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Geochemistry of trace elements and uranium in Devonian shales of the Appalachian Basin

by

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Abstract

This final report summarizes the chemical data for 17 cores from Kentucky (1), West Virginia (1), Pennsylvania (4), Ohio (4), New York (3), Tennessee (3) and Illinois (2). Major elements, for example Si and Al, show changes related to stratigraphic boundaries when the effect of organic matter, sulfur, and carbonate are removed. The geochemical associations of trace elements with organic carbon and sulfide sulfur are shown in down-hole plots, minor or trace element vs organic C or sulfide S plots, and by statistical correlation. The uranium and molybdenum are most strongly related to organic carbon. Based on down-hole plots and statistics, sulfur seems to control the abundance of Hg, As, Cu, and Pb in some cores, and organic matter shows some control over Cu and Ni. Vanadium and zinc are usually related to organic carbon or sulfur or both. Carbon and sulfur contents and their ratios can be used to infer an environment of deposition using C/S plots and to show trace element pathway during deposition and diagenesis.

Introduction

The U. S. Geological Survey in cooperation with Morgantown Energy Technology Center, U.S. Department of Energy, is characterizing Devonian 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 (which are presently sub economic) and can be used to recognize possible environmental problems caused by such elements as As and Hg. These chemical data are useful in stratigraphic correlations; and particularly for geochemical assessment of source rocks, and characterization of depositional environment for oil and gas potential or resources.

Chemical data and geochemical controls and affinities of 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 in other Devonian samples (Leventhal, 1978, 1979, 1980).

This report includes chemical data from 17 cores (fig. 1) which completes the analytical work that was initiated as part of Eastern Gas Shales Program. Previous reports (see References) presented data and interpretation of some aspects of the work.

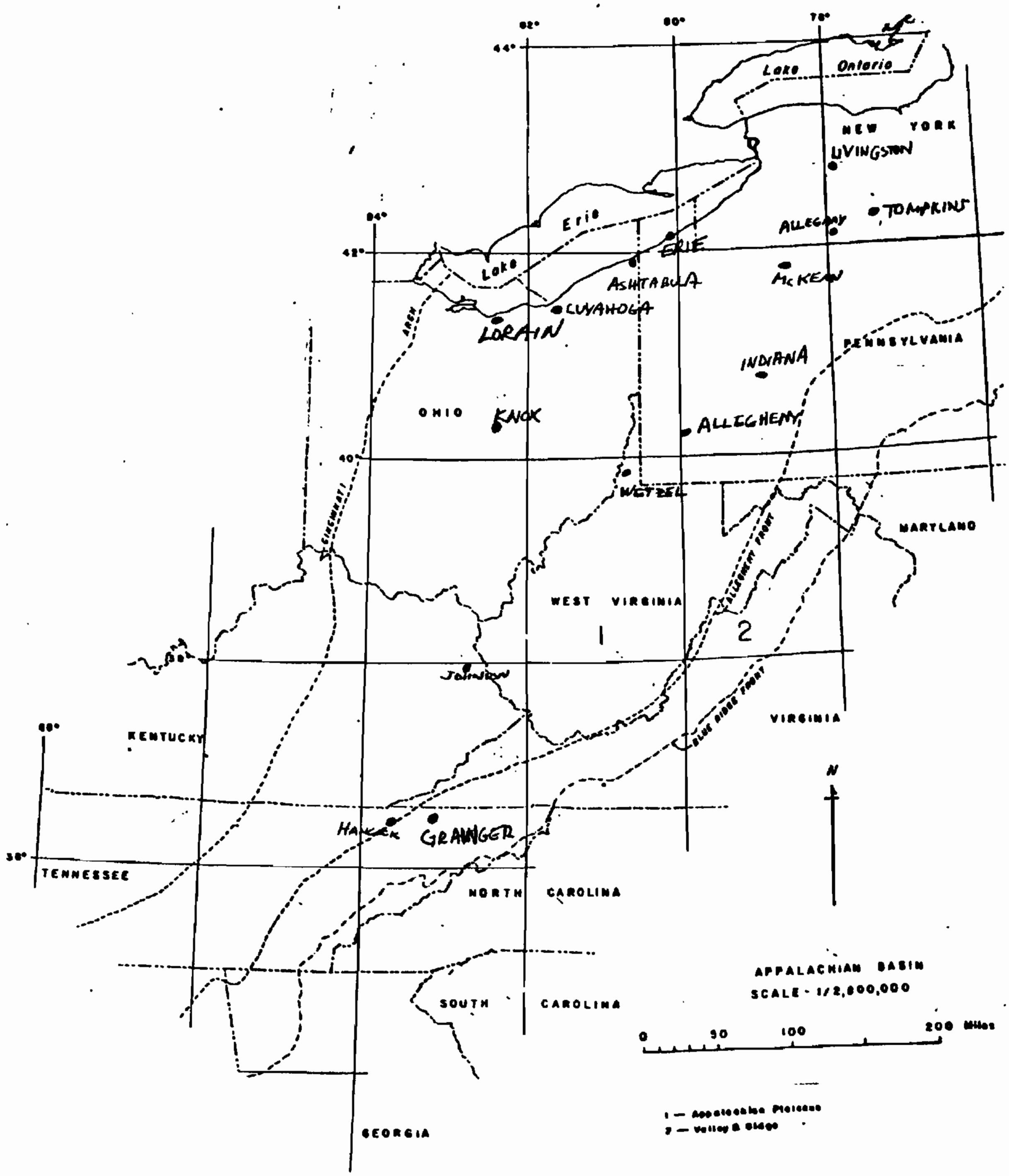


Figure 1.--Map showing Appalachian basin and location of cores.

Sample locations, cored intervals, and stratigraphy (See figure 2)

Wetzel County, W VA (EGSP WVA-7, API 47-103-20645; 39°41'N, 80°49'W), Rhinestreet 6103-6226; Genesee 6272-6372; Sample at 6426 may be part of Tully and 6474 may be Mahantango or the latter two may be carbonate rich and organic rich portions of Genesee.

Johnson County, KY (EGSP KY4). Bedford 987; Cleveland 1046; Chagrin 1099; Huron 1204-1402 (1352 and 1402 are lower Huron). Olentangy, 1453.

Allegany County, NY, (EGSP NY-1, API 31-003-13549, 77°50W, 42°21'N) Angola 1002, Rhinestreet 1542, 1744, 2049, 2301; at Middlesex -- Genesee boundary 2496, Geneseo 2743-2874, Hamilton 2975-3480, Marcellus below 3480.

McKean County, PA, (EGSP-PA-1, API 37-073-36302), Gardeau or Rhinestreet 3517; Saw Mill 4577, Penn Yan 4627, 4679; or 4577 to 4679 could be Middlesex; Mahantango 4829 to 5083. Sample 5133 could be Marcellus.

Allegheny County, PA, (EGSP-PA-2, API 37-003-20980) Genesee Fm 6967-7072, 7072 is Burket or Genesee; Hamilton Fm, Mahantango 7189-7290; Marcellus, 7465. Samples 7342 and 7415 could be Marcellus based on organic carbon, but Mahantango based on uranium.

Erie County, PA (EGSP-PA-3, API 37-049-20846, 42°10N, 80°7'W) Angola 545 to 735, Rhinestreet 949-995; Tully 1045, Mahantango 1191, 1241 could be Marcellus or Mahantango. Shale at 405 is not identified.

Indiana County, PA (EGSP-PA-4, 40°35N, 79°11W), shale samples at 7375 and above not identified. Genesee 7475-7526; Tully 7576; samples 7627 to 7975 are Mahantango.

Generalized correlation of Devonian shale units studied for clay mineralogy
[Modified from Oliver and others, 1969]

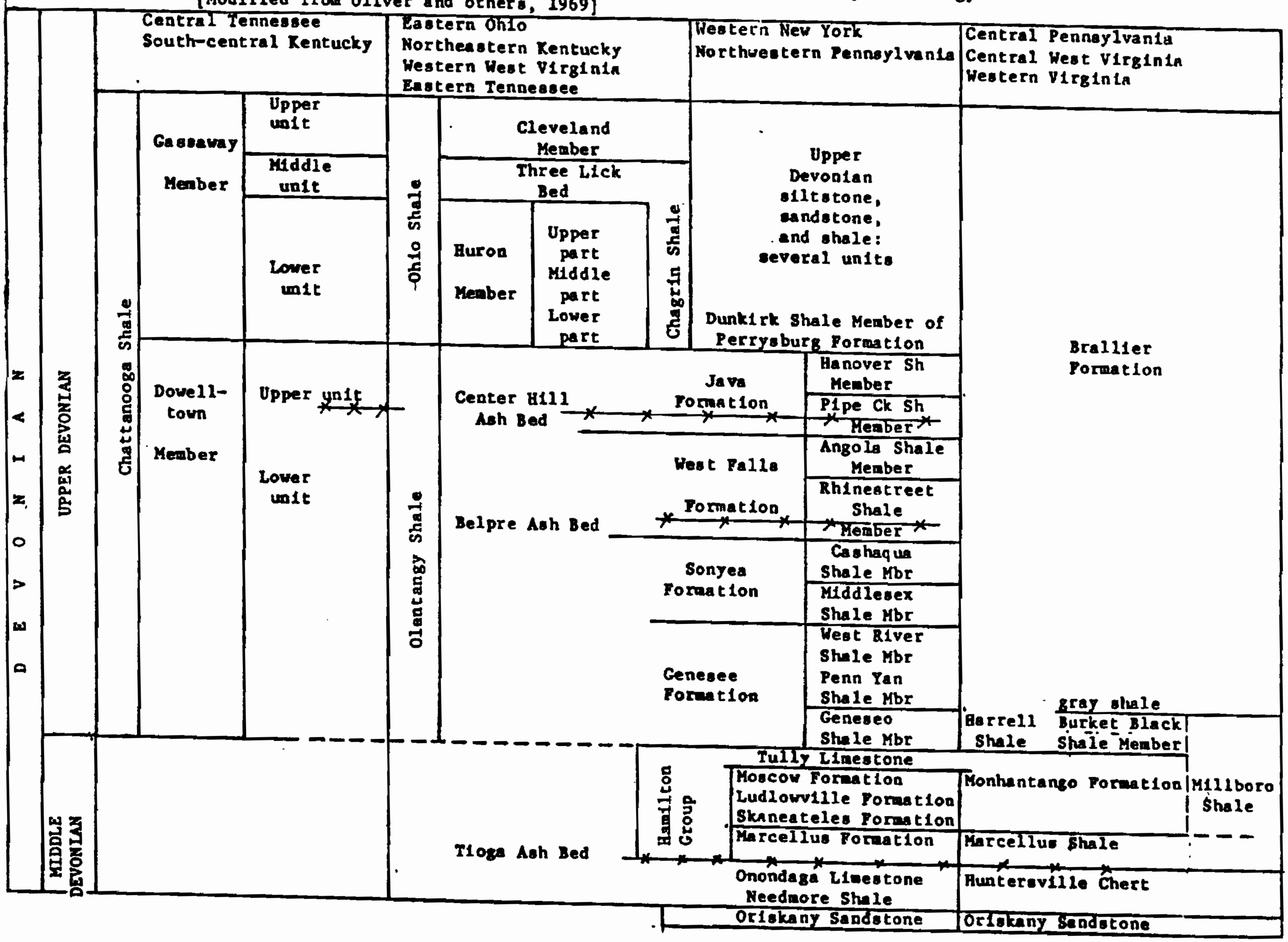


Figure 2.—Stratigraphy of upper and middle Devonian sediments in Appalachian basin (from Roen and Hosterman, 1980).

Knox County, OH (EGSP OH-3; 82°30W, 40°24'N, API 34-083-22599). Sample 577 is near the Bedford - Cleveland contact; Chagrin 627-677; Huron 727-1027 (1027 is Lower Huron); Hanover Sh 1078; Angola (or Olentangy) 1181-1231.

Ashtabula County, OH, (EGSP-OH-4 API 34-007-21087, 41°57'N, 80°33'W). Ohio Sh 523; Java - West Falls 761-1125, Marcellus 1175, Onondaga 1325.

Lorain County, OH, (EGSP-OH-5, API 34-093-21100) Cleveland 416; Chagrin 466-745; Lower Huron 764-1015; sample 1065 could be Lower Huron or Java; Java 1086-1190; Rhinestreet 1216; Deleware limestone sample at 1267.

Livingston County, NY, (Stewart 6701, API 31-031-14100, 42°45'N, 77°50'W) Hamilton 77-511, 530 transitional, Marcellus 543-576.

Tompkins County, NY, (Cargill 17, Lansing Township, API 31-109-13173) Genesee Fm 77-113; Geneseo, 149-240; Hamilton 299-1300, 1339 transitional, Marcellus 1360-1429.

Cuyahoga County, OH, (Cleveland Salt #1, API 34-035-01001) Cleveland or Chagrin 101-188, Upper Huron 285-361, Middle Huron 391-447, Lower Huron 490-705, Java Fm 712-750, Hamilton 813-923.

Hardin County, IL, (EGSP, IL-4, Sec 36 T11S, R7E) New Albany Shale; Grassy Creek and Selmier Shale.

Wayne County, IL, (EGSP IL-5, Sec 17, T3S, R8E) New Abany Shale: Grassy Creek 5066-5166, Selmier 5126; Blocher Shale 5265.

Hancock County, TN, (EGSP-Tenn-3, API 41-067-01001) Sunbury 132-235, Cleveland 235-336, Three Lick Bed 336-358, Upper Huron 372-392, Middle Huron 392-544, Lower Huron 544-650; Java 656-732, Rhinestreet 732-742.

Grainger County, TN, (EGSP Tenn-6, API 47-057-1001 Lower Huron 281-372, Java-West Falls 441-469.

Grainger County, TN, (EGSP-Tenn-7, API 47-057-1002) Price 50, Brea 100-149, Sunbury 200-250, Bedford 300-350, Middle Huron 406-603, Lower Huron 650-700, Java - West Falls 750-800, Rhinestreet 825.

Methods and results

Tables 1-17 present the new data for core samples. The analytical chemical methods, and their precision and accuracy are given in earlier reports (Leventhal and others, 1978) and can also be seen from the replicate analysis of samples (submitted as blind splits) in some of the tables. Total C and S were measured by high-temperature combustion, carbonate C by titration or gravimetric CO_2, and organic C by difference or by wet oxidation. U was measured by delayed-neutron analysis. Quantitative determination of SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MgO, Na_2O, and K_2O were measured by X-ray fluorescence on the ash. Ni, Cu, Zn, Co, and V were measured either by semiquantitative emission spectroscopy or by atomic-absorption spectrophotometry. Hg and As were measured by flameless atomic-absorption spectrophotometry. Mo was determined by emission spectroscopy or colorimetrically. Loss on ignition (LOI) was measured gravimetrically. In general, based on splits and replicates, the results are precise to the following degree (in percent):

±2-5	U, S, C (organic), SiO_2, Al_2O_3, K_2O, MgO, CaO, TiO_2
±5-10	Ni, Cu, Cd, Zn, Co, Na_2O, C (carbonate), V, LOI Mo, Th, Fe_2O_3, As, Hg, Zn
±33	Semiquantitative emission spectroscopy results

Table 1.--Chemical data for Johnson Co., KY.

Kentucky 4, Johnson County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon;

	quantitative								Semi-quantitative								Quantitative								
	percent								parts per million								parts per million					percent			
	xray fluorescence								6 step emission spectroscopy																
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
987	59.3	20.7	5.2	4.28	1.3	0.22	0.3	1.04	300	50	100	N	150	30	300	200	56	16	0.05	37	6.9	0.51	0.43	0.40	6.9
1046	64.2	14.4	4.8	3.71	1.3	.27	.5	.82	200	20	100	10	150	30	700	200	177	18	.03	20	6.9	2.98	1.59	.08	8.5
1099	60.4	15.3	5.2	3.78	1.3	.88	.5	.89	300	20	100	100	150	20	700	200	171	19	.04	11	16	2.93	1.67	.25	9.8
1156	57.1	16.7	6.6	3.98	1.4	.86	.4	.85	200	30	100	50	150	30	300	150	450	21	.05	23	15	2.65	2.84	.25	9.6
1204	57.8	17.5	7.1	4.31	1.4	.34	.4	.78	300	30	100	30	100	30	200	150	58	18	.03	8	9.7	1.51	2.76	.30	8.4
1254	60.8	14.7	6.1	3.75	1.3	.32	.4	.74	200	30	100	30	100	20	200	150	130	17	.02	12	13	3.84	2.40	.30	10.2
1303	57.5	15.3	7.5	3.95	1.4	.36	.4	.74	300	30	100	100	100	30	200	150	89	18	.04	11	17	4.15	3.40	.31	11.3
1352	60.5	12.4	6.3	3.33	1.2	1.41	.4	.69	300	30	100	70	100	20	200	200	130	--	.05	20	28	4.32	3.00	.22	10.9
1402	56.7	14.2	6.2	4.16	1.3	.36	.4	.70	200	50	150	150	150	30	200	200	106	--	.06	20	37	6.58	3.08	.09	13.7
1453*	54.6	17.5	6.2	4.27	3.0	3.07	<.2	.84	1000	15	100	N	70	30	200	200	63	15	.03	4	3.3	.12	0.10	1.35	7.9

* 1453 has 0.1% P_2O_5; all others <0.1% P_2O_5.

Table 2.--Chemical data for Wetzel Co., W VA.

West Virginia 7, Wetzel County

[—, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected; 6272G, grey color; 6272B, black color]

	quantitative percent								Semi-quantitative parts per million									Quantitative parts per million				percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
6122	61.9	19.1	4.9	4.21	1.6	0.83	0.5	0.94	500	10	100	N	30	N	200	200	N	15.2	—	—	4.2	0.17	.07	0.35	5.2
[6172	54.9	19.8	8.5	4.66	1.7	0.22	.4	.84	300	20	150	N	70	30	300	100	N	17.5	—	—	7.6 }	0.49	2.59	.04	7.3
6172]	55.2	20.0	8.9	4.69	1.6	0.22	0.4	0.86	300	30	70	N	70	30	300	150	N	19.5	—	—	7.5 }				
6222	57.2	16.7	6.2	3.89	2.3	3.20	.5	.81	300	20	100	5	70	30	300	150	N	15.6	—	—	3.6	1.11	1.00	0.80	7.0
[6272G	57.0	18.5	7.4	4.33	2.0	1.53	.4	.77	300	30	100	N	70	30	300	100	N	14.5	—	—	6.6	0.62	1.7	0.40	6.3
6272B]	57.5	19.0	7.3	4.43	2.0	.53	.5	.77	100	20	70	5	50	30	300	100	N	14.3	—	—	7.49	1.10	1.7	0.15	6.7
6322	57.5	18.3	6.7	4.38	2.0	1.41	.5	.74	500	20	70	N	70	50	300	150	N	12.6	—	—	3.64	0.63	1.47	0.36	6.0
6372	54.3	19.6	7.3	4.55	2.4	2.29	.4	.83	500	20	70	N	70	N	300	150	N	16.0	—	—	3.27	0.26	0.21	0.52	6.4
6426	26.7	8.50	2.6	2.13	1.6	29	<.2	.36	2000	10	70	N	30	N	70	50	N	7.08	—	—	1.95	0.52	0.48	5.46	25.6
6474	51.6	13.0	4.5	3.18	1.9	9.08	.4	.69	200	20	150	7	70	30	200	150	N	12.6	—	—	6.37	3.25	1.00	1.97	12.0

Analytical split

Different Lithology

8

Table 3.—Chemical data for McKean Co., PA.

Pennsylvania 1, McKean County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected.]

	quantitative								Semi-quantitative								Quantitative								
	percent								parts per million								parts per million					percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
3517*	57.1	20.0	7.79	4.49	2.2	0.46	0.6	1.02	1500	20	70	N	100	15	300	200	89	18	0.01	11	3.7	0.25	0.10	0.53	5.2
4577	64.8	14.1	5.23	3.23	1.7	1.18	.5	.70	300	20	150	10	100	30	300	200	192	15	.06	8	6.1	1.90	1.37	.49	6.2
4627	65.1	13.5	5.07	2.97	1.7	1.98	.8	.92	500	20	150	10	100	30	200	300	50	14	.06	12	5.8	1.45	1.21	.71	5.4
4679	55.0	14.5	4.96	3.36	2.1	6.44	.6	.80	700	15	150	N	100	30	200	150	71	14	.04	53	4.0	1.51	0.93	1.24	8.8
4729	51.4	14.7	4.53	3.54	2.0	7.56	.4	.75	700	15	150	10	100	20	200	150	180	14	.05	18	5.6	3.00	0.84	1.44	11.2
4779	58.4	18.9	7.61	4.18	2.1	.77	.7	1.0	1000	20	50	N	50	10	200	200	84	12	.02	10	3.6	1.96	1.34	2.25	5.5
4829	36.1	9.5	2.92	2.24	2.1	22.3	.4	.35	1000	10	100	N	50	10	150	70	350	9	.03	23	6.1	.90	0.39	4.57	21.1
4879	55.2	16.9	5.75	3.98	2.2	5.02	.5	.62	500	20	70	N	100	30	200	100	52	11	.02	31	3.0	.75	0.70	1.08	7.8
4929	50.9	13.0	4.47	3.08	1.9	11.2	.4	.45	700	10	70	N	70	20	150	100	91	8	.01	41	2.7	1.13	0.47	1.60	12.0
4979	21.4	6.00	2.70	1.37	1.5	34.0	<.2	.23	2000	10	50	N	50	10	100	70	26	5	.02	18	1.8	.30	0.30	6.13	29.3
5033	38.2	10.1	3.63	2.42	1.9	20.9	.2	.37	1000	10	70	N	50	10	150	70	32	10	.01	56	1.7	.55	0.51	4.46	19.0
5083	52.8	14.2	4.81	3.45	1.8	8.07	.4	.51	300	15	100	10	70	20	200	70	35	12	.04	13	3.6	1.97	1.17	1.74	9.6
5083	52.8	14.2	4.8	3.45	1.7	8.16	0.4	.50	300	20	100	7	70	30	200	70	36	10	.03	20	3.6				9.7
5133	58.4	16.3	4.84	4.00	1.6	1.95	.5	.59	150	20	150	30	100	30	300	100	100	13	.08	28	10.1	3.02	1.35	.4	8.8

Analytical split

* 3517 has 0.1% P_2O_5; all others <0.1% P_2O_5.

