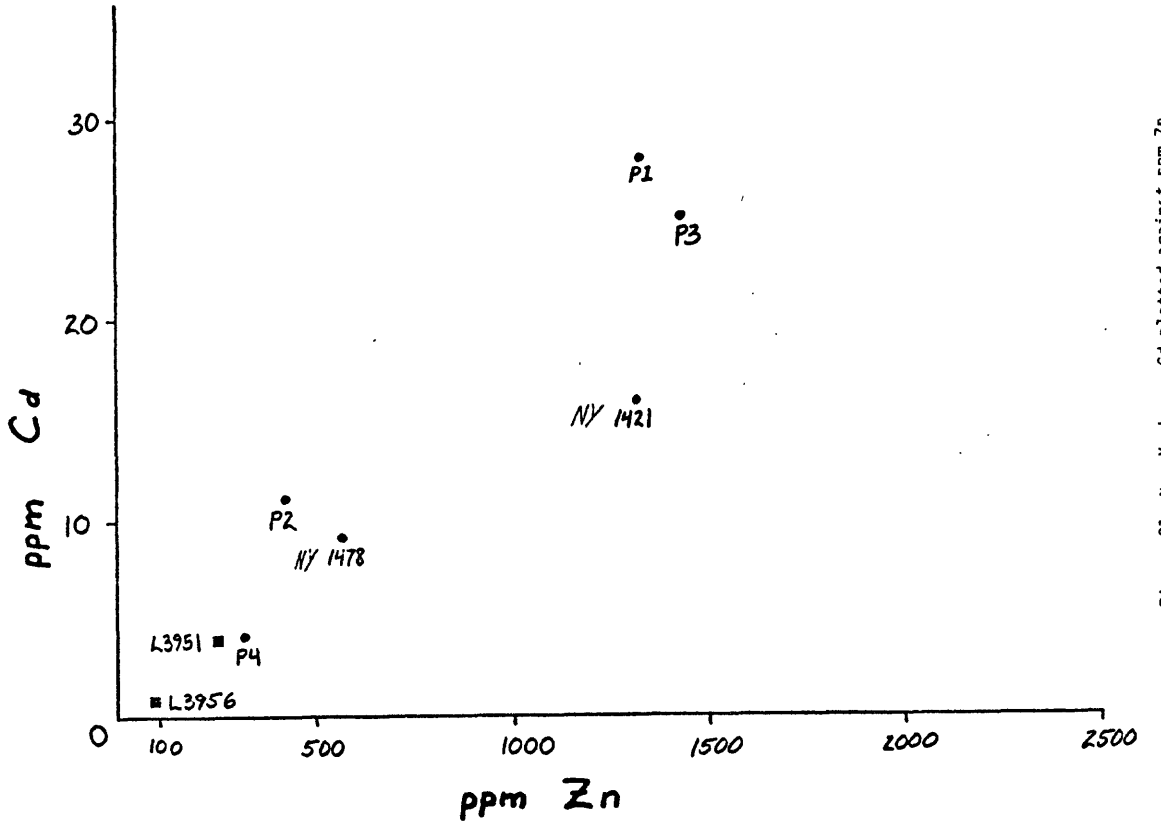

Figure 21. New York ppm Cd plotted against ppm Zn

Figures 22 through 25 show down-core plots for the continuous section of black shale from Perry County, Kentucky. Figure 22 shows that organic carbon is the major constituent that controls the abundance of U, Mo, and V. Figure 23 shows that the major constituent pyrite (FeS_2) controls the abundance of As and Hg and sometimes (top of core), but not always (bottom of core), Pb and Sb. Figure 24 shows that Zn, Cd, and Ag follow the pyrite at the top of the core. Mixed controls are evidenced for sample 7, where maxima occur for organic C and Ti and trace elements Co, Ni, and Zn. Mixed controls are also operating for sample 16, where the minor element abundances of organic C, S, Fe, and Ti are high, along with Co, Ni, Mn, Zn, Sb, and Pb. A similar treatment of minima values can be used, giving the same associative relations.

A composite of Figures 22 to 25 is given on Figure 26.