Table 4.—Chemical data for Allegheny Co., PA.

Pennsylvania 2, Allegheny County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected]

	-quantitative percent								Semi-quantitative parts per million								Quantitative parts per million					Quantitative percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
6967	61.4	16.6	6.0	3.78	1.9	1.54	0.5	0.89	500	20	100	N	70	30	200	300	56	16	0.07	14	4.8	0.75	1.22	0.47	5.3
7017	57.9	14.4	5.3	3.40	2.0	4.97	.5	.78	700	20	100	3	100	20	200	200	57	14	.05	3	4.2	1.22	1.03	.87	6.9
7072	57.8	13.0	7.0	3.16	1.3	1.0	.4	.59	150	30	300	100	200	100	700	150	34	--	.17	14	29	6.87	3.70	.25	13.5
7189	58.3	17.8	6.3	4.16	2.0	1.42	.5	.77	700	20	100	15	100	30	500	150	3600	15	.06	13	4.3	1.30	.94	.56	6.1
7240	56.6	18.6	6.9	4.35	2.2	2.15	.4	.83	1000	30	100	N	100	30	300	150	67	16	.03	6	3.3	.47	.88	.77	5.7
7290*	59.6	16.5	6.8	3.62	2.0	2.95	.4	.86	1000	30	50	N	100	10	300	300	67	16	.02	7	3.3	.56	.51	.64	5.3
7342	54.2	13.7	9.7	3.38	1.3	1.91	.4	.52	150	20	300	70	200	100	500	70	41	12	.13	40	11	3.89	5.10	.72	11.6
7415	55.7	17.5	8.1	4.42	1.5	.64	.4	.70	200	30	200	70	200	50	500	150	44	16	.11	19	8.9	2.41	3.83	.22	8.4
7465	52.1	12.1	7.1	3.40	1.2	2.59	.5	.49	100	30	300	200	300	30	1500	100	1000	--	.21	78	67.7	9.63	5.00	.15	17.0

* 7290 has 0.1% P_2O_5; all others < 0.1% P_2O_5.

Table 5.--Chemical data for Erie Co., PA.

Pennsylvania 3, Erie County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected]

	quantitative								Semi-quantitative								Quantitative								
	percent								parts per million								parts per million					percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
405	55.5	18.3	7.9	4.29	2.0	1.81	0.5	0.89	500	20	70	N	50	15	200	150	N	17.2	--	--	3.1	0.09	1.97	0.25	5.8
545	59.5	16.8	6.4	4.09	1.8	.54	.4	.84	300	30	70	20	100	20	200	200	N	16	--	--	7.5	1.76	1.88	.05	7.6
595	61.4	14.7	5.8	3.62	1.6	.41	.4	.79	300	15	100	15	70	30	150	200	N	17	--	--	10.2	3.38	1.88	.29	9.0
645	46.7	12.2	4.5	2.97	1.8	14.5	.3	.70	1000	10	15	N	20	15	70	150	N	12.0	--	--	3.2	.07	.03	3.10	14.2
735	55.1	16.7	5.3	4.27	2.3	5.41	.4	.80	500	15	70	N	50	15	200	150	N	11.9	--	--	3.8	.08	.07	1.24	7.8
945	57.1	17.6	6.7	4.61	2.1	.57	.4	.80	200	30	100	15	150	70	200	150	N	18.0	--	--	9.3	2.79	1.63	.07	8.7
995*	66.7	11.9	4.7	3.24	1.2	1.17	.3	.54	100	10	100	30	100	30	300	100	N	--	--	--	19.1	3.02	2.03	.09	8.1
1045	4.0	1.1	.7	.25	1.0	48.9	--	--	300	N	15	N	7	N	10	15	N	--	--	--	1.4	.8	.44	10.1	40.2
1191	50.5	17.4	5.6	4.55	2.4	6.96	.2	.62	300	20	50	N	70	10	200	100	N	12.8	--	--	2.5	.31	.70	1.46	8.9
1241	43.2	13.3	5.4	4.19	2.3	6.69	.2	.55	150	15	200	50	150	15	300	100	N	13	--	--	11.1	8.06	2.73	1.21	17.9

* 995 has 0.5% P_2O_5; all others <0.1% P_2O_5.

Table 6.--Chemical data for Indiana Co., PA.

Pennsylvania 4, Indiana County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected; L, detected, but low; 7975S is shale; 7975P is pyrite rich; G, greater than 15 percent]

	quantitative								Semi-quantitative								Quantitative								
	percent								parts per million								parts per million					percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
7125*	57.5	18.3	7.7	3.94	2.5	1.23	0.6	0.86	700	20	70	N	70	15	200	150	--	14.4	--	--	3.4	0.28	0.18	0.30	5.1
7175*	59.0	17.8	7.3	3.81	2.3	1.12	.5	.90	700	20	70	N	50	10	200	150	--	13.5	--	--	3.4	.29	.25	.51	4.9
7226*	51.5	19.9	9.7	4.14	2.9	1.78	.4	.87	700	15	100	N	50	10	200	100	--	16.0	--	--	3.3	.25	.26	.51	6.4
7274	--	--	7	--	1	.7	--	.3	700	20	70	N	50	30	150	100	67	16.6	.02	17	4.3	.31	3.84	.77	--
7375*	59.4	16.2	6.7	3.65	2.2	1.83	.6	.88	700	20	70	N	70	30	200	100	--	13.4	--	--	3.6	.45	1.69	.69	5.8
7475	59.8	12.9	4.8	2.86	2.0	5.53	.6	.77	500	15	70	L	50	30	150	200	--	8.92	--	--	4.0	.93	.900	1.48	7.4
7526	--	--	5	--	1	.7	--	.3	500	15	70	N	50	20	150	100	52	10.9	.06	7	3.5	1.23	.91	1.90	--
7576	18.3	5.32	2.7	1.20	1.2	36.2	L	.21	1500	5	15	N	15	N	70	50	--	4.7	--	--	1.2	.15	.839	7.98	29.5
7627	58.1	19.1	6.8	4.36	2.0	.64	.5	.82	300	20	70	L	100	50	300	150	--	13.6	--	--	3.5	.5	1.37	.10	5.6
7676	58.0	20.5	6.4	4.75	1.9	.30	.6	.91	200	20	100	N	70	15	200	150	--	16.3	--	--	4.0	.39	.66	.04	5.5
7726	57.6	19.8	7.1	4.47	2.0	.58	.5	.89	300	20	70	N	70	10	300	150	--	14.1	--	--	3.6	.39	.67	.05	5.4
7775	57.8	19.2	7.0	4.40	2.0	.56	.5	.89	300	30	50	N	70	30	200	150	--	13.9	--	--	3.6	.52	1.01	.05	5.6
7825	56.8	20.0	6.6	4.67	2.0	.94	.5	.89	700	30	50	N	70	10	300	200	--	16.2	--	--	3.7	.31	.31	.14	5.5
7874	57.1	19.9	6.8	4.71	1.8	.50	.4	.84	200	30	70	5	100	50	300	150	--	16.7	--	--	4.5	.79	1.41	.07	6.3
7926	57.4	18.6	5.9	4.44	1.9	1.89	.5	.76	300	20	100	3	70	30	300	150	--	12.9	--	--	4.4	.90	1.09	.30	6.6
7975S	G	--	6	--	.7	2	--	.6	300	15	100	7	70	30	200	100	62	10.0	.07	13	5.6	1.9	1.3	0.61	--
7975P	6	--	G	--	.3	2	--	.1	150	10	100	N	50	30	70	20	35	5.11	.02	30	1.63	0.83	>13.	0.63	--

SEMI QUANTITATIVE

*7125, 7175, 7226, and 7375 have 0.1% P205; all others <0.1% P205.

Table 7.--Chemical data for Knox Co., OH.

Ohio 3, Knox County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected; L, detected, but low]

	Quantitative								Semi-quantitative								Quantitative								
	percent								parts per million								parts per million					percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
577	54.2	19.0	9.9	3.69	1.7	0.31	0.2	0.89	1000	30	70	N	50	30	150	100	270	16.6	0.03	63	4.8	0.17	0.32	0.82	8.8
627*	61.8	18.8	5.1	4.08	1.6	.31	.4	.94	200	20	50	N	50	10	300	200	120	14.4	.01	16	3.5	.22	.59	.03	5.4
627*	61.5	18.7	5.2	4.03	1.6	.36	.5	.93	200	20	50	N	50	10	200	150	162	14.4	.02	18	3.5				5.5
677	55.0	21.0	7.5	4.59	1.7	.09	.3	.91	150	30	50	5	70	30	300	150	125	17.7	.02	43	5.7	1.02	3.47	.03	7.7
727	58.3	20.5	5.9	4.37	1.6	.15	.4	1.02	200	20	50	L	50	20	200	150	104	16.6	.02	47	4.7	.65	1.69	.19	6.8
777	57.8	17.0	5.7	3.82	1.6	.27	.4	.87	150	20	50	70	100	20	300	150	162	15	.03	20	14.2	4.12	1.37	0.10	10.7
877	62.3	14.0	4.8	3.36	1.3	.57	.3	.68	150	20	70	30	70	15	150	100	138	--	.03	27	16.5	4.90	1.58	.18	10.7
927	57.1	16.6	6.8	3.88	1.5	.25	.3	.72	150	30	100	30	100	30	150	100	272	--	.02	51	14.4	4.11	2.63	.13	10.6
977	60.0	13.9	7.2	3.46	1.4	.38	.3	.63	150	20	70	70	50	20	150	100	52	--	.03	50	16.4	4.18	3.30	.18	9.8
1027	59.8	9.3	7.0	2.25	1.0	.97	.2	.50	150	20	70	70	50	20	100	100	74	--	.08	51	41.1	8.84	4.06	.12	16.3
1027	59.8	9.3	6.9	2.25	1.0	.97	<.2	.51	150	20	70	100	50	10	70	70	84	--	.05	27	39.6				16.5
1078	63.6	12.8	5.3	3.19	1.5	1.40	.4	.72	300	20	70	30	100	20	200	150	114	--	.05	36	21.7	3.12	1.68	.42	9.0
1127	55.6	14.0	6.2	3.58	1.6	.84	.4	.68	200	30	150	100	100	30	200	150	110	--	.06	34	32.5	7.65	2.79	.28	14.2
1181	56.4	19.0	5.2	4.70	2.1	2.69	--	.92	300	15	30	N	50	10	200	150	72	17.2	.03	17	3.7	.40	.16	1.02	6.2
1231	61.1	18.1	5.0	4.73	2.1	1.44	.3	.87	300	15	70	N	50	10	150	150	129	16.3	.04	12	2.8	.18	.10	.40	5.2

Analytical split

analytical split

* 627 has 0.2% P_2O_5; all others <0.1% P_2O_5.

Table 8.--Chemical data for Ashtabula Co., OH.

Ohio 4, Ashtabula County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected; L, detected, but low]

	quantitative								Semi-quantitative								Quantitative							
	percent								parts per million								parts per million				percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
523	56.0	19.5	8.1	4.67	2.0	0.23	0.4	0.86	300	30	70	10	70	30	200	150	123	16.6	0.01	31	5.0	0.76	2.56	0.06	6.8
761	58.6	17.2	7.6	4.20	1.8	.35	.5	.85	300	30	100	7	70	30	200	200	115	14.8	.02	30	6.2	.96	2.86	.13	6.8
811	60.8	16.6	6.6	4.11	1.7	.22	.5	.81	200	30	100	20	70	30	300	200	95	15	.02	21	7.6	1.34	2.03	.13	7.2
861	48.1	12.5	9.2	3.08	1.8	1.44	.3	.65	300	20	200	5	100	100	150	150	57	12	.03	83	8.8	9.70	5.16	.38	19.2
955	57.1	18.0	7.7	4.48	2.1	.39	.5	.90	200	50	70	L	100	50	300	200	78	17.8	.06	33	5.8	1.00	2.62	.12	7.1
1085	59.7	17.9	5.6	4.73	2.2	1.27	.5	.87	300	20	150	N	50	20	300	150	80	11.6	.02	2	4.0	.10	.12	.28	4.7
1125	56.9	16.6	5.8	4.37	2.1	2.82	.5	.77	300	20	150	5	70	30	200	150	358	11	.04	13	8.0	1.67	1.05	.28	7.5
1175*	64.9	12.1	4.4	3.39	1.3	.96	.4	.55	150	15	150	50	150	20	500	150	2090	--	.11	22	23.3	4.15	1.84	.09	9.4
1325	47.7	15.6	4.7	4.14	2.2	9.88	.3	.61	500	20	100	L	70	15	300	100	71	8.6	.02	5	3.7	1.43	.67	1.44	11.3

* 1175 has 0.4% P_2O_5; all others <0.1% P_2O_5.

Table 9.--Chemical data for Lorain Co., OH.

Ohio 5, Lorain County

[—, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected]

	Quantitative (percent)								Semi-quantitative (parts per million)								Quantitative (parts per million)					Quantitative (percent)			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
416	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.58	2.58	0.37	—
466	59.0	18.2	7.0	4.20	1.7	0.18	0.5	.86	200	20	50	10	70	20	200	150	76	15	.02	35	5.0	.26	3.54	.15	7.0
516	62.4	11.3	5.2	2.27	2.6	4.60	0.5	.78	700	10	30	N	20	10	70	150	77	10	<.01	12	3.2	.11	0.33	1.67	7.9
565	56.5	19.1	7.7	4.08	1.5	.13	0.4	.99	150	30	50	10	100	30	150	150	113	17	.02	40	5.8	.57	2.90	0	8.4
613	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.51	1.17	.09	—
665	58.8	17.1	7.4	3.82	1.7	.58	0.5	.84	300	15	50	10	50	20	150	100	141	15	.03	33	6.2	1.33	1.09	.09	7.4
715	60.1	16.1	6.3	3.89	1.6	.32	0.4	.81	300	20	70	20	70	20	150	100	109	16	.02	27	11.0	1.94	1.68	.11	9.0
764	61.6	13.8	5.2	3.34	1.3	.34	0.4	.70	150	20	70	30	100	15	150	100	74	21	.04	25	19.4	4.45	1.87	.06	11.5
815	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.71	2.54	.12	—
861	60.7	12.8	6.1	3.25	1.5	1.27	0.3	.60	200	15	50	30	50	20	70	100	40	—	.03	26	15.1	4.23	2.47	.43	10.9
861	60.9	12.8	6.3	3.28	1.5	1.28	0.3	.61	300	15	70	30	50	15	70	100	42	—	.03	25	14.4				10.6
915	62.8	10.6	6.1	2.63	1.1	.41	0.3	.59	150	20	70	50	50	10	70	100	82	—	.04	31	22.9	6.20	3.14	.06	13.1
965	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3.93	2.28	.11	—
1015	59.4	13.6	6.7	3.60	1.3	.38	0.3	.67	150	20	100	50	70	30	100	100	51	—	.06	37	28.2	4.85	3.39	.19	12.1
1065	58.0	17.2	5.6	4.57	2.3	2.59	0.4	.84	500	20	70	N	50	20	150	150	56	—	.03	12	5.1	.22	0.94	.48	5.8
1116	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.37	2.63	.17	—
1167	59.2	18.6	5.4	5.04	2.3	1.46	0.3	.92	300	15	50	N	50	N	150	150	78	13	<.01	2	2.9	.11	0.05	.48	5.3
1216	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.75	0.68	3.94	—
1267	36.1	12.2	3.4	3.29	1.9	19.7	<.2	.43	300	7	30	N	30	N	100	70	40	14	.02	4	2.5	1.06	0.79	4.06	18.5

Analytic Split

Table 10.--Chemical data for Grainger Co., TN (core 7).

Tennessee 7, Grainger County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected; L, detected, but low]

	quantitative percent								Semi-quantitative parts per million								Quantitative parts per million					Quantitative percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
50	71.5	13.1	4.7	3.14	1.4	.12	.7	1.02	200	15	10	N	30	10	150	300	75	13	<.01	5	4.0	.33	.05	.01	2.9
100	85.5	6.08	2.8	1.30	.51	.16	.5	.94	150	7	7	N	20	N	70	1500	57	20	<.01	4	5.6	.20	.04	.11	1.3
149	81.2	8.98	2.3	2.15	.58	.09	.6	.87	70	10	15	N	30	20	150	700	40	16	.01	11	4.2	.35	.32	<.01	1.8
200	55.3	20.1	6.6	4.45	1.4	.13	.3	.87	150	20	100	30	100	30	700	150	380	17	.04	30	9.7	2.10	2.88	<.01	9.4
250	61.6	11.8	3.5	2.90	1.0	.72	.4	.60	100	10	150	100	150	10	700	150	590	--	.10	18	14.4	7.38	1.66	.16	15.0
300	64.2	16.2	4.3	3.67	1.5	.73	.6	1.02	700	30	70	N	70	30	150	300	370	15	.04	10	4.2	1.06	.15	.32	5.8
350	55.8	18.5	8.8	4.24	1.6	.41	.3	.89	700	15	150	N	30	N	150	150	56	14	.01	6	3.3	.21	.13	.87	7.8
406	74.5	7.79	6.2	1.57	.60	.54	1.0	.72	100	7	70	15	70	50	100	300	19	11	.03	28	9.2	.94	4.45	.19	5.3
450*	60.5	18.5	5.3	4.31	1.8	.72	.5	.94	700	15	50	N	50	N	150	150	65	17	.01	12	3.7	.30	.17	.30	5.5
506	62.7	16.0	6.4	3.50	1.2	.15	.7	1.02	150	20	70	10	70	30	100	200	49	15	.03	31	8.2	.83	2.73	.11	6.6
550	59.2	16.4	6.5	3.99	1.5	.19	.6	.92	150	20	70	30	70	30	150	150	87	17	.03	23	12.7	2.30	2.58	.13	8.6
603	59.0	16.9	6.8	4.15	1.7	.25	.5	.84	200	20	70	10	70	30	150	150	129	14	.02	29	7.8	1.20	2.51	.19	7.4
650	59.2	15.2	6.9	3.51	1.9	1.65	.6	.87	500	20	70	15	70	30	150	150	118	16	.04	31	12.9	1.19	2.17	.65	7.3
700	55.2	16.0	6.6	4.04	1.6	.69	.5	.80	300	30	100	50	100	30	200	150	129	--	.07	22	27.5	5.44	2.84	.47	12.7
750	57.5	20.8	5.7	4.89	1.8	.23	.3	.91	200	15	100	L	50	30	150	100	74	20	.04	12	9.6	.54	1.12	.03	5.8
800	46.1	16.1	6.4	4.00	1.8	10.4	.2	.70	1000	10	30	N	30	10	100	100	79	12	<.01	2	2.7	.10	.02	1.82	11.9
825*	49.4	18.7	6.2	4.15	1.8	1.07	.3	.81	200	15	200	15	150	150	200	100	630	19	.08	20	11.6	6.65	2.06	.30	14.8
825*	48.6	18.4	6.8	4.07	1.8	1.02	.3	.81	200	15	200	20	150	150	200	100	650	17	.08	28	11.9				15.2

Analytical split

*Samples at 450 and 825 ft have 0.1% P_2O_5; all others <0.1% P_2O_5.

Table 11.--Chemical data for Grainger Co., TN (core 6).

Tennessee 6, Grainger County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon]

	-quantitative percent								Semi-quantitative parts per million									Quantitative parts per million					Quantitative percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
281*	53.4	13.1	8.7	3.18	1.3	0.68	0.6	0.79	200	50	100	70	150	30	150	200	57	--	0.12	67	44.7	6.94	4.94	0.31	15.7
348*	44.0	16.4	6.5	3.82	1.4	1.50	.2	.66	150	20	200	100	150	150	700	150	78	--	.07	43	44.8	13.69	3.02	.04	22.1
372	55.1	15.7	6.0	4.47	1.4	.33	.4	.79	150	20	150	100	150	50	200	150	124	--	.07	22	32.2	5.93	2.92	.12	13.2
441	54.5	19.4	5.6	4.58	1.4	.27	.3	.90	150	50	100	30	150	50	700	150	590	18	.08	24	17.0	4.67	1.66	.02	10.6
469*	46.0	17.2	9.8	3.88	1.5	1.08	.3	.69	150	20	300	10	200	200	300	150	1600	13	.08	61	13.2	7.55	4.31	.05	16.7

*281 has 0.1% P_2O_5; 348 has 0.86% P_2O_5; 469 has 0.62% P_2O_5; 372 and 441 <0.1% P_2O_5.

table 12a.--Chemical data for Hancock Co., TN.