The element abundances are all related to the land source of the elements and the depositional environment. The depositional environment is controlled first by the organic carbon, which controls the sediment-water interface redox potential. As long as the redox is sufficiently negative, sulfate-reducing microorganisms can provide sulfide ions to react with Fe to form iron sulfides. The organic matter and sulfides can act as scavengers for trace elements. The Ti may be a measure of detrital input, which can be a source of, or act to, dilute the other elements.

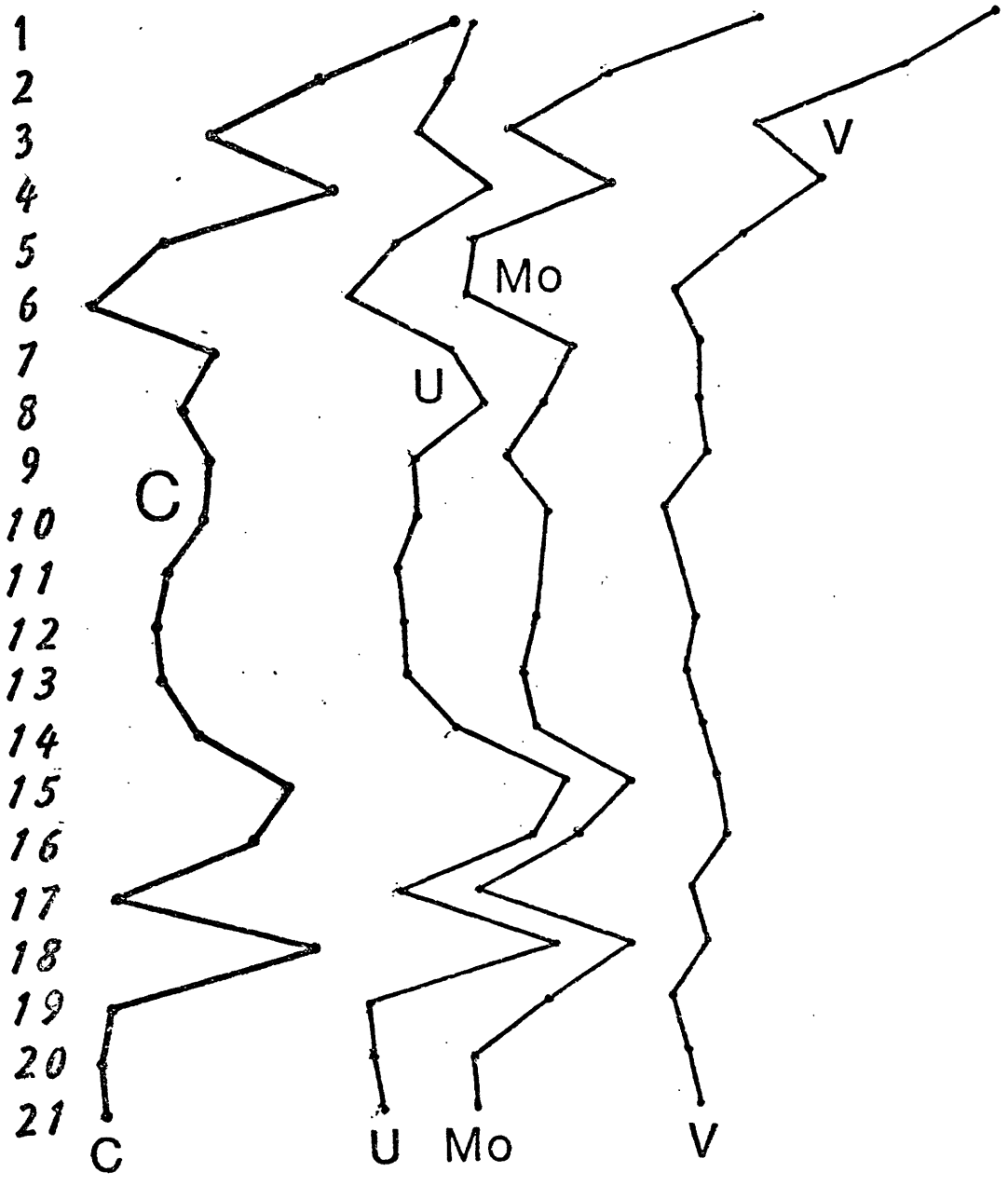

Figure 22. Down-hole plot of C, U, Mo, and V, Perry County, Kentucky (Numbers refer to samples listed on Tables 1 and 2)