Hancock County, Tenn., TDG-DOE #3
[-- not determined]

Depth ft	Quantitative percent							Semi-quantitative parts per million							Quantitative parts per million									Quantitative percent		
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Mg*	CaO	TiO_2	Mn	Ba	Cr	Pb	Sr	Zr	Co	Cu	Mo	Ni	V	Zn	Th	Hg	U	Org C	S	CO_3C
143.3	55	20	5.6	4.4	.7	<.1	.88	160	500	150	20	100	150	15	26	<10	81	395	208	18	1.3	6.3	1.29	1.79	<.01
193.8	56	18	4.9	4.0	.7	.2	.74	97	500	100	15	100	100	13	55	18	135	895	365	18	.1	12.2	4.87	1.72	.04
244.8	57	15	7.0	3.5	.7	.5	.90	730	500	70	10	150	150	81	59	<10	110	325	366	14	.08	5.0	2.73	.31	.74
264.2	57	14	5.2	3.0	.5	2.1	.84	115	500	100	20	150	200	13	76	<10	114	230	332	16	.08	9.2	5.48	2.12	.07
315.0	62	11	6.4	2.5	.5	.9	.82	115	300	70	10	70	200	9	49	23	104	500*	296	—	.08	17.5	5.18	3.41	.18
461.2	59	16	6.5	3.9	.7	<.1	.94	240	300	70	20	100	150	18	29	<10	66	165	65	14	.05	6.9	1.38	2.20	.14
500.8	55	17	7.0	4.3	.7	.4	.87	250	500	70	15	150	150	19	50	<10	62	150	99	14	.05	7.6	1.86	3.13	.21
555.0	52	13	9.3	3.3	.7	.6	.78	175	300	50	15	100	150	38	79	130	99	185	68	—	.11	44.	8.25	7.10	.14
741.7	61	18	3.8	4.8	.7	.1	.99	125	500	100	15	150	200	14	93	<10	87	235	72	19	.11	9.7	1.86	.92	<.01

* Semi-quantitative emission spectroscopy, other majors (in %) by XRF

264 - 2.% P_2O_5, all others <.1% P_2O_5

193.8 - 1 ppm Ag, others <1ppm

143.3 - Hg is really this high

193.8 - 6 ppm Cd; 315.0 - 4 ppm Cd, others <1 ppm

Table 12b.--Chemical data for Hancock Co., TN.

Hancock County, Tenn., TDG-DOL #3

[G, greater than 10%; N, below detection (usually 5 ppm); L, at detection limit; --, not analyzed]

	Semi-quantitative omission spectroscopy																Quantitative				
	percent						ppm										ppm		percent		
Depth ft	Fe	Ca	K	Al	Mg	Ti	Mn	Ba	Co	Cr	Cu	Mo	Ni	Pb	V	Zr	U	Th	Org C	S	Carb C
132	3	.3	3	7	.7	.3	300	200	15	70	50	N	70	15	70	150	3	14	.43	3.01	.18
152*	3	.05	7	G	.7	.3	100	700	15	150	50	30	70	30	500	150	7	16	1.17	1.79	.03
172	3	.15	3	10	.7	.3	100	500	15	70	70	70	150	30	300	150	17	--	3.98	2.36	.07
192*	3	.15	3	10	.7	.3	70	500	15	150	150	50	150	20	700	100	14	--	6.04	2.11	.07
212*	3	.15	3	G	.7	.3	70	700	15	100	100	30	150	30	500	100	7	11	3.98	2.38	.11
232	3	.15	3	10	.7	.3	100	500	15	70	70	70	200	15	500	150	23	--	6.26	1.82	.04
252	1.5	.07	3	G	.7	.3	150	700	15	70	50	N	30	L	150	150	3	17	1.01	.14	.14
273	1.5	.07	3	7	.7	.15	70	300	7	70	70	5	30	10	70	70	6	16	4.97	1.60	.07
293*	1.5	.3	3	7	.7	.3	70	1000	15	150	70	15	150	10	300	200	10	11	7.13	1.06	.21
313*	2	.07	3	10	.7	.3	70	300	15	150	70	30	100	15	500	200	13	16	5.48	1.37	<.01
333	3	.03	5	10	.7	.3	150	500	20	70	70	15	150	30	300	150	10	13	1.97	2.30	<.01
337	3	.07	5	10	.7	.3	300	700	15	70	30	N	50	L	150	150	3	16	.25	.23	.29
350	3	.03	5	10	.7	.3	70	500	15	70	50	5	70	15	300	150	11	18	1.59	1.14	.04
372	3	.07	3	G	.7	.3	70	500	20	70	70	30	100	15	200	200	15	18	3.24	2.39	<.01
390	3	.1	3	7	.7	.7	70	500	20	70	70	30	100	15	200	300	19	--	3.76	2.37	.03
410	3	.05	3	7	.7	.5	150	500	20	70	70	30	70	15	150	200	8	14	2.00	2.81	.07
430	3	.07	5	G	1.5	.3	200	500	15	70	50	3	30	15	150	150	5	15	.41	.94	.11
450	3	.07	3	10	.7	.3	150	500	15	70	70	15	70	15	150	150	6	14	.93	2.18	.13
470	3	.03	3	7	1	.3	200	300	15	50	50	7	30	20	70	150	5	16	.96	2.51	.11
490	3	.07	3	10	1	.3	200	700	20	70	70	15	70	20	150	150	5	17	1.24	2.53	.11
510	3	.07	3	G	1.5	.3	150	700	20	70	50	30	70	15	150	150	6	13	1.34	2.50	.07
530	3	.15	3	10	1	.3	150	700	20	70	70	30	70	15	150	150	9	17	2.31	2.85	.10
550	3	.15	3	7	.7	.3	150	300	30	50	70	70	100	15	150	150	33	--	6.56	5.08	.11
570	3	.15	3	10	1	.3	150	700	15	70	50	N	30	L	150	150	6	16	3.94	.40	.22
574	3	.3	3	7	.7	.3	300	700	30	70	70	70	150	30	150	150	30	--	5.79	2.57	.40
596	5	.15	3	7	.7	.3	150	300	50	50	150	70	150	70	150	150	24	--	11.10	5.23	.04
616	3	.15	3	7	.7	.3	150	300	50	70	100	70	150	20	150	150	29	--	6.62	3.76	.14
636	3	.3	3	10	.7	.3	150	300	30	70	100	70	100	20	150	150	27	--	5.15	2.60	.15
649*	3	.15	3	10	.7	.3	150	500	20	70	100	70	100	30	150	150	33	--	7.17	4.47	<.01
656	3	.15	3	G	1	.3	200	500	15	70	30	N	70	20	150	150	3	14	.13	.70	.15
676	3	3.	3	10	1.5	.3	700	300	10	70	70	N	30	L	150	100	2	13	.26	.05	1.96
697	3	.3	3	G	1.5	.3	150	300	15	70	150	N	100	20	150	150	4	15	.27	.21	.14
717	3	.3	3	10	1.5	.3	300	500	15	70	30	N	70	10	150	150	2	15	.33	.03	.25
737*	7	.15	3	7	.7	.3	150	300	50	70	150	70	300	70	300	150	22	--	8.66	8.75	.04

* Ag - 152 ft., 0.7 ppm; 192, 1.5; 212, 1.5; 293, 0.7; 313, 0.7; 737, 0.5

Cd - 192 ft., 100 ppm

Zn - 192 ft., 3000 ppm; 212, 200; 649, 1500; 737, 500

Table 13.—Chemical data for Cuyahoga Co., OH.

Cleveland Salt Co. #1, Cuyahoga County, Ohio

[G, greater than 10%; N, below detection (usually 5 ppm); L, at detection limit; —, not analyzed]

	Semi-quantitative Emission spectroscopy																Quantitative				
	percent						ppm										ppm		percent		
Depth ft	Fe	Ca	K	Al	Mg	Ti	Mn	Ba	Co	Cr	Cu	Mo	Ni	Pb	V	Zr	U	Th	Org C	S	Carb C
101	3	.07	3	10	1.5	.5	150	300	15	70	30	7	70	15	150	150	4	12	.70	1.66	.04
116	3	.07	3	G	.7	.5	150	300	15	70	30	N	70	10	150	150	3	15	.36	.51	.03
130	3	.15	3	G	.7	.5	150	300	15	70	30	N	50	N	150	150	4	16	.36	.12	.07
138	3	.07	3	7	.7	.3	150	300	15	70	30	15	70	30	100	150	6	14	1.66	1.89	.07
151	3	.15	3	7	.7	.3	100	300	15	70	50	30	70	10	150	150	9	11	2.78	1.53	<.01
165	3	.07	3	G	1.5	.3	150	300	15	70	30	N	70	N	150	150	3	16	.37	.14	<.01
180	3	.1	3	7	.7	.3	150	300	15	70	30	20	70	30	150	150	6	14	2.2	1.76	.07
188	3	.15	3	7	.7	.5	150	500	15	70	30	15	70	20	100	150	8	15	.57	1.47	.03
285	3	.15	3	7	.7	.3	100	300	15	50	30	30	70	10	150	150	17	—	5.73	1.31	.03
350	3	.15	3	7	.7	.3	150	300	15	70	50	30	70	20	150	150	11	—	3.0	2.26	<.01
361	3	.15	3	7	.7	.3	150	300	30	70	70	30	70	30	150	150	8	13	2.99	3.03	.21
391	3	.15	5	G	1.5	.3	200	300	15	70	50	N	50	10	150	100	5	12	1.74	.28	<.01
415	3	.15	3	10	1	.3	150	300	15	70	30	N	30	L	150	150	4	13	.43	.32	<.01
422	3	.5	3	7	1	.3	150	300	20	70	70	70	70	30	150	150	15	—	5.60	2.64	.20
447	3	.15	5	7	1	.3	150	300	15	70	30	5	30	15	150	150	6	14	.31	.86	.07
490	3	.15	3	7	.7	.3	150	300	15	70	70	30	70	30	100	150	11	12	3.47	3.12	.07
494	3	.15	3	7	.7	.3	150	300	15	50	70	30	70	150	70	150	15	—	5.92	3.02	.04
509	3	.3	3	7	.7	.3	150	300	20	70	70	70	100	30	150	200	30	—	6.42	2.92	.07
546	3	1.5	3	10	1.5	.5	200	300	15	70	50	N	30	N	150	150	4	14	.34	.45	.52
559	3	.3	3	7	.7	.5	150	500	30	70	70	70	150	30	150	150	24	—	5.93	1.90	.11
590	3	.3	3	7	.7	.3	150	300	15	70	70	30	70	20	150	150	15	—	3.17	1.38	.18
602	3	.7	3	7	.7	.5	150	300	30	70	70	70	70	30	150	150	15	—	6.87	2.37	.10
632	3	.15	3	7	.7	.3	150	300	30	70	70	70	100	30	150	150	25	—	8.26	2.52	<.01
662	3	.15	3	7	.7	.3	150	300	30	50	150	70	70	30	150	150	24	—	7.60	2.62	<.01
701	3	.3	3	7	.7	.3	150	300	20	70	70	30	100	30	150	100	15	—	7.92	1.55	.14
705	7	.7	3	7	.7	.3	150	200	30	30	150	15	150	150	100	150	12	13	15.31	2.29	.06
712	3	1.5	3	7	1	.3	200	300	15	70	30	N	30	N	70	70	3	16	.27	.20	.48
727	3	.3	5	7	1	.7	150	300	30	70	150	15	150	30	150	150	9	16	4.0	2.01	<.01
737	3	.7	3	10	1	.5	150	300	15	70	150	N	70	10	150	150	5	13	.37	.31	.28
750	7	.7	3	7	1	.5	150	300	30	70	150	70	150	70	300	150	18	20	6.48	2.98	.17
813	3	10	3	7	1	.3	1500	150	30	70	20	N	70	10	150	100	2	9	.48	.34	4.50
874	1.5	7	3	7	1	.15	700	200	5	70	30	N	30	15	70	70	2	11	.90	1.01	2.92
904	.7	7	3	7	1	.07	300	200	3	30	20	N	10	10	30	15	2	10	3.43	.46	2.19
923	3	7	3	7	1	.3	200	300	15	70	30	5	70	10	150	70	2	8	1.09	.55	1.82

Zn - 300 ppm at 285 and 923.

Table 14.--Chemical data for Tompkins Co., NY.

Cargill #17, Tompkins County, New York (Lansing Township)
[G, greater than 10%; N, below detection (usually 5 ppm); L, at detection limit; —, not analysed]

	Semi-quantitative Emission Spectrography																Quantitative				
	percent						ppm										ppm		percent		
Depth ft	Fe	Ca	K	Al	Mg	Ti	Mn	Ba	Co	Cr	Cu	Mo	Ni	Pb	V	Zr	U	Th	Org C	S	Carb C
77	3	.7	3	10	1.5	.7	700	500	20	70	70	N	70	10	150	150	4.0	16	.33	.15	.22
93	3	.3	3	7	1.5	.5	300	300	15	70	70	N	70	30	150	150	4.2	15	1.61	.58	<.01
113	3	.3	5	G	1.5	.7	500	500	30	100	70	N	70	L	150	150	3.8	18	.33	.17	.18
149	3	1.5	3	10	1.5	.7	300	300	15	70	70	7	70	30	150	300	4.8	13	1.01	1.40	.42
180	3	1.5	3	7	1	.7	150	300	15	100	70	15	70	20	200	150	5.2	16	1.59	1.53	.43
210	3	.7	3	G	1.5	.3	150	500	15	100	70	10	70	15	200	150	5.0	15	1.40	1.16	.21
240	3	1.5	3	G	1.5	.3	150	500	20	100	70	15	150	70	150	150	5.9	15	1.39	1.94	.39
299	3	1.	5	10	1.5	.5	300	500	20	100	30	N	70	N	150	100	3.6	16	.39	.40	.29
350	3	.7	3	10	1.5	.3	300	500	30	70	150	N	70	15	150	150	3.2	14	.35	.48	.24
400	3	1.5	5	G	1.5	.3	200	500	20	150	30	N	70	15	150	150	3.1	13	.41	.62	.35
449	3	1.5	3	G	1.5	.7	300	500	20	100	70	N	70	15	150	150	3.5	15	.31	.28	.46
510	3	1.	5	10	1.5	.7	500	500	20	100	30	N	70	15	150	150	3.4	15	.33	.22	.36
550	3	1.	3	G	1.5	.5	300	300	15	150	15	N	70	15	150	150	3.7	14	.38	.38	.35
600	3	1.5	3	10	1.5	1.	500	500	30	70	30	N	70	15	150	150	3.7	13	.33	.38	.43
650	3	.5	3	10	1.5	.7	300	300	15	70	15	N	70	10	150	300	3.5	14	.34	.53	.14
701	3	3.	3	7	.7	.3	300	300	15	100	30	N	30	N	150	300	3.3	13	.27	.08	1.12
750	3	.7	3	10	1.5	.3	300	300	15	100	30	N	70	N	150	200	3.3	14	.56	.45	.28
800	3	.3	3	10	1.5	.3	700	300	15	70	30	N	70	15	150	150	3.0	14	.72	.67	1.18
850	3	.7	3	7	1.5	.3	300	300	15	70	30	N	70	20	150	150	3.6	14	.57	.84	.38
900	3	.7	3	7	1.	.3	150	300	15	100	50	N	70	30	150	150	3.8	14	.81	.85	.29
950	3	10.	3	7	1.	.3	1000	300	10	70	30	N	70	15	150	70	2.5	8	.57	.42	4.96
1000	3	7.	3	7	1.	.3	700	300	15	70	30	N	70	30	150	150	3.2	10	.62	.71	2.78
1050	3	3.	5	10	1.5	.3	500	300	20	100	30	N	70	L	150	70	3.0	12	.69	.39	1.21
1100	3	3.	3	7	1.5	.3	500	300	30	70	30	N	70	15	150	150	3.1	14	.58	.48	.63
1150	3	2.	3	10	1.5	.3	300	300	15	70	30	N	70	10	150	150	3.2	13	.52	.31	.71
1200	3	3.	3	10	1.5	.3	700	300	15	100	30	N	70	N	150	150	3.2	13	.57	.21	.90
1250	3	3.	3	7	1.5	.3	300	500	15	70	30	N	70	30	150	70	3.0	11	.64	.85	1.06
1300	3	10.	3	7	1.	.3	700	700	15	70	20	N	70	30	100	100	1.9	8	.28	.66	4.39
1339	3	1.	5	7	1.5	.3	150	1000	15	100	70	20	70	30	150	70	6.1	12	1.94	1.20	0.39
1360	7	.3	3	7	.7	.3	100	7000	30	70	150	50	150	30	150	100	14	18	3.65	4.99	.15
1380	3	.7	3	7	.7	.3	150	500	30	70	150	150	150	30	300	150	29	—	5.37	2.83	.18
1403	3	7.	3	5	.7	.3	100	300	15	70	300	70	300	15	700	70	25	—	9.23	2.91	2.15
1420	2	7.	3	3	.7	.15	70	300	15	30	150	50	150	20	150	70	53	—	8.12	5.95	2.26
1429	.7	7.	2	1.5	.7	.1	70	150	3	30	150	7	70	15	70	70	11	—	4.56	1.65	4.49

Zn: L at 900 ft, 200 ppm at 1420 ft; Ag: .5 ppm at 1380 ft, 1.5 ppm at 1403 ft, 1 ppm at 1420 ft, .7 ppm at 1429 ft

Table 15.--Chemical data for Livingston Co., NY.

Stewart 6701, Livingston County, N. Y.
[G, greater than 10%; N, below detection (usually 5 ppm); L, at detection limit; --, not analyzed]

	Semi-quantitative emission spectroscopy																Quantitative				
	percent						ppm										ppm		percent		
depth ft	Fe	Ca	K	Al	Mg	Ti	Mn	Ba	Co	Cr	Cu	Mo	Ni	Pb	V	Zr	U	Th	Org C	S	CO3
77.7	3.	3.	3	10	1.5	.3	150	300	15	100	15	N	70	N	150	100	3.4	10.1	.42	.39	.92
80.8	3.	1.5	3	G	1.5	.3	150	300	15	100	20	N	70	N	150	150	2.7	11.1	.28	.38	.48
108	3.	3.	3	10	1.5	.15	150	300	15	100	20	N	70	N	150	70	3.9	10	.32	.17	.83
120.3	3.	2.	3	G	1.5	.3	150	300	15	100	30	N	70	N	150	150	3.1	10.4	.32	.12	.72
139.7	3.	3.	3	10	1.5	.3	150	300	15	70	30	N	70	N	150	150	2.7	9.6	.19	.12	1.29
155.9	1.5	G	3	3	.7	1.5	1000	150	5	30	7	N	30	N	30	30	1.2	4.9	<.01	.22	6.72
168	1.5	7.	3	3	.7	1.5	300	150	7	30	20	N	30	10	70	70	1.3	6.4	.05	.36	4.26
179	1.5	7.	3	10	1.5	.3	300	300	15	70	15	N	30	N	150	70	2.8	10.5	.01	.27	2.06
201.4	1.5	3.	5	7	1.	1.5	150	300	3	50	30	N	15	N	70	30	3.3	10.9	.64	.38	1.33
215.8	.7	7.	3	3	1.	.07	700	150	N	30	15	N	7	N	15	30	2.3	6.7	.18	.49	5.31
229	1.5	7.	3	7	1.5	.15	300	300	3	50	30	N	30	10	50	30	3.8	8.9	.71	.49	2.35
235.8	3.	7.	3	10	1.5	.3	200	300	20	100	50	7	70	30	150	150	4.0	9.7	2.01	.84	1.39
260.7	3.	1.5	3	7	1.5	.3	150	300	20	100	30	N	70	30	150	150	3.7	12.8	.81	2.00	.44
269.8	3.	2.	3	10	1.5	.3	150	300	15	100	50	N	70	L	150	100	3.2	12.0	.60	.74	.66
288	1.5	7.	3	7	.7	.15	150	300	15	70	15	N	30	N	150	70	2.6	9.2	.26	.61	3.91
300	.7	7.	3	3	1.5	.07	300	200	3	30	50	N	15	15	30	30	3.6	8.1	1.91	.73	3.50
318.1	3.	10.	3	7	1.5	.3	300	200	10	70	30	3	70	10	70	70	4.3	6.6	1.72	.43	3.25
333.6	3.	7.	3	7	1.5	.3	300	200	20	70	70	N	70	15	70	70	3.0	9.9	1.06	.56	2.75
348	3.	7.	5	7	1.	.3	200	200	15	70	70	3	70	10	150	70	2.8	7.9	1.14	.40	2.13
368	3.	7.	5	7	1.	.3	150	300	10	70	50	N	70	15	150	70	2.8	10.9	.92	.59	2.31
384	3.	10.	3	7	1.	.3	300	200	10	70	30	N	50	10	150	70	2.7	7.5	.64	.40	3.98
398	3.	7.	3	7	1.5	.3	200	200	10	70	30	N	50	N	150	70	2.7	8.6	.82	.44	2.87
403	3.	10.	3	7	1.5	.3	150	200	15	70	30	N	30	N	150	70	1.9	8.4	.12	.41	5.13
425	3.	10.	3	7	1.5	.3	200	200	10	70	30	N	50	15	150	70	2.4	7.3	.48	.50	4.28
442	3.	10.	3	7	1.	.3	300	300	15	70	70	7	70	10	150	70	3.6	8.7	1.31	.57	4.06
455	3.	7.	3	7	1.	.3	300	200	10	70	70	7	70	N	150	70	3.7	6.7	1.46	.50	4.52
469	1.5	G	3	5	1.	.2	500	300	5	70	70	N	30	N	100	70	2.3	6.2	.77	.46	6.55
491	.3	7.	3	3	1.	.07	300	150	N	15	50	N	7	N	15	30	2.4	8.6	1.00	.40	5.36
506	1.	7.	3	3	1.	.15	200	300	3	30	50	N	15	N	30	30	2.9	9.4	1.59	.41	3.42
511	2.	G	3	3	1.	.2	300	700	10	70	30	3	30	N	70	70	2.3	5.8	1.10	.38	5.65
530	1.5	7.	3	7	1.	.2	150	300	7	70	100	15	70	30	150	70	7.3	10.4	2.96	1.24	2.29
543	3.	.5	3	7	1.	.3	100	300	30	70	150	50	150	30	150	70	19.9	6.3	6.25	2.99	.11
543.5	3.	.5	5	7	1.	.3	100	300	20	100	150	70	150	30	300	100	16.6	6.3	5.16	2.43	.11
564*	3.	.3	3	7	.7	.3	100	200	30	70	300	150	300	30	300	150	83.7	17.	12.00	6.27	.06
576*	2.	7.	3	3	.7	.15	150	150	20	30	300	100	300	30	300	70	53.8	13.	14.14	5.90	2.07

* Zn: 700 ppm at 564 ft and 576 ft; Ag: 0.7 ppm at 564 ft; 2 ppm at 576 ft

Table 16.--Chemical data for Alleghany Co., NY.

New York 1, Allegany County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected]

	quantitative								Semi-quantitative									Quantitative							
	percent								parts per million									parts per million				percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	Mn	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
1002	58.6	17.8	7.6	4.22	1.9	0.66	0.5	0.84	300	20	10	N	70	50	200	150	N	14	--	--	3.4	1.13	1.98	0.16	6.4
1542	57.0	20.1	7.7	4.42	2.0	.18	.5	.94	500	30	50	N	100	50	300	200	N	15	--	--	4.0	.26	1.08	.03	5.5
1744	55.5	21.3	7.6	4.63	2.1	.21	.5	.95	700	30	70	N	100	30	300	200	N	16	--	--	4.0	.33	0.69	.04	5.9
2049	54.6	19.5	9.2	4.20	2.1	.60	.4	.92	1500	20	200	N	70	10	200	200	N	15	--	--	3.5	.17	0.11	.66	6.8
2301	58.4	18.0	7.5	3.84	2.3	1.05	.6	.85	1500	20	150	N	70	N	200	200	N	14	--	--	3.2	.18	.14	.37	5.6
2496	58.4	18.6	7.0	4.14	2.0	.59	.6	.87	500	20	100	10	100	50	300	200	N	14	--	--	4.8	.77	1.50	.13	6.0
2743	53.0	14.5	5.2	3.18	2.3	7.60	.6	.79	700	20	100	N	70	20	200	200	N	11	--	--	3.3	1.00	.75	1.42	9.4
2843	63.3	14.9	5.8	3.29	1.9	.66	.7	.87	300	20	100	50	100	30	200	300	N	15	--	--	8.1	2.17	1.52	.23	6.9

Table 17.--Wayne and Hardin Counties, IL.

Illinois 5, Wayne County

[--, not analyzed; LOI, loss on ignition; org C, organic carbon; CO_3C, carbonate carbon; N, not detected; L, detected, but low]

	quantitative percent								Semi-quantitative parts per million								Quantitative parts per million					Quantitative percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	MnO	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
5066	58.0	13.2	4.0	4.34	2.0	1.62	0.4	0.66	500	10	150	20	100	20	700	150	L	16	--	--	16.1	6.89	1.10	0.45	12.8
5116	59.6	11.7	7.8	3.50	1.3	.39	.5	.62	200	30	150	70	100	30	150	150	N	--	--	--	35.7	4.46	4.12	.05	12.5
5116	59.2	11.7	8.1	3.50	1.3	.40	.5	.61	200	30	150	70	100	30	150	150	N	--	--	--	33.6				12.6
5166	53.1	16.6	6.0	4.87	2.0	.57	.6	.68	200	30	150	70	100	30	300	150	N	--	--	--	36.1	5.71	2.09	.18	13.0
5216	55.5	14.6	4.5	4.50	2.3	1.48	.7	.70	200	15	150	50	150	30	700	150	N	24	--	--	23.8	5.30	1.46	.37	12.5
5265	45.9	9.24	2.1	3.05	3.0	13.7	.5	.39	300	15	200	20	100	20	300	100	N	11	--	--	8.39	1.68	.05	1.93	17.0

Analytical split

Illinois 4, Hardin County

	quantitative percent								Semi-quantitative parts per million								Quantitative parts per million					Quantitative percent			
depth (ft)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	Na_2O	TiO_2	MnO	Co	Cu	Mo	Ni	Pb	V	Zr	Zn	Th	Hg	As	U	org C	S	CO_3C	LOI
84	48.5	13.6	5.6	4.34	2.6	3.4	4.6	0.68	500	30	150	15	100	50	300	150	46	16	.09	54	13.15	6.19	2.5	1.80 * 1.80	11.7
137	40.6	11.5	5.0	4.04	5.4	10.3	3.8	.59	700	10	70	N	50	N	300	150	64	18	.03	36	3.8	0.53 * 0.50	.54	3.37 * 3.46	15.5
198	64.4	9.7	3.5	3.83	2.1	2.2	2.9	.47	200	15	100	30	150	20	300	100	193	6	.05	46	5.1	3.98	.92	1.40 * 1.36	7.6

* analytical split

Discussion

Down-hole plots

Figures 3-13 show the down-hole plots of results for 11 of the cores. These plots allow an easy assessment of the organic carbon and sulfur controls of trace elements such as U, Mo, V, Cu, and Ni, and the carbonate control of Mn. As and Hg are often positively correlated with S, but not always.

Johnson County (KY-4) shows generally good correlation between organic C, U and Mo; however, the higher level of organic carbon at 1046 ft in the Cleveland shale is not reflected in higher U or Mo. The V does show the higher levels at 1046, however. Hg, As, and Co show high values at the top of the core in the Bedford shale (987 ft) without accompanying high C or S values. It is possible they are in a separate sulfide phase, although Pb and Zn are not high on this sample. The high at 1402, near the base of the Huron shale shows well in C, S, U, Mo, Hg, As, Co, and Ni. Note the high Mn, CaO, and CO_3 at the bottom of the core (1453 ft) in the Olentangy shale.

The chemistry and stratigraphy are related as can be seen on Table 18 for Johnson Co., KY. Major constituents have been recalculated to remove organic carbon, carbonate, and sulfur using the following relation: subtract [organic C x 1.3 + CO_3C x $\frac{44}{12}$ + S] from the total and recalculate to 100 percent. The major components SiO_2 and Al_2O_3 show the stratigraphic changes between 987 and 1046, 1099 and 1156, and 1402 and 1453, between the Bedford and Cleveland, Chagrin and Huron, and Lower Huron and Olentangy, respectively. Similarly the Huron-Lower Huron boundary between 1303-1352 may be recognized, but less clearly. The uranium and organic carbon also show these changes as expected, because since the rock color is based on the organic content and the radioactivity (on the geophysical gamma-ray log) is based on the uranium content.

Johnson Co, Ky Fig 3

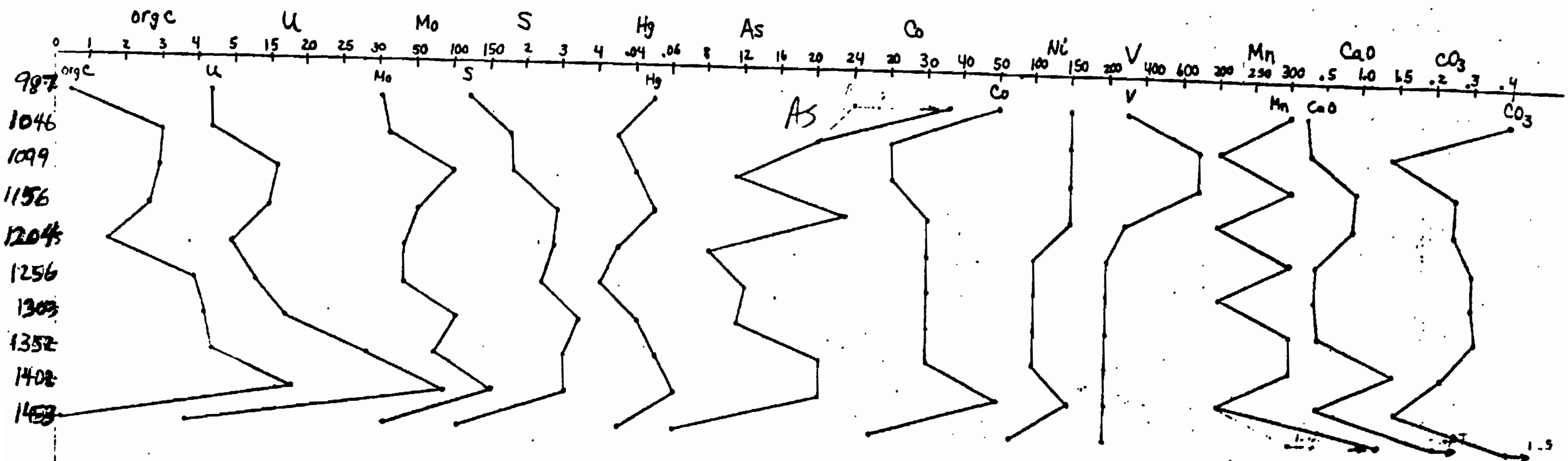


Figure 3.--Down-hole plot of chemical analysis from Johnson Co., KY ore. Chemical elements grouped by geochemical affinity; increasing concentrations to the right.

Table 18.--KY 4, Johnson County recalculated values (corrected for organic, carbonate and S)

ft depth	recaluated % SiO_2	% Al_2O_3	ppm U	% Organic C	Formation
987	60.8	21.2	6.9	0.51	Bedford
1046	67.9	15.2	6.9	2.98	Cleveland
1099	64.3	16.3	16	2.93	
1156	61.2	17.9	15	2.65	Huron
1204	61.2	18.5	9.7	1.51	
1256	66.0	16.0	13	3.84	
1303	63.2	16.8	17	4.15	
1352	66.2	13.6	28	4.32	Lower Huron
1402	63.5	15.9	37	6.58	
1453	57.4	18.4	3.3	0.12	Olentangy

Wetzel County (WV-7) shows the expected general relations with covariance between organic carbon, uranium, and molybdenum at 6474 ft, although U and Mo are quite low. Three samples contain carbonate, the sample at 6426 shows increased Mn, but the samples at 6172 and 6474 show no increases. The sample at 6272 was subdivided based on its color, into black and gray portions. Despite the visual observations there is slightly difference except that 6272B has more organic carbon (1.1) and a little more U, Ni, Cu, Co, and Mo, whereas 6272G has more CaO and CO_3C has higher Mn.

McKean County, PA-1) core shows increases in organic carbon, U, Mo, and Hg at 4629 and 5133. The 5133 sample also shows increased As and S and may be near the top of the Marcellus shale. The samples at 4679 and 5033 show high As which doesn't relate to organic or sulfide changes, but there is enough of either organic C or S to easily account for the As. The high sulfide (and Fe) are not accompanied by increases in trace elements at 4779 and 4879. Part of the reason for lack of obvious trace-element control by organic carbon in these samples may be relatively low organic content. Some of the samples (carbonate-rich shales) show increased amounts of Mn (4979, 5033, 4829); however, higher Mn is also present in samples at 4779 and 3517 which do not contain increased carbonate.

Allegheny County,(PA-2) shows good covariance between organic carbon, U, V, Mo, Cu, Ni, Hg, and S at 7072, 7342, and 7465 ft. The 7465 sample (Marcellus shale) which has the greatest amounts also shows high levels of Zn and As. The high Zn (3600 ppm) at 7189 ft in the Mahantango shale is unusual because that sample contains only 0.94 percent S, [but has a high iron content, 6.3 percent as Fe_2O_3] indicating that the sample as a whole is not strongly sulfidized. Based on organic and sulfur contents the 7342 and 7415

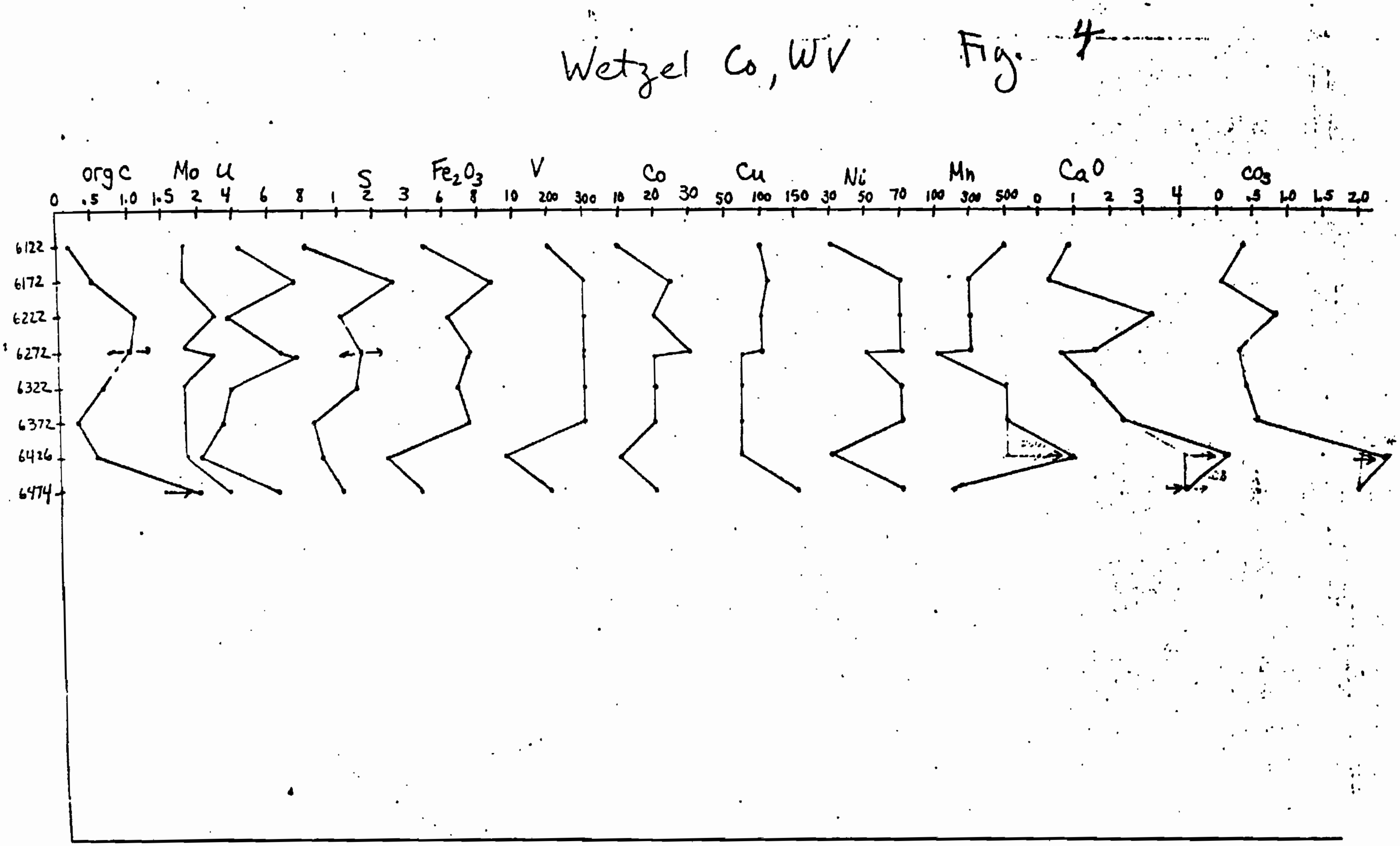


Figure 4.--Down-hole plot of chemical analysis from Wetzel Co., W VA core.

Figure 5 McKean Co, PA

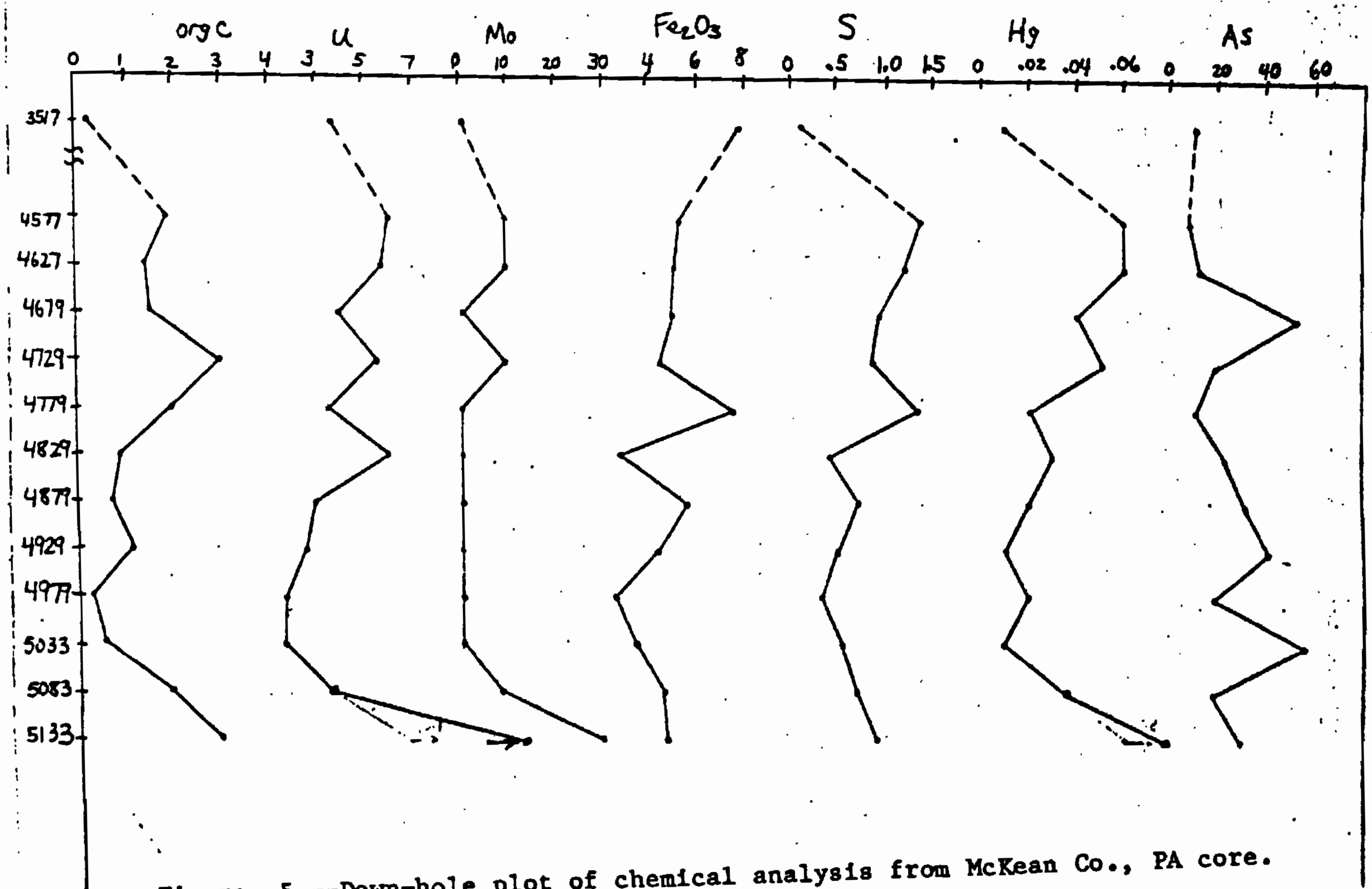


Figure 5.--Down-hole plot of chemical analysis from McKean Co., PA core.