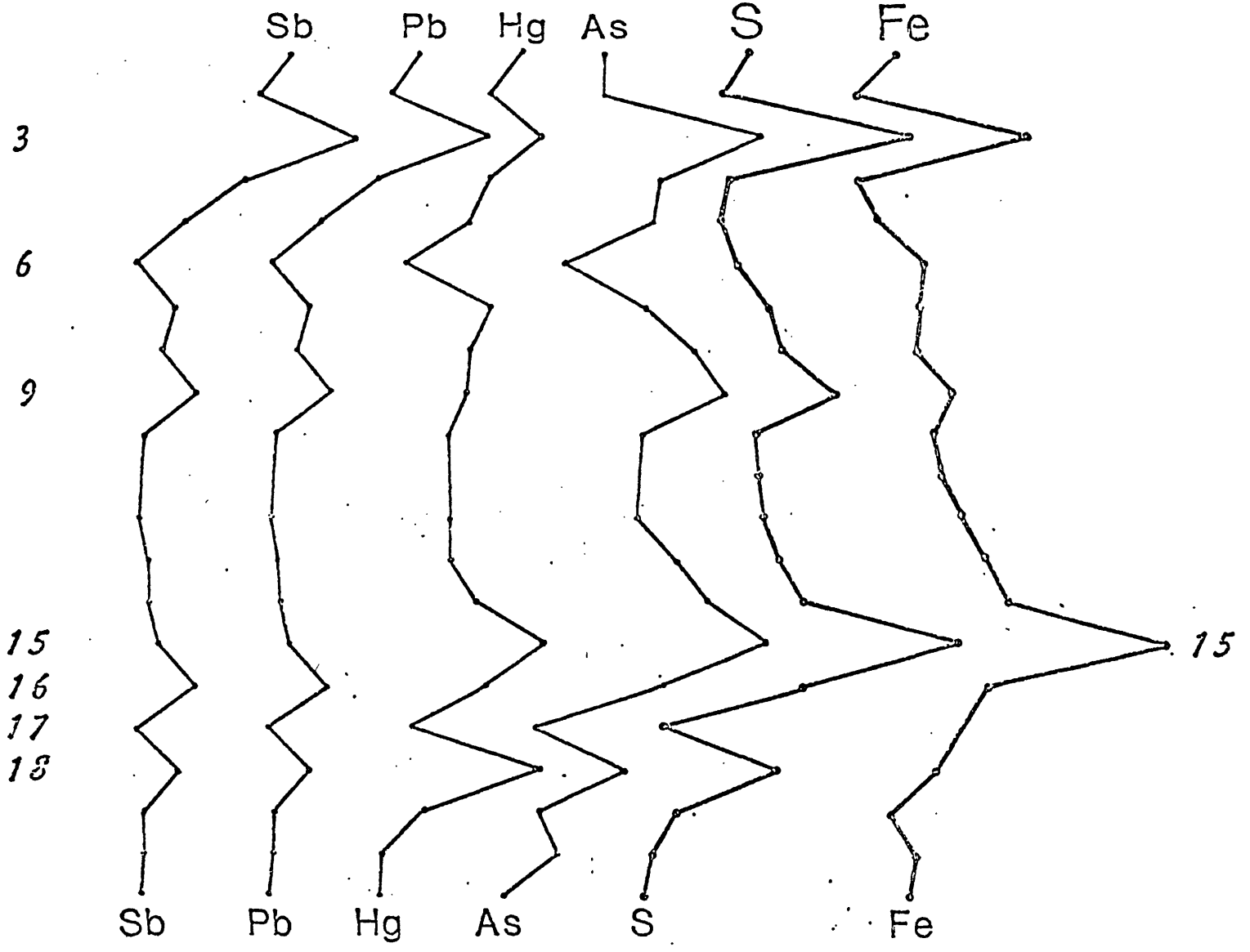

Figure 23. Down-hole plot of S, Fe, A, Hg, Pb, Sb, Perry County, Kentucky
(Numbers indicate samples, (Tables 1 and 2), with high or low values).

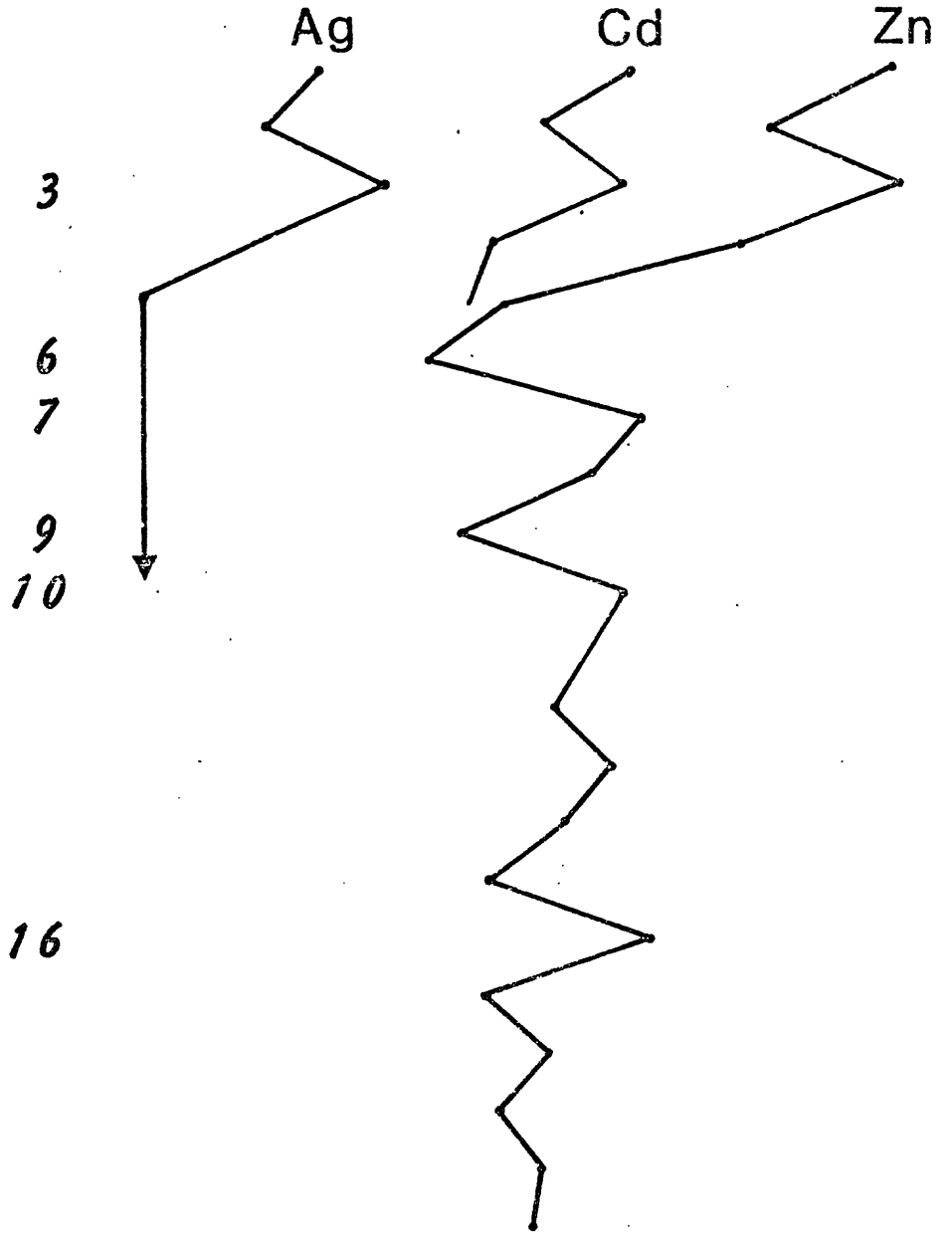

Figure 24. Down-hole plot of Ag, Cd, Zn, Perry County, Kentucky
(Numbers indicate samples, (tables 1 and 2), with high or low values).