PA 1

Figure 6 Allegheny Co, PA

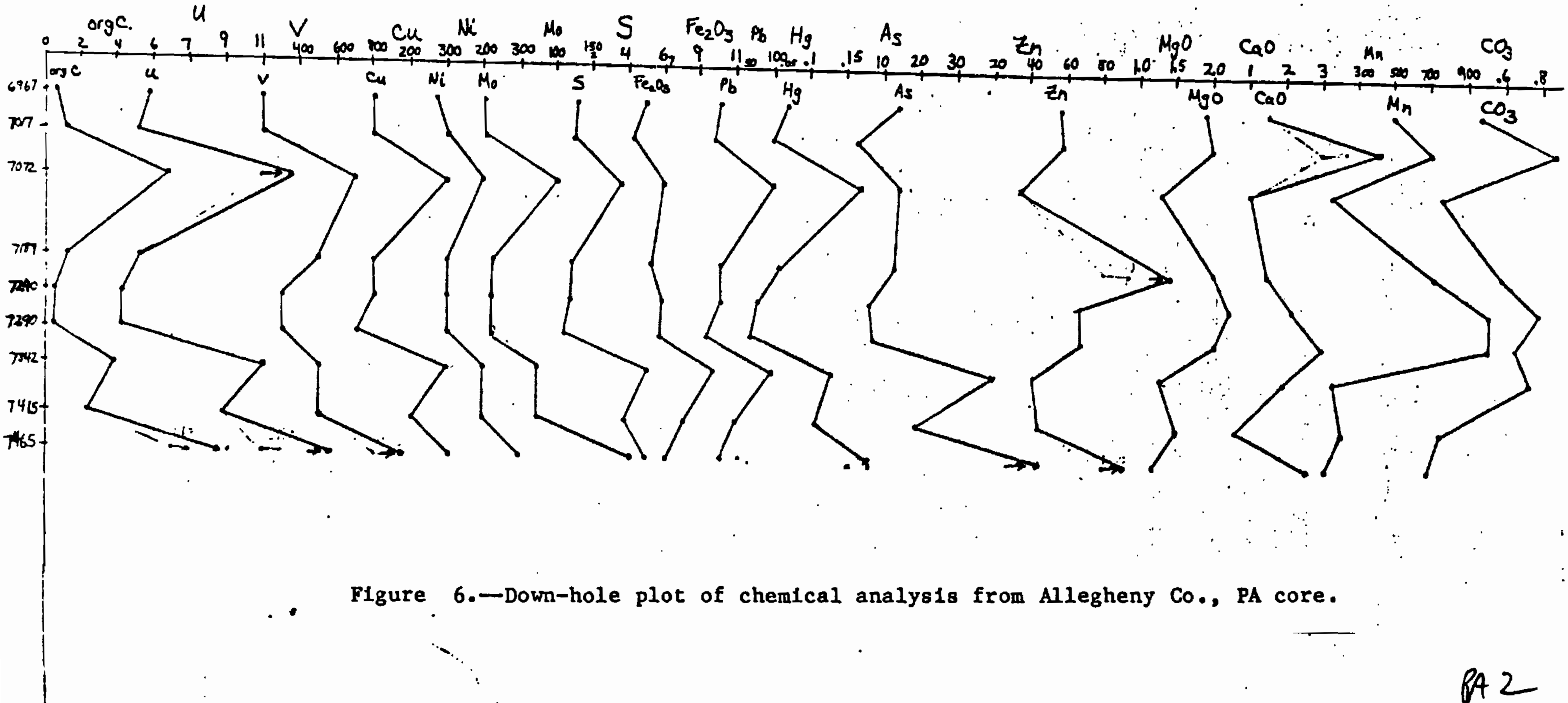


Figure 6.—Down-hole plot of chemical analysis from Allegheny Co., PA core.

PA 2

samples could be classified as Marcellus, but, their uranium contents are lower than most Marcellus samples.

Erie County, (PA-3) shows covariance between organic carbon, U, and Cu at 595, 995, and 1241. Samples 545, 995, and 1241 show covariance between organic carbon, U, Cu, S, V, Ni and Mo. The sample at 995, with the highest U (19.1 ppm) doesn't show the highest organic carbon or sulfur, but does contain 0.5 percent P_2O_5 (other samples have <0.1 percent). Based on organic C the 1241 sample is probably Marcellus, but its uranium content is much lower than most Marcellus samples.

Indiana County, (PA-4) shows relatively low organic carbon and sulfur contents. The deep burial has given the layers of organic matter a carbonized appearance in samples 7475, 7525, and 7874 which contain higher carbon contents. Sample 7975 was separated into two portions, one of which contained a pyrite-rich zone which appears to be a portion of an approximately ~4-cm nodule. The pyrite-rich sample has a higher As content, but Hg, Pb, and Zn which are sometimes associated with sulfide are lower than the adjacent shale. The shale portion has higher organic content and higher U, Mo, and V as well as those elements mentioned above.

Knox County, OH-3) samples at 777, 1027 and 1127 show covariance in high values of organic carbon, U and Mo. Hg and S show increases in the latter two samples. The high S at 677 does not clearly affect any trace elements. The 577 sample shows high As and Zn but they are not associated with organic C or S; the CO_3C in this sample is higher as is Mn, but not CaO, which suggests a mixed carbonate (Ca, Mn, Mg, Fe?). High Zn at 927 occurs with high organic C and S. The stratigraphy is not agreed upon. The Ohio stratigraphic nomenclature choice (by Roy Kepferle, USGS) would fit very nicely with the

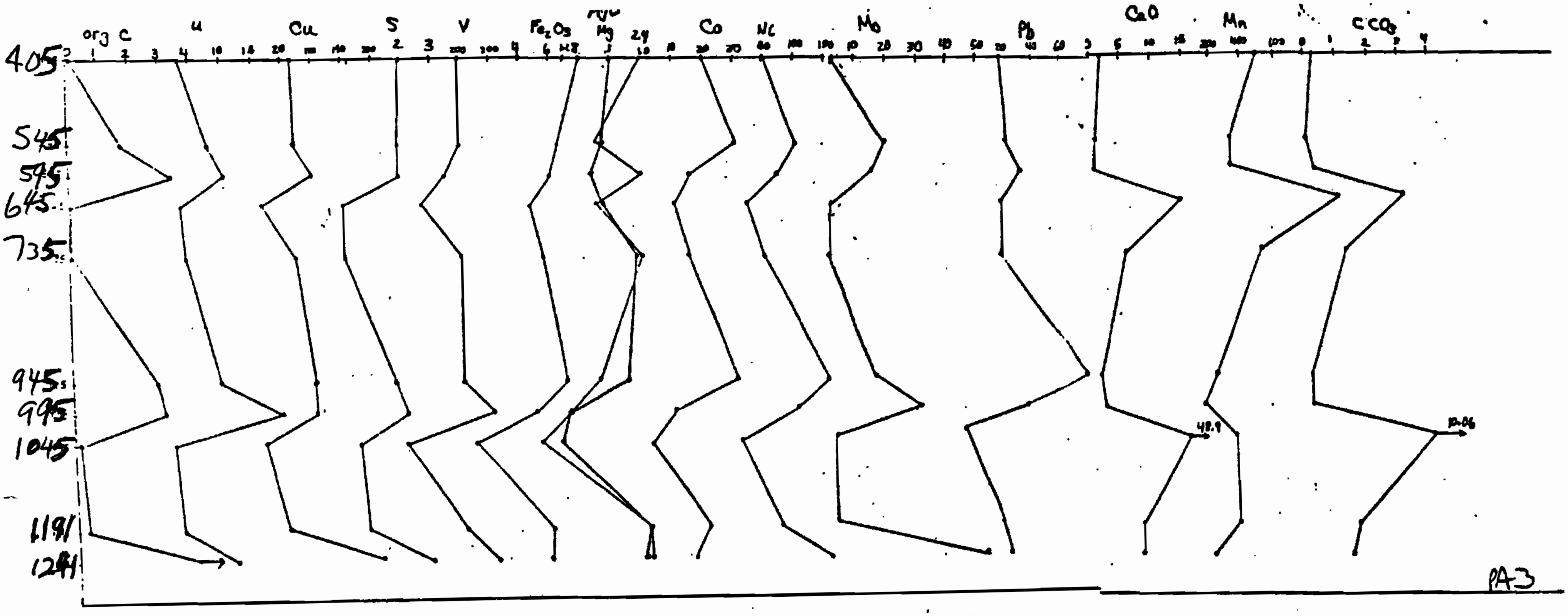
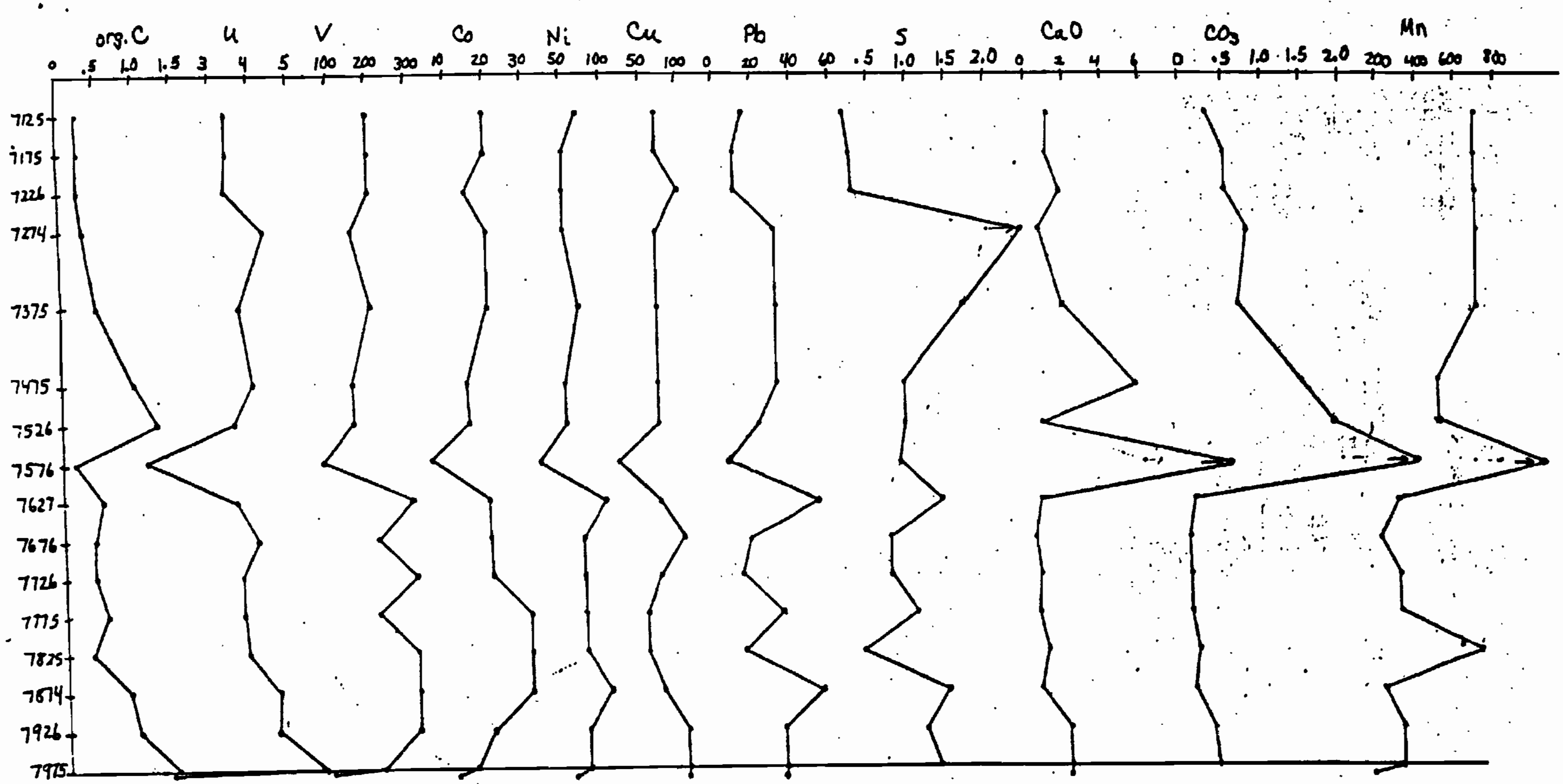


Figure 7.--Down-hole plot of chemical analysis from Erie Co., PA core.

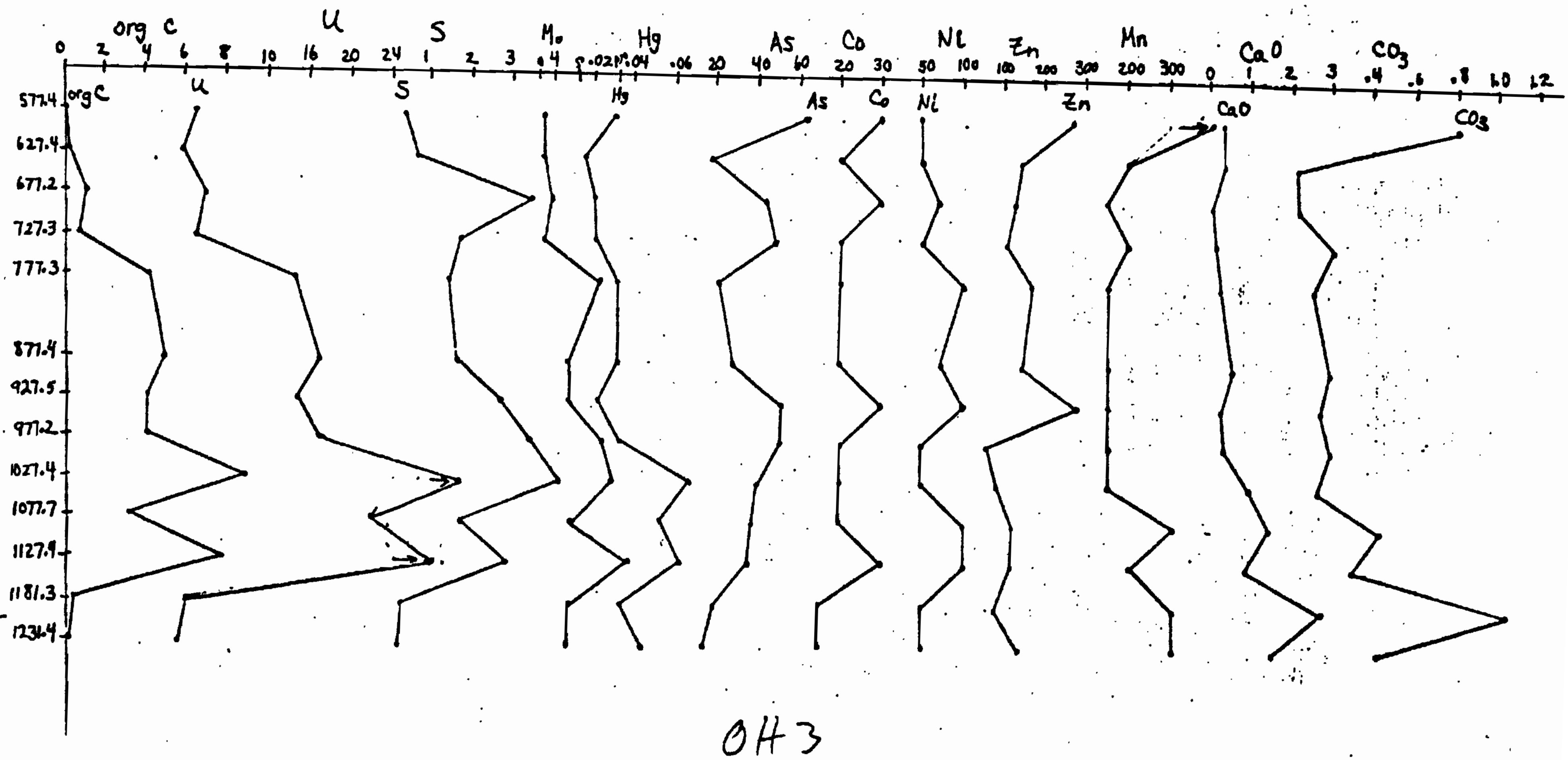
Fig 8. Indiana Co, Pa



PA 4

Figure 8.--Down-hole plot of chemical analysis from Indiana Co., PA core.

Figure 9.—Down-hole plot of chemical analysis from Knox Co., OH core.



chemistry; top of the Huron member of the Ohio shale at between 777 and 877 and the bottom of the Huron between 1127 and 1181 which is only slightly different from the New York nomenclature (see fig. 2 and core descripton, p. 4). Table 19 shows the major elements (recalculated, without organic matter, carbonate and sulfur) which shows changes at these intervals. Likewise the uranium and carbon levels remain high down to 1127. The uranium and organic carbon contents do not define the top of the Huron.

Ashtabula County, (OH-4) samples at 861 and 1175 show higher amounts of organic carbon and sulfur accompanied by U and As. The 1175 sample (but not 861) shows high amounts of Mo, V, Zn, and Hg. This higher level of trace elements seems to be typical of the Marcellus Shale. The carbonate rich sample (Onondaga limestone) at 1325 shows higher Mn than the rest of the samples but it is only 500 ppm. The sample at 1175 also contains 0.4 percent P_2O_5, which may account for the much higher uranium contents (but it is only 23 ppm).

Lorain County, (OH-5) core shows a good covariance between organic carbon and U and Mo. In sample 466 and 565 the high S, As, Fe, Pb, Hq, V, Cu, and Co contrasts with the low values for sample 516. All of these samples are quite low in organic C, and the S control is evident. The sample at 1015 shows high organic C and S accompanied by U, Mo, Cu, Ni, Pb, As, and Hg. Compared to 466 and 565 (both with higher S), it appears the U and Mo are related to the organic C, whereas the other trace metals are more closely associated with S. As with other samples the bulk chemistry (SiO_2 and Al_2O_3) can be related to the stratigraphy. Table 20 shows this.

Table 19.--Recalculated values for Knox County, Ohio (OH-3)

depth ft	% SiO_2 recalculated	% Al_2O_3 recalculated	U ppm	% C org.	Formation	
577	56.1	19.7	4.8	0.17	Cleveland/Bedford	
627	62.3	18.9	3.5	0.22	Chagrin	↑
677	57.7	22.0	5.7	1.02	↓?	
727	60.2	21.2	4.7	0.65		
777	61.9	18.2	14.2	4.12		
877	67.7	15.2	16.5	4.90		Huron
927	61.9	18.0	14.4	4.11	Huron	
977	65.6	15.2	16.4	4.18		
1027	69.4	10.8	40.3	8.84	Lower Huron	
1078	68.2	13.7	21.7	3.12	Hanover	
1127	63.3	15.9	32.5	7.65		↓
1181	58.9	19.8	3.7	0.40	Olentangy	
1231	62.2	18.4	2.8	0.18	(Angola)	

OH4

Fig 10 Ashtabula Co, OH

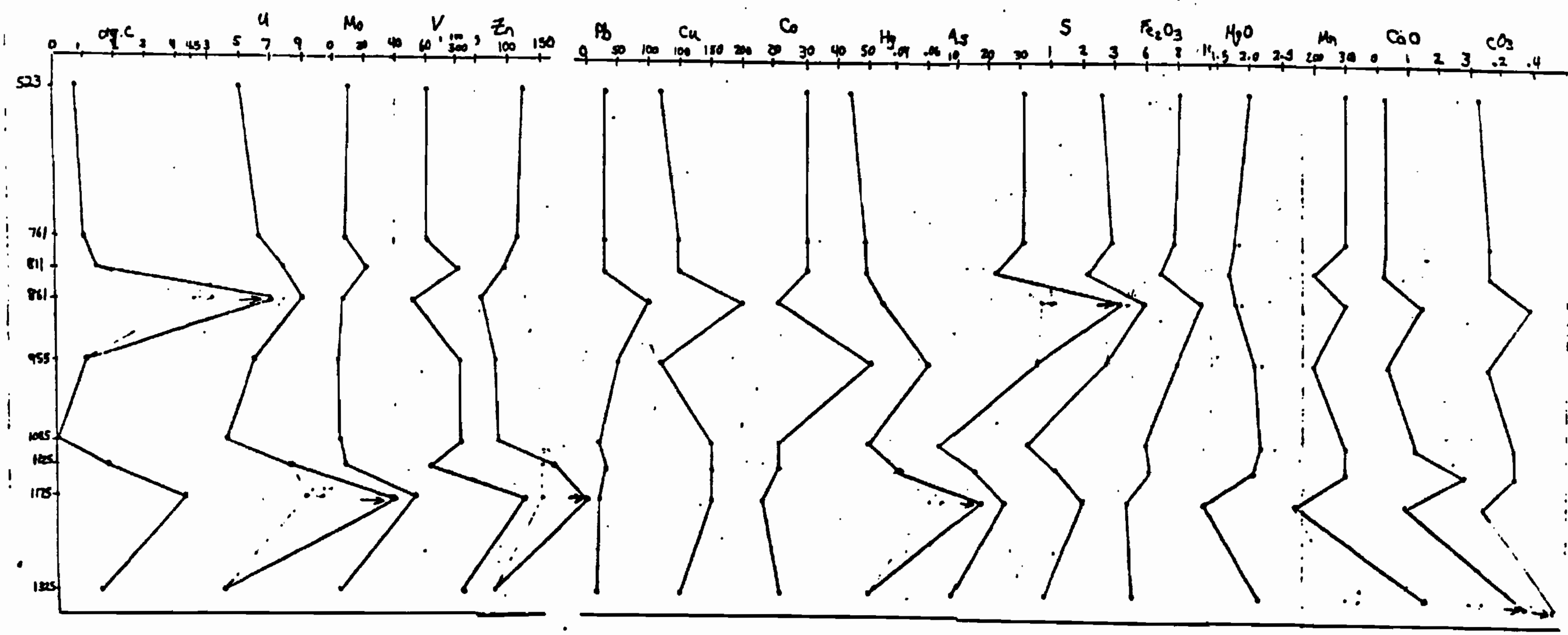
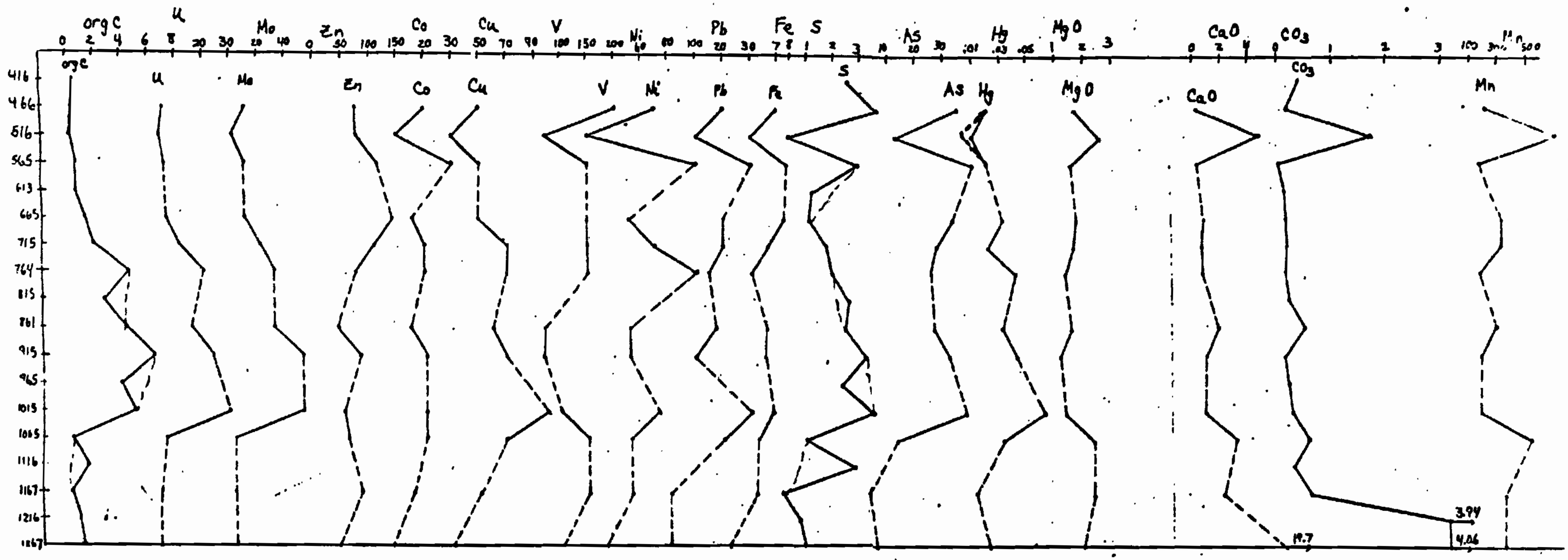


Figure 10.—Down-hole plot of chemical analysis from Ashtabula Co., OH core.