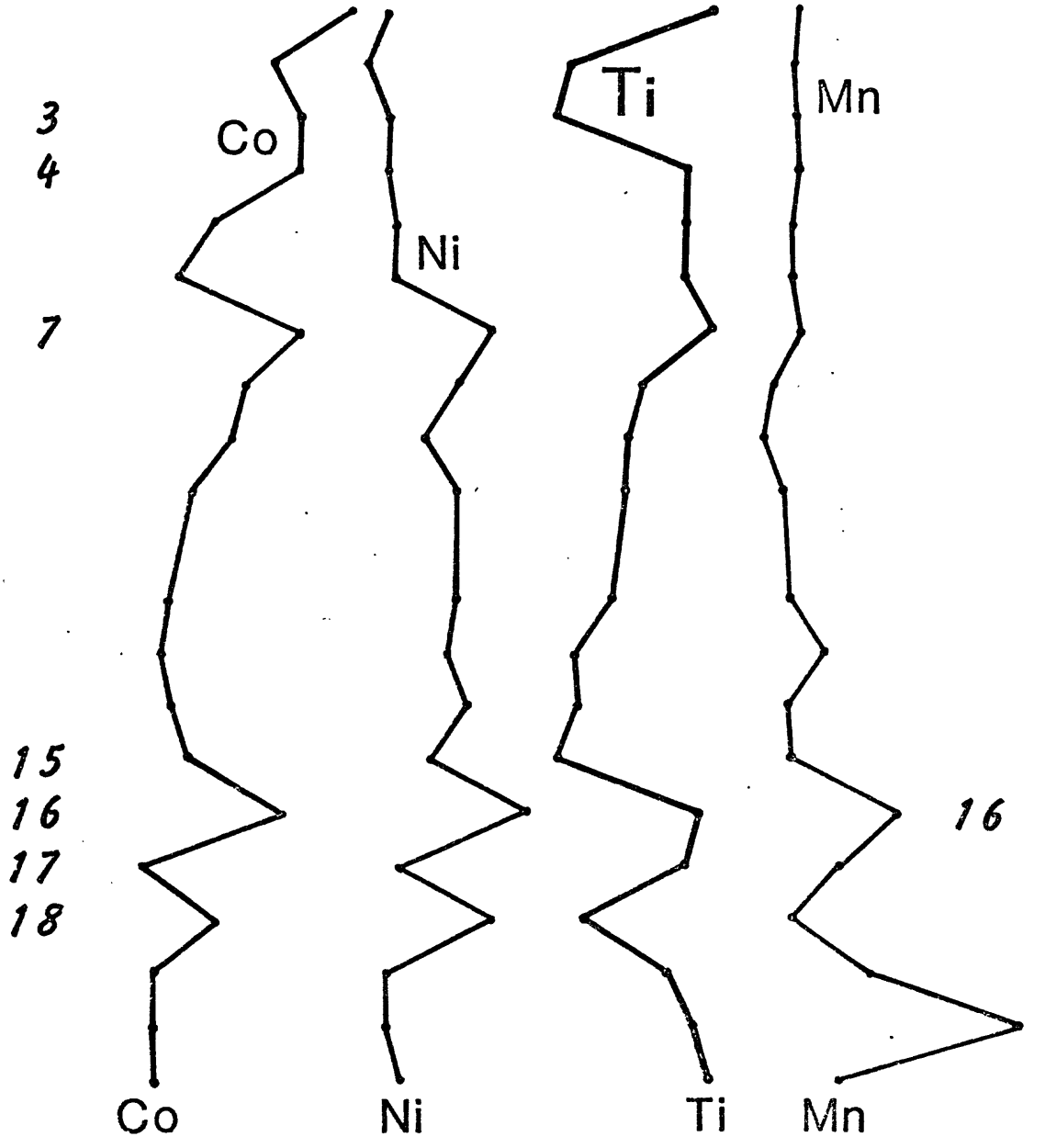

Figure 25. Down-hole plot of Ti, Mn, Ni, Co, Perry County, Kentucky
(Numbers indicate samples, (Tables 1 and 2), with high or low values).

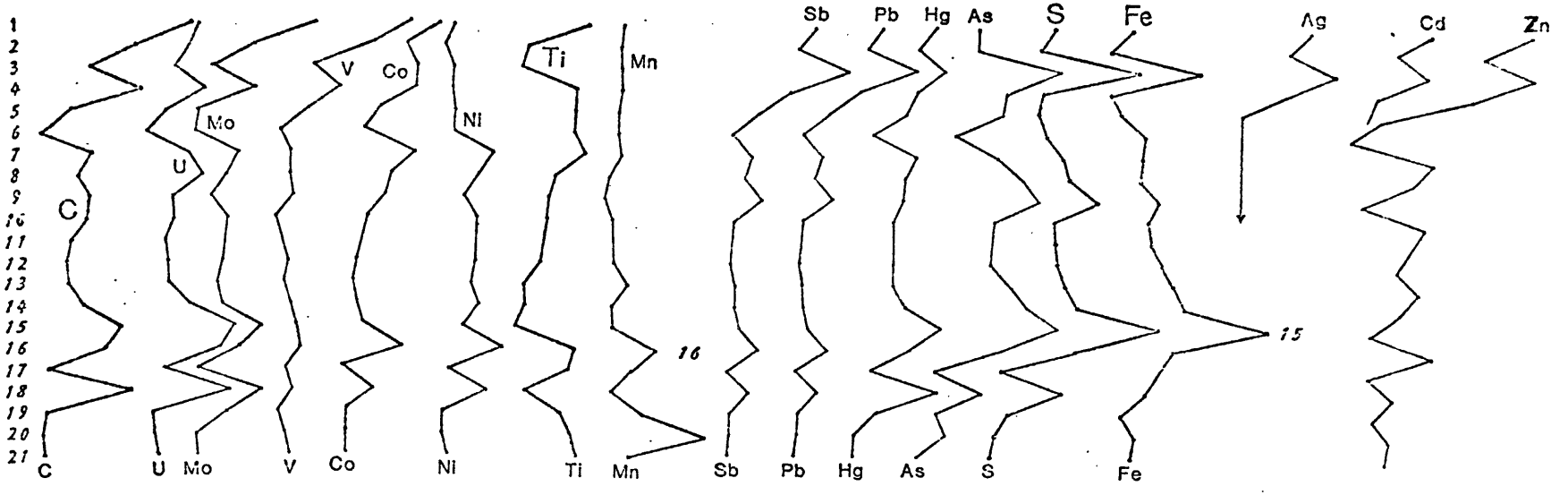

Figure 26. Composite plot of Figure 22-26.
(Numbers refer to samples, listed on Tables 1 and 2)

Acknowledgements

The author thanks M. B. Goldhaber for discussion and suggestions. Tom Knapp, Mark LeFont, and Philip Saletta helped with data tabulation.

Thanks to J.G. Crock, J.A. Thomas, G.E. Riddle, W. Mountjoy, H.Millard, N.M. Conklin, J.S. Wahlberg, and R. MacGregor, (Branch of Analytical Laboratories), for sample preparation and analyses.

References

Bryer, C.W. and Trumbo, D.B., 1976, Lithologic description of the Devonian shale in the Hazard, Kentucky area. Morgantown Energy Research Center Report, 23 p.

de Laguna, W., 1972, Hydraulic fracturing test at West Valley, New York. ORNL-4827, U.S. Atomic Energy Commission, 64 p.

Leventhal, J.S., and Goldhaber, M.B., 1977, New data for uranium, thorium, carbon, and sulfur in Devonian Black Shale, from West Virginia, Kentucky and New York. First Eastern Gas Shale Conference, Morgantown, West Virginia MERC SP 77/5 p. 183-222

Leventhal, J.S., Crock, J.G., Mountjoy, W., Thomas, J.A., Shaw, V.E., Briggs, P.H Walberg, J.S., and Malcolm, M.J., 1978, Preliminary analytical results for a new U.S. Geological Survey Devonian Ohio Shale standard SDO-1 from U.S. Geol. Survey, Denver. U.S. Geol. Survey Open File Rept. 78-447. 11p.

Provo, L.J., Kepferle, R.C., Potter, P.E., 1977. Three Lick Bed: Useful stratigraphic marker in the Upper Devonian shale in eastern Kentucky. ERDA-MERC/CR-77-2, Morgantown, W. Va, 55 p.