Fig 11 Lorain Co OH



OHIO 5

Figure 11.--Down-hole plot of chemical analysis from Lorain Co., OH core.

Table 20.--Recalculated values for Lorain County, OH

depth ft	% SiO_2 recalculated	% Al_2O_3	U ppm	% C org.	Formation
466	61.6	19.0	5.0	0.26	
516	66.5	12.0	3.2	.11	
565	58.6	19.8	5.8	.57	Chagrin
665	60.7	17.6	6.2	1.33	
715	62.9	16.8	11.0	1.94	
764	66.5	14.9	19.4	4.45	
861	66.6	14.0	14.7	4.23	Lower Huron
915	70.0	11.8	22.9	6.20	
1015	65.6	15.0	28.2	4.85	
1065	59.7	17.7	5.1	0.22	Java
1167	60.4	19.0	2.9	0.11	
1267	42.3	14.3	1.0	1.06	Rhinestreet

Grainger County, (TN-7) samples show varying amounts of C and S. Samples at 200 and 406 show high levels of S, the former also with moderate organic C. The 250 sample has higher organic C, and lower S. The As shows a peak at 200, whereas U, Mo, Hg, Zn, and Cu peak at 250, showing the major As control by S, and control of the others by organic carbon. The sample at 406 is interesting, relative to those above and below: it shows increases in organic C by a factor of about 4 (but to only 0.94 percent), whereas the S increases by a factor of about 20 (to high 4.45 percent). The trace elements increase by the factors of 2 for Mo and Ni, 3 for Hg, As, and U, and 5 for Pb. Thus the trace element increase is proportional to the organic increase, but it is not clear whether the organic C or S is in control or how they work together.

Grainger County, (TN-6) has only 6 samples, but the results are quite interesting. The high organic sample at 348 (Lower Huron) also shows high U, Mo, Pb, and V. However, the sample at 469 (Rhinestreet ?)with high organic doesn't show the expected high Mo or U; it does show high S, Pb, Cu, As, Zn, and Ni. The high S sample at 281 shows high As and Hg. Part of the unusual non-organic(?) effect in these samples could be related to the P_2O_5 content which is at or above 0.1 percent P_2O_5 in 348, 469 and 281. The presence of phosphate in these samples may be the initial control in removing the uranium, so that organic matter can not exert its usual control. Another possible explanation is the type of organic matter, since it has been shown that marine organic matter is associated with lower U contents (Leventhal, 1981, in press).

Data for the other cores are given in tables 12-17 and are not presented as down-hole plots, but they show the same relations that have been discussed above.

Tenn 7

Fig 12 Grainger Co TN Core 7

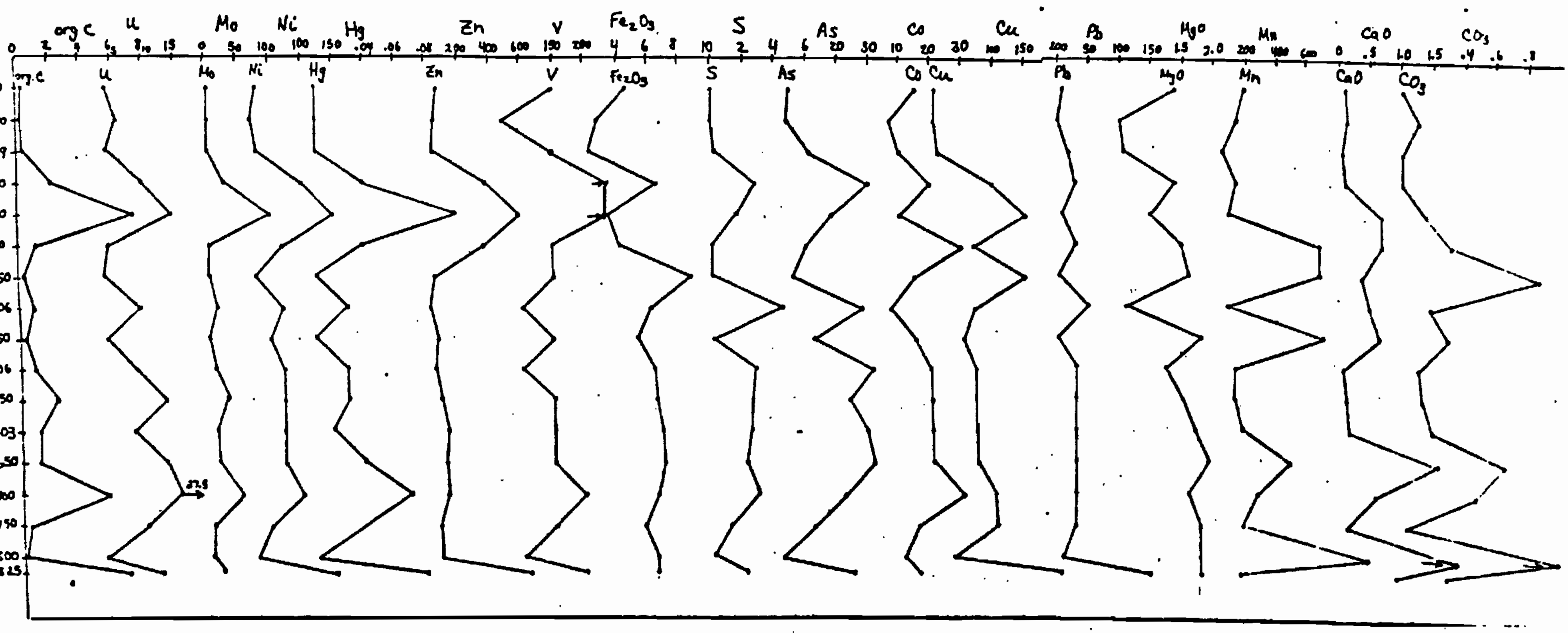


Figure 12.--Down-hole plot of chemical analysis from Grainger Co., TN core 7.

Fig 13— Grainger Co TN, Core 6

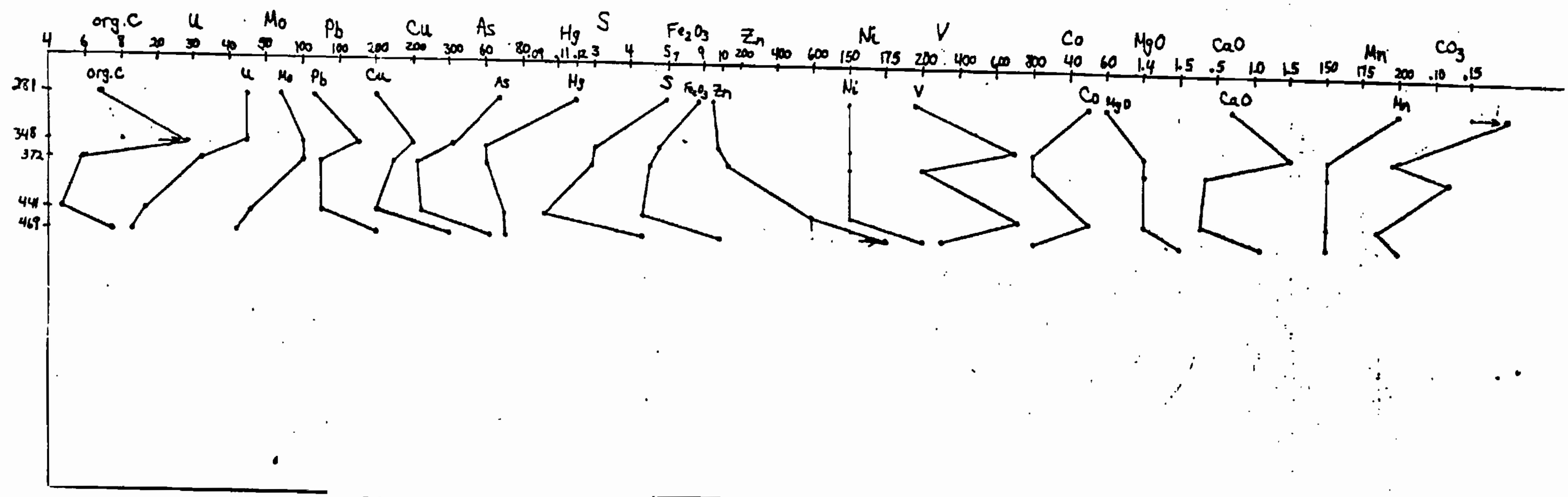


Figure 13.--Down-hole plot of chemical analysis from Grainger Co., TN core 6.

Hancock County, (TN-3) was analyzed as two sets. Table 12a gives the quantitative data for trace elements Co, Cu, Mo, Ni, V, Zn, and Hg. Table 12b gives these elements only by semiquantitative spectroscopy, and for different depths. The relationship of increased organic matter and uranium is evident in these samples, often with increased amounts of V, Mo, and Ni. Both V and U show the highest values of any of the cores that have been analyzed. The sample at 143 ft has 1.3 ppm Hg, the highest for any analyzed black shales in this program, and Zn and Ag also show high values (see table 12b) of 3000 and 1.5 ppm. The sample at 192 ft has 100 ppm Cd.

The Cuyahoga County, Ohio core (Table 13) shows samples with ~6 percent organic carbon, 100-150 ppm Ni and Mo and up to 30 ppm U, one sample shows 300 ppm V. The Tompkins County, NY, core (Table 14) shows several high U, organic carbon, Mo, Cu, Ni, Ag, and V values near the bottom in the Marcellus shale. The Livingston County, NY (Table 15) core also shows high values in the Marcellus shale. The Allegany County, (NY-1) (Table 16) core shows generally low values in U until the Marcellus shale at 3480 plus is encountered. The Illinois core samples (Table 17) contain high amounts of U, As, or V in certain samples, usually associated with high values of organic C or sulfur.

Element graphs

For compactness of presentation the organic carbon (or sulfur) vs trace elements are plotted for all the cores on one figure for each trace element. The large array of points makes it difficult to see clear trends in many cases. An exception is uranium vs organic carbon, where there is a clear visual correlation (fig. 14). In this case the correlation coefficient

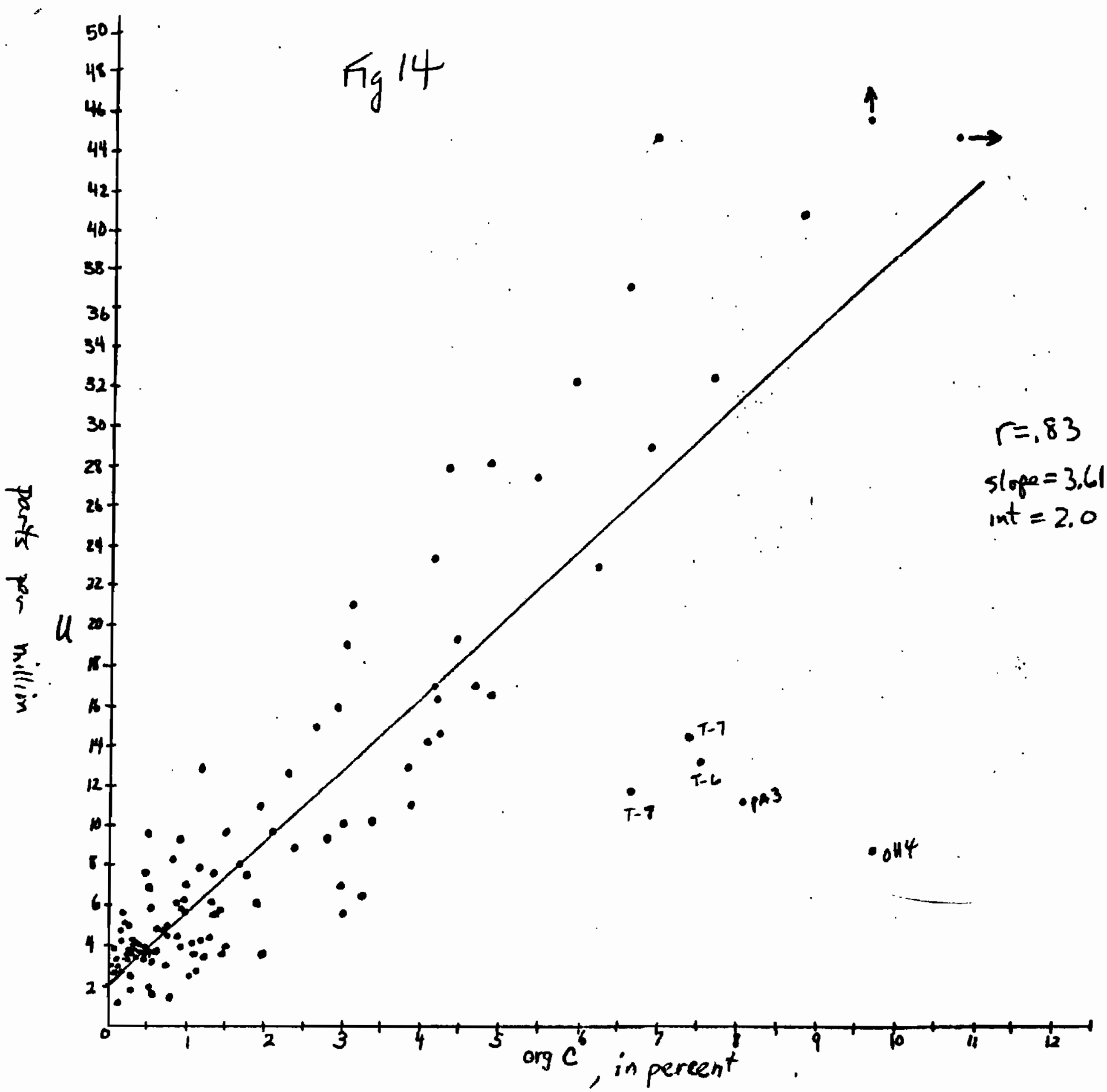


Figure 14.--Plot of organic C vs U.

(linear-least-squares), r, is 0.83 for 117 samples, which is statistically significant at greater than the 99.9-percent level. In addition, statistical treatment of samples from individual cores with 10 or more samples (PA-1, PA-4, TN-7, OH-3, KY-4) show r values (.70, .63, .71, .96, .89, respectively) which are significant at the 99 percent level (except PA-3, r = .64, which is at the 95-percent level).

Organic carbon vs Mo also shows a strong correlation as seen on figure 15. The statistical data on separate cores show r values of 0.83 to 0.95 for OH-3, PA-3, OH-4 (one high-carbon sample omitted), KY-4 and PA-2. For these cores, with 9 or more samples each, the correlation coefficients show a significance at the 99-percent level.

In the case of organic carbon vs Mo and U, the best-fit line goes through the origin of the graph - indicating a purely organic control, that is to say without organic matter there would be only very low levels (<2 ppm) of uranium and molybdenum present.

The organic carbon correlation with Cu and Ni is not as clear on the figures (16 and 17) nor is it as statistically significant. The correlation coefficient for all the samples is statistically significant (organic C vs Ni, r = 0.57 for 62 samples significant at the 99-percent level) but for individual cores may not be highly significant. Thus the organic carbon is only explaining approximately 30 percent (r^2) of the variance in Ni or Cu. However, it is clear that few samples with high organic C values (greater than 5 percent) have low Ni or Cu values.

It should be noted that, in contrast to Mo and U (figs. 14 and 15), a best-fit line for organic C vs Ni (or Cu) (figs. 16 and 17) would not go through zero, but would intercept the Y axis at ~ 55-65 ppm. This can be

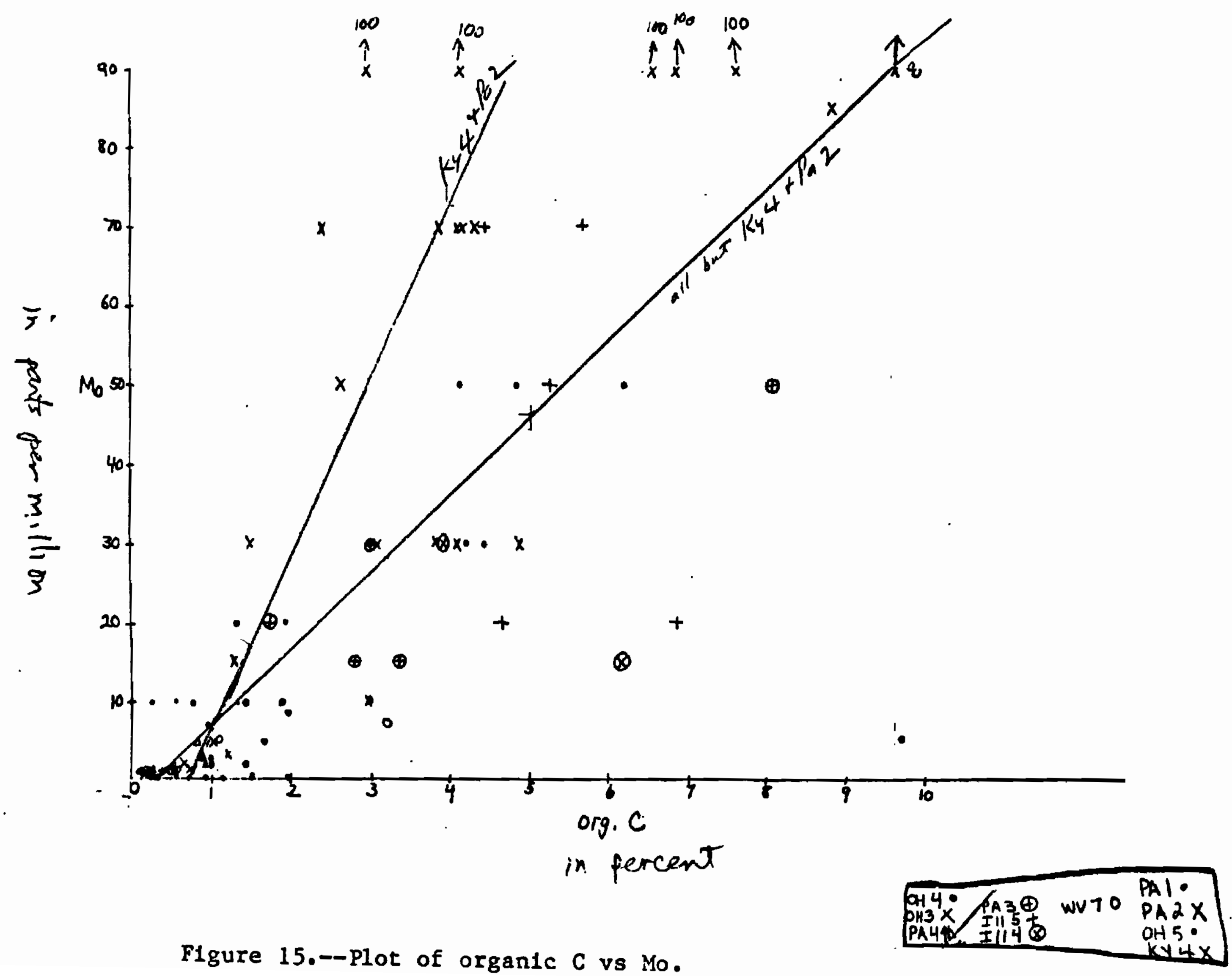


Figure 15.--Plot of organic C vs Mo.

Fig 16

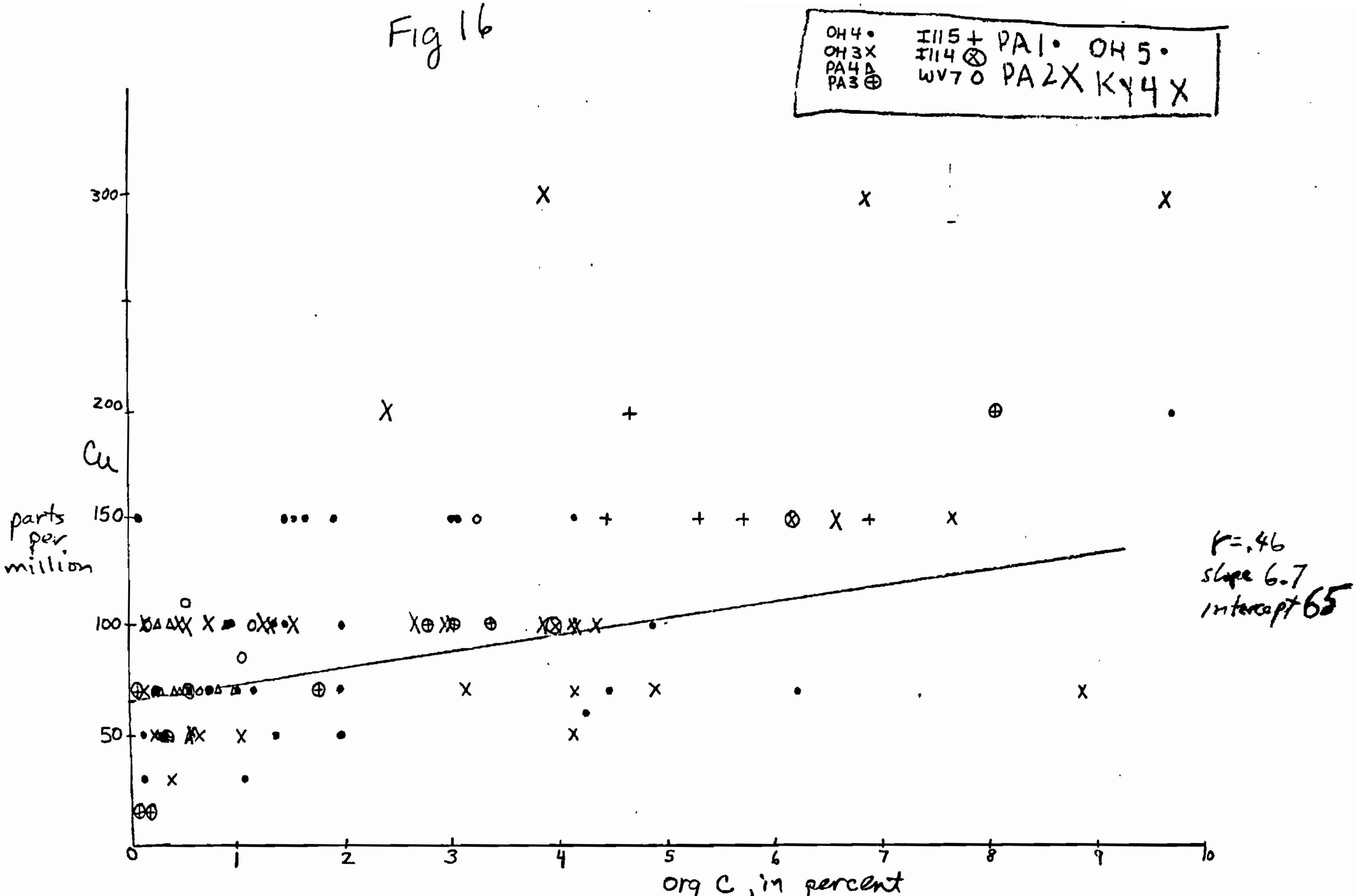


Figure 16.--Plot of organic C vs Cu.

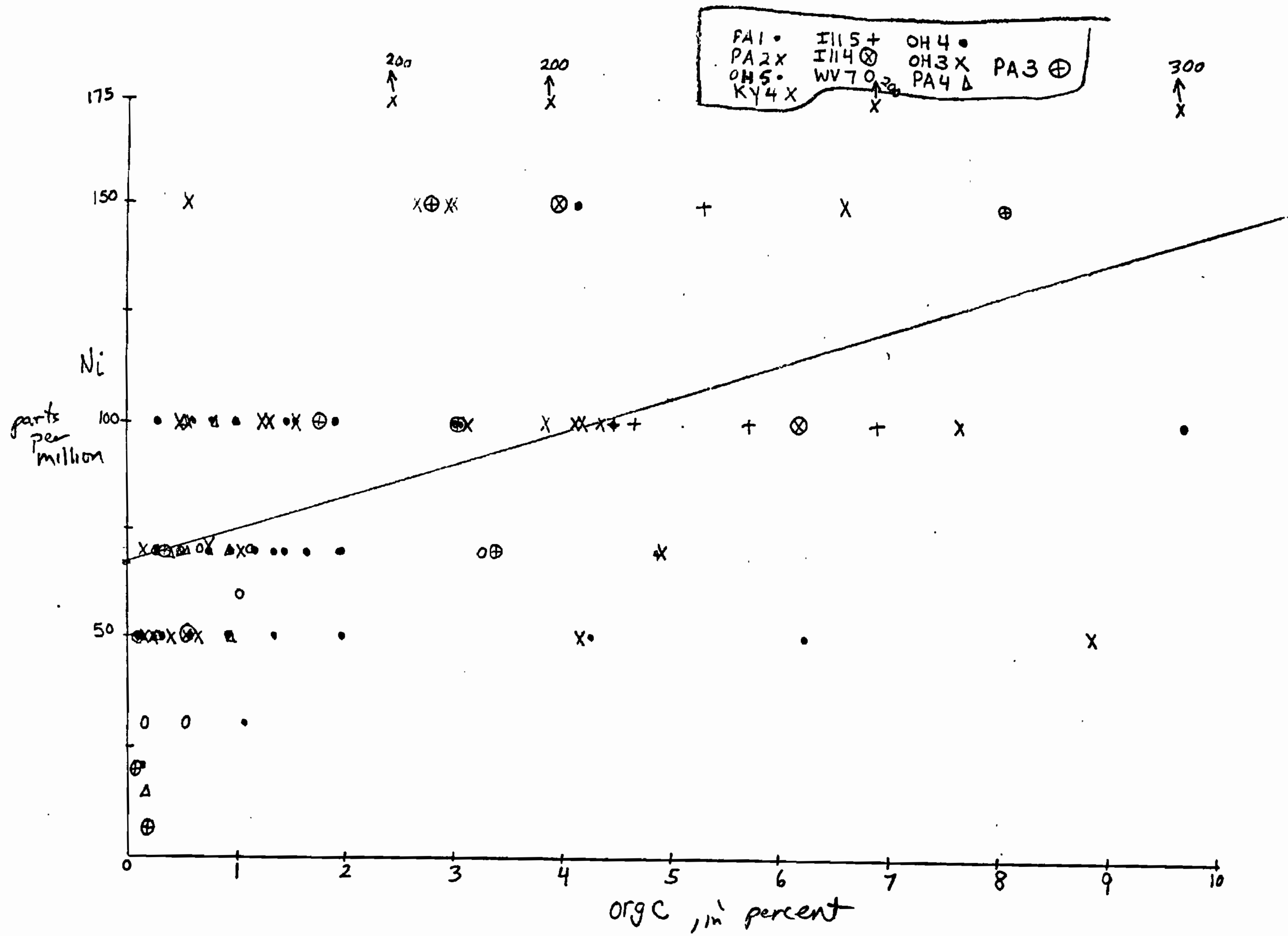


Figure 17.--Plot of organic C vs Ni.

interpreted to indicate that in the absence of organic carbon, 55-65 ppm of the trace element would be incorporated in minerals (such as clays or perhaps iron oxides).

Organic carbon is somewhat related to As and Hg, but the relationship only explains 20-30 percent of the variance. However, figures 18 and 19 show very few low metal values associated with high (>5 percent) organic C values.

Sulfur appears to be important in controlling the abundance of Hg, As, and Pb. The As relation (fig. 20) is quite strong for certain cores ($r = 0.98$ for OH-4, $r = 0.90$ for TN7), but low for others OH-3 ($r = 0.45$) and nonexistent for others KY-4 ($r = -.12$). Overall, the r value for 73 samples is 0.45, which is statistically significant, but only explains ~20% of the variance.

Mercury shows a similar relation to sulfur (fig. 21). Certain cores, PA-1 and PA-2, show high correlations ($r = 0.73$ and 0.88, respectively), but the correlation is low for others (OH-3, $r = 0.33$; KY-4, $r = 0.25$) and nonexistent for others (OH-4, $r = 0.01$). Overall, for 78 examples, the $r = 0.48$ which means or it explains ~25 percent of the variance. It should be noted that many samples with >2 percent sulfur have only low (.02 - .03 ppm) levels of Hg. A possible explanation is that these sulfides formed somewhat later (diagenetically) in an environment lower in Hg. Petrographic-mineralogic work on thin sections and sulfur isotopes can help evaluate this.

Sulfur plays a role in the abundance of Pb and Cu. In certain cores, for example PA3 for Cu and OH4 for Pb, it is highly significant (99-percent level) statistically, but for most it explains only 30 percent of the variance. Figures 22 and 23 show these data.

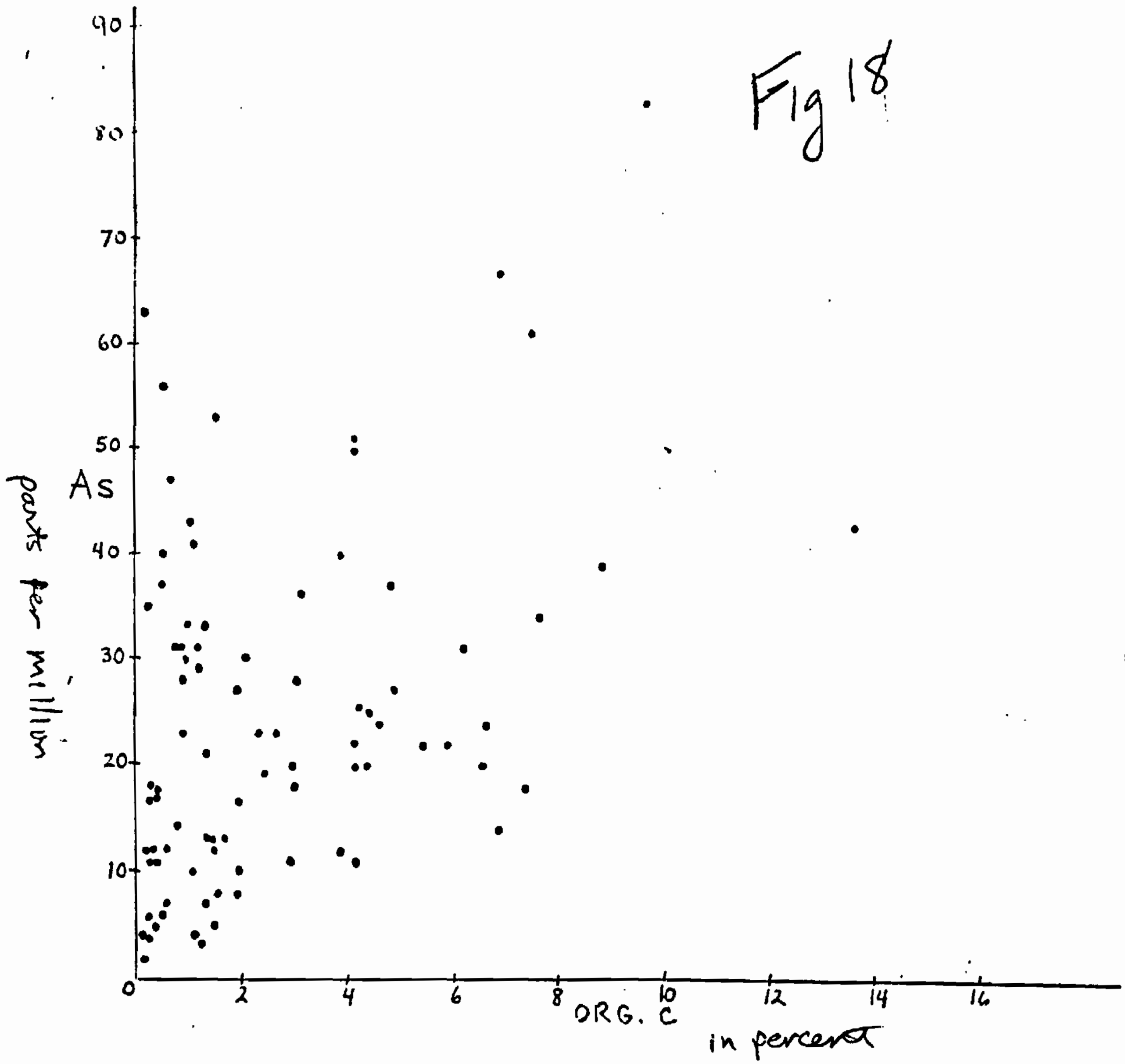


Figure 18.--Plot of organic C vs As.

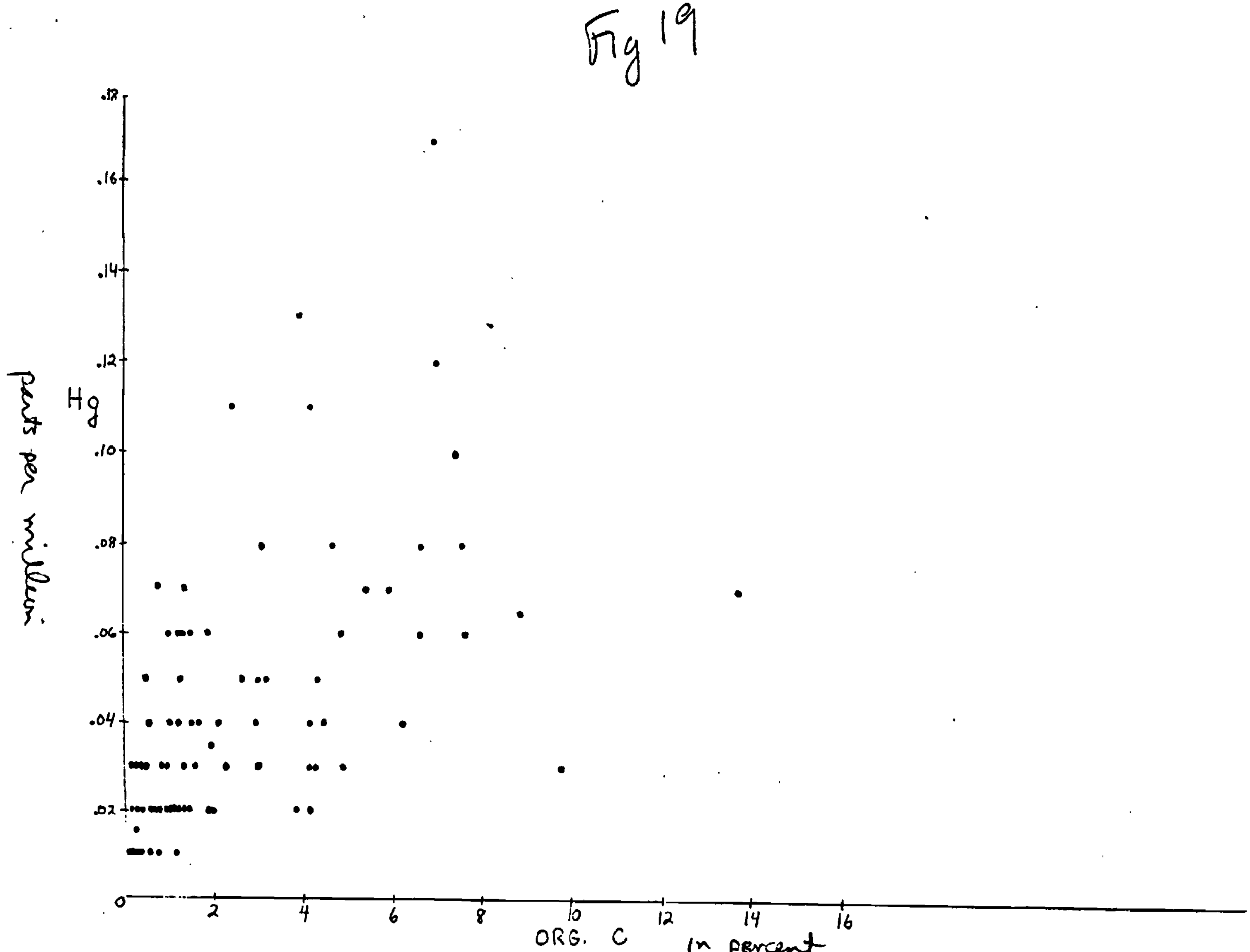


Figure 19.--Plot of organic C vs Hg.

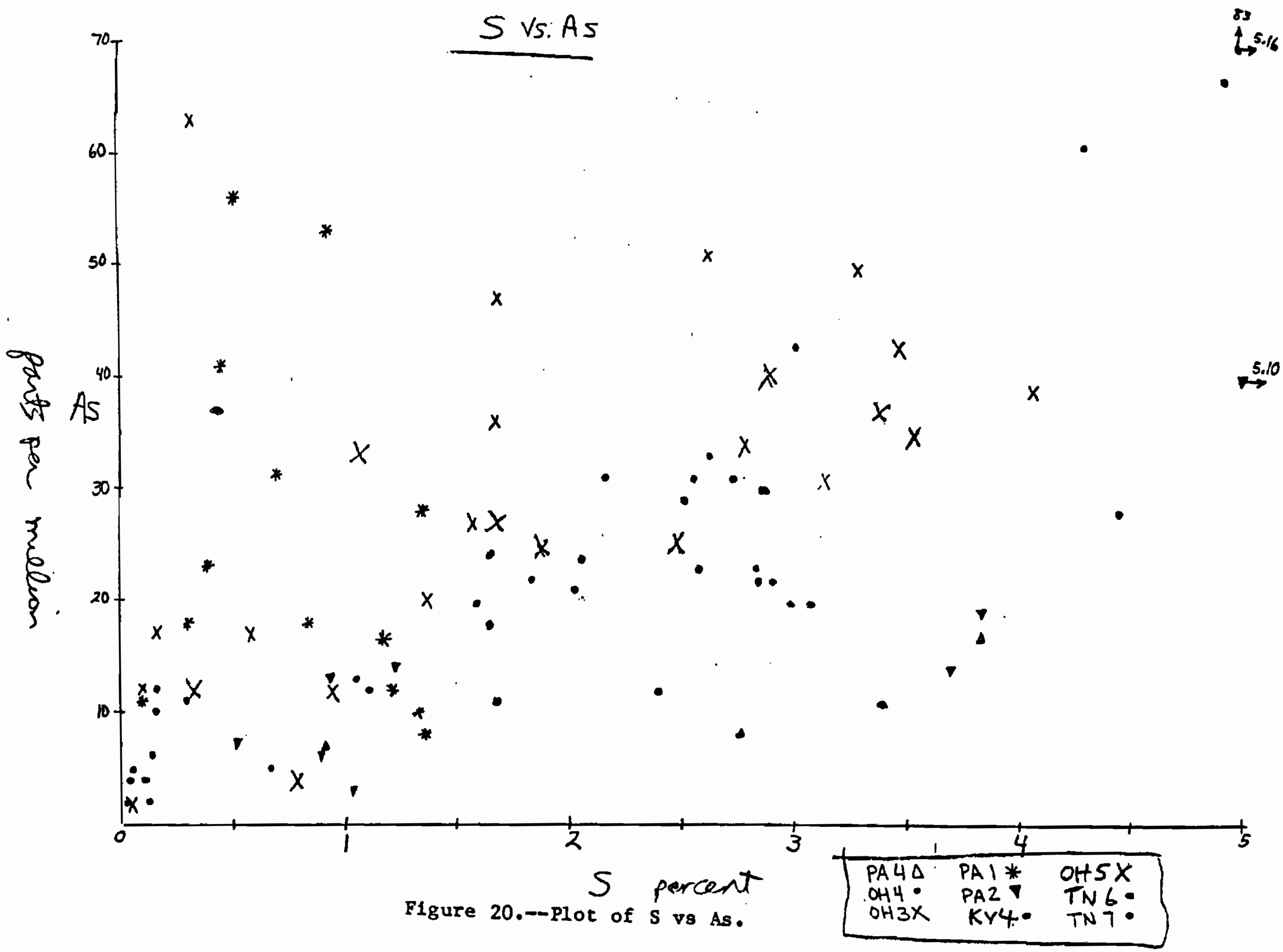


Figure 20.--Plot of S vs As.

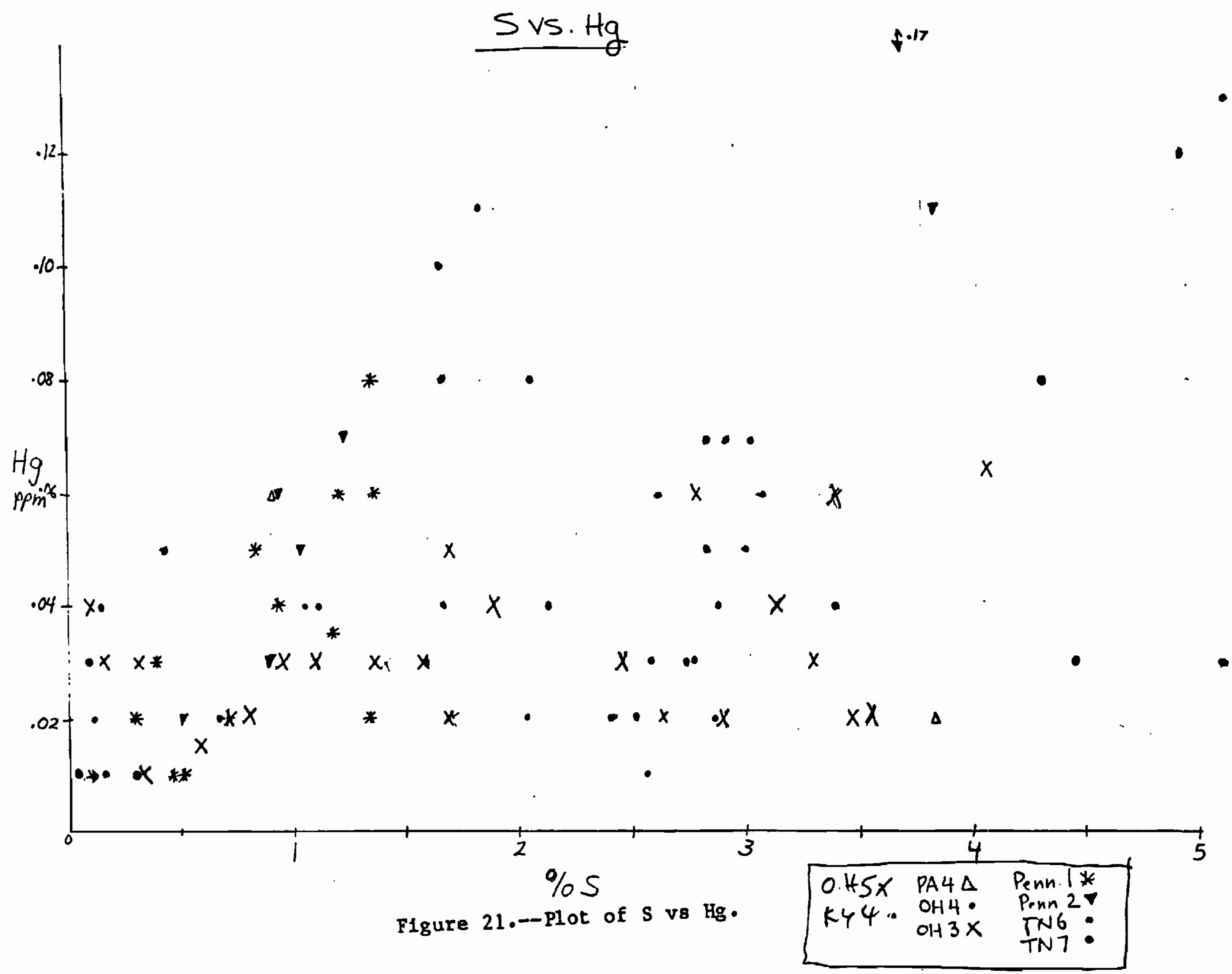


Figure 21.--Plot of S vs Hg.

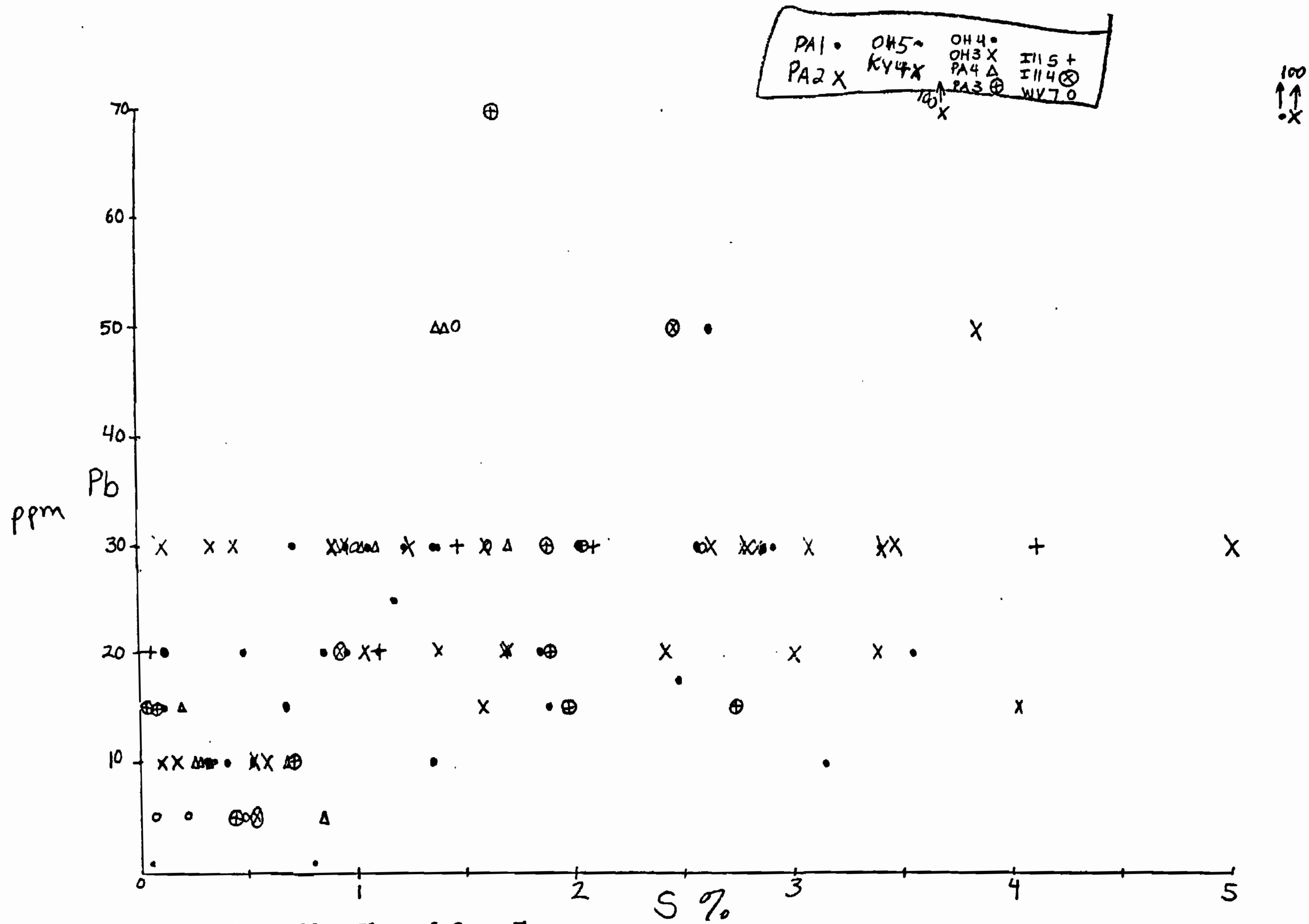


Figure 22.—Plot of S vs Pb.

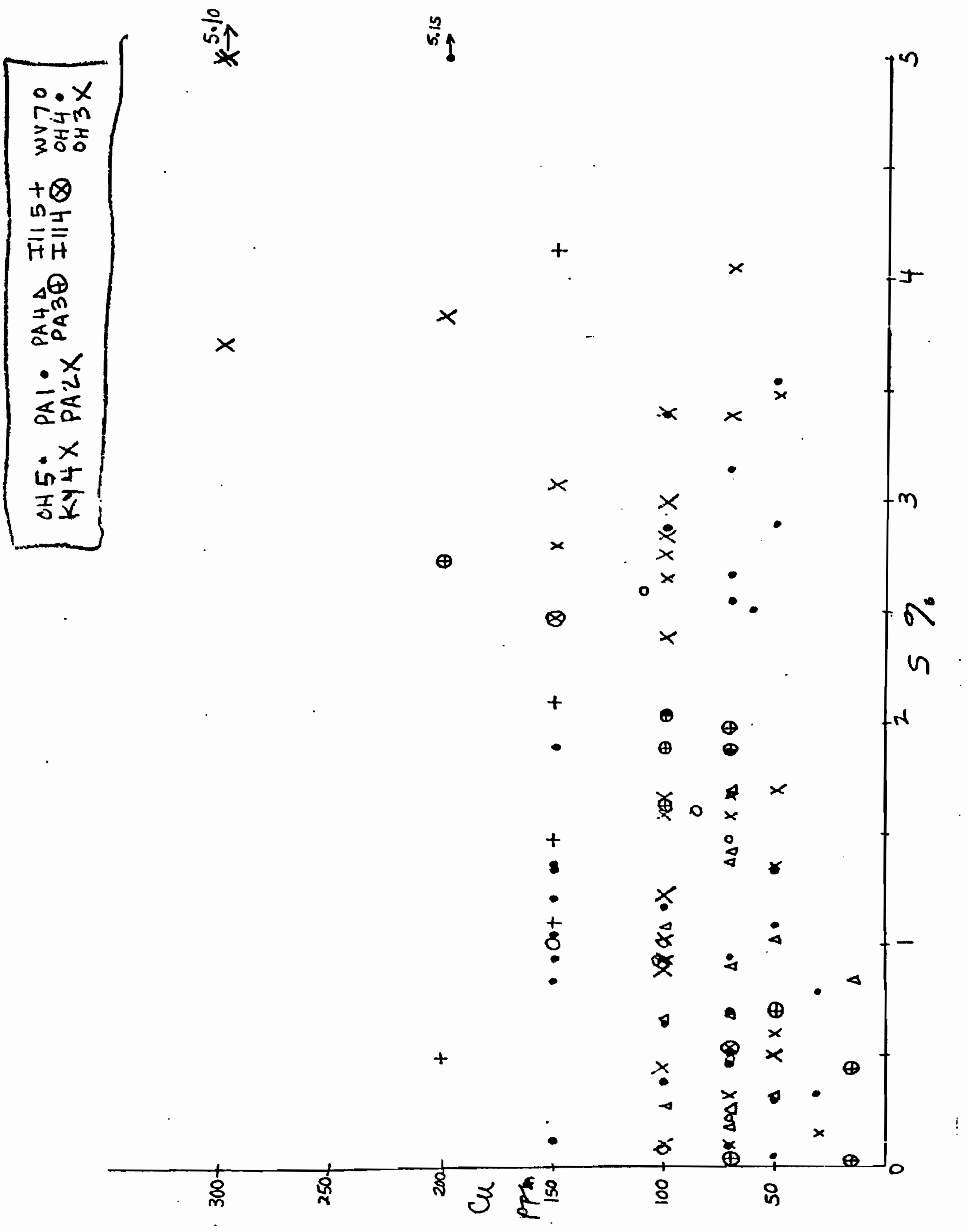


Figure 23.--Plot of S vs Cu.

Organic carbon and sulfur both seem to show an influence on cobalt; figures 24 and 25 show the plots. What is clear is that there are no low Co values associated with high C or S (the lower right part of both figures). Certain cores show high correlations; for example, the 16 samples from Wetzel County, W VA, and Hardin and Counties, Illinois give r value of 0.78 for S vs Co.

The organic C vs V relationship is not clear (fig. 26), because even some high organic values show low V and the converse is also seen. The correlation coefficients for Erie Co., PA is 0.56, significant at the 95 percent level. For 42 samples from the W VA, IL and Erie and Indiana Counties, PA cores, the r value is 0.51, significant at the 99 percent level but explaining only ~ 25 percent of the relationship.

Zinc is influenced in certain samples (approximately 10) by both the organic carbon (fig. 27) and sulfur (fig. 28). Most of the samples do not show a relationship. Two samples (one each from Allegheny County, PA and Ashtabula County, OH) show very high Zn values (3600 and 2100 ppm, respectively), but these samples are not the highest in C or S. Two other samples high in Zn do show high C and S values (Allegany County, (NY-1), 7465 ft; Grainger County, (TN-6), 469 ft) and high Zn (1000 and 1600 ppm, respectively). Of these 4 high values, two are in the Marcellus Shale which may indicate a stratigraphic-time control relating to a high Zn source. It is also the Allegheny County, PA sample at 7465 in the Marcellus Shale that has the highest V content (1500 ppm).

The relation between carbonate carbon and manganese is shown on figure 29. There are few samples (only 2) that are high in carbonate but not in Mn. For the 32 samples from Hardin County, IL; Erie County, PA; Knox and Ashtabula Counties, OH the correlation coefficient, r, is 0.72, which is significant at the 99-percent level. The correlation was computed without two

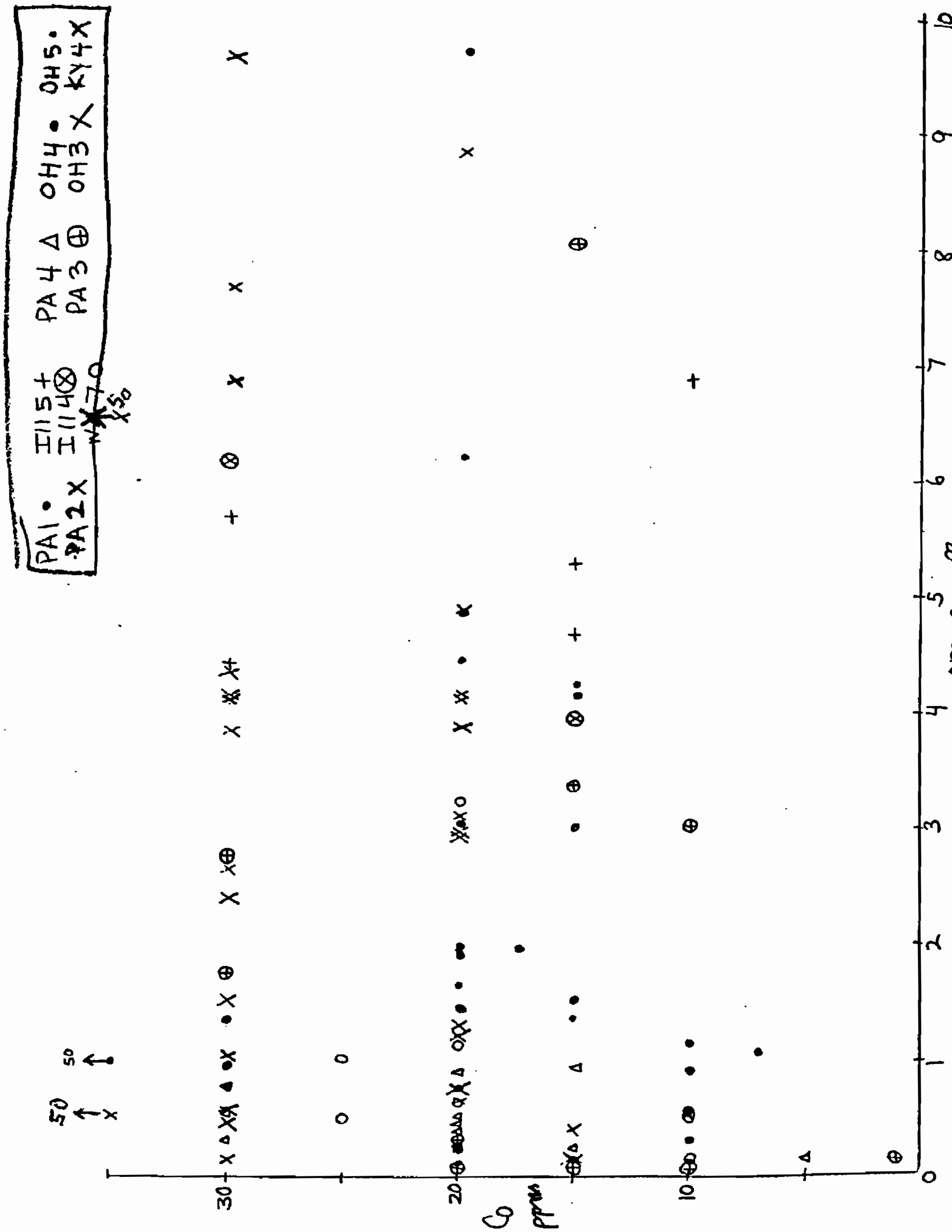


Figure 24.--Plot of organic C vs Co.

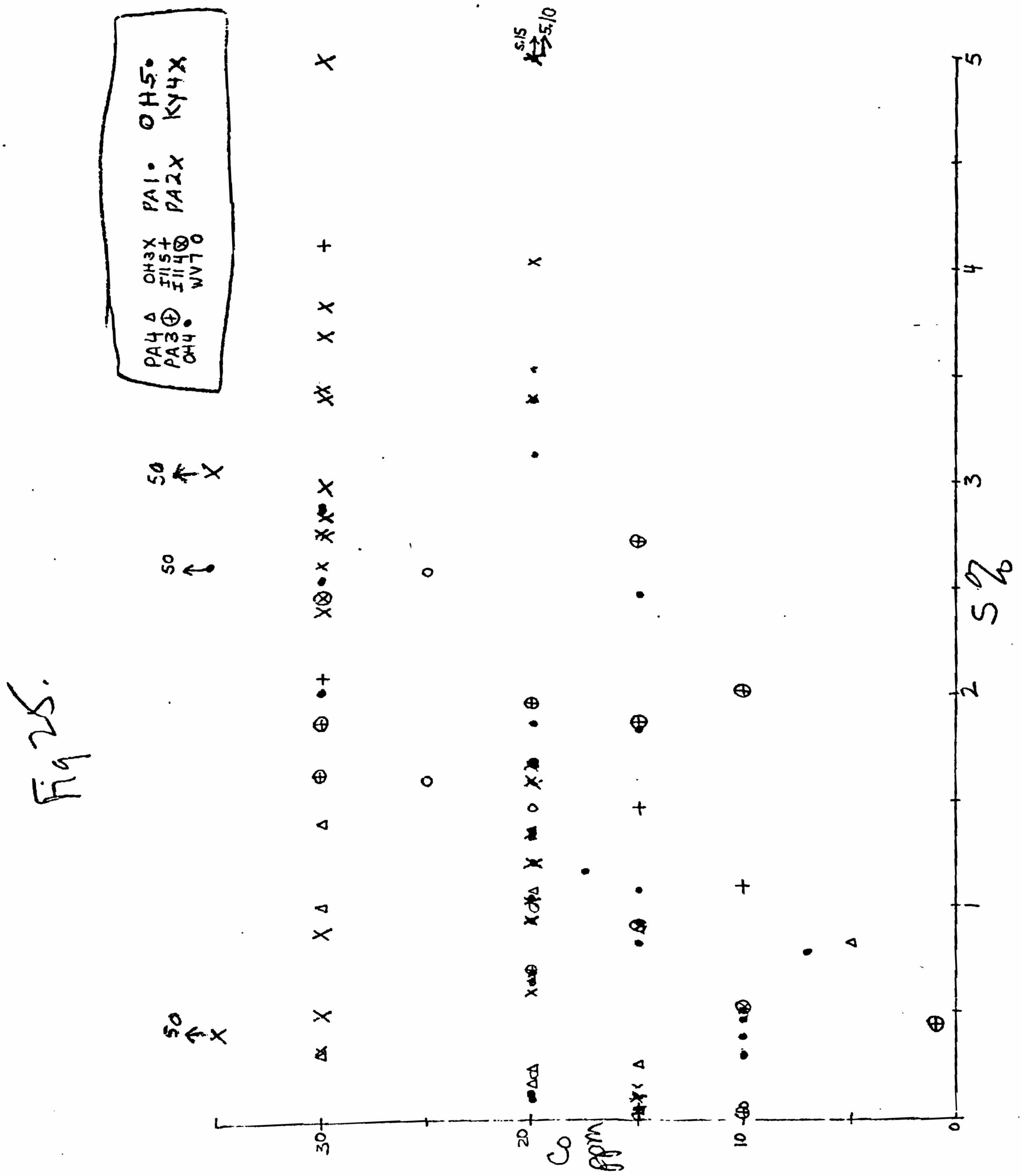


Figure 25.--Plot of sulfur vs Co.

Fig 26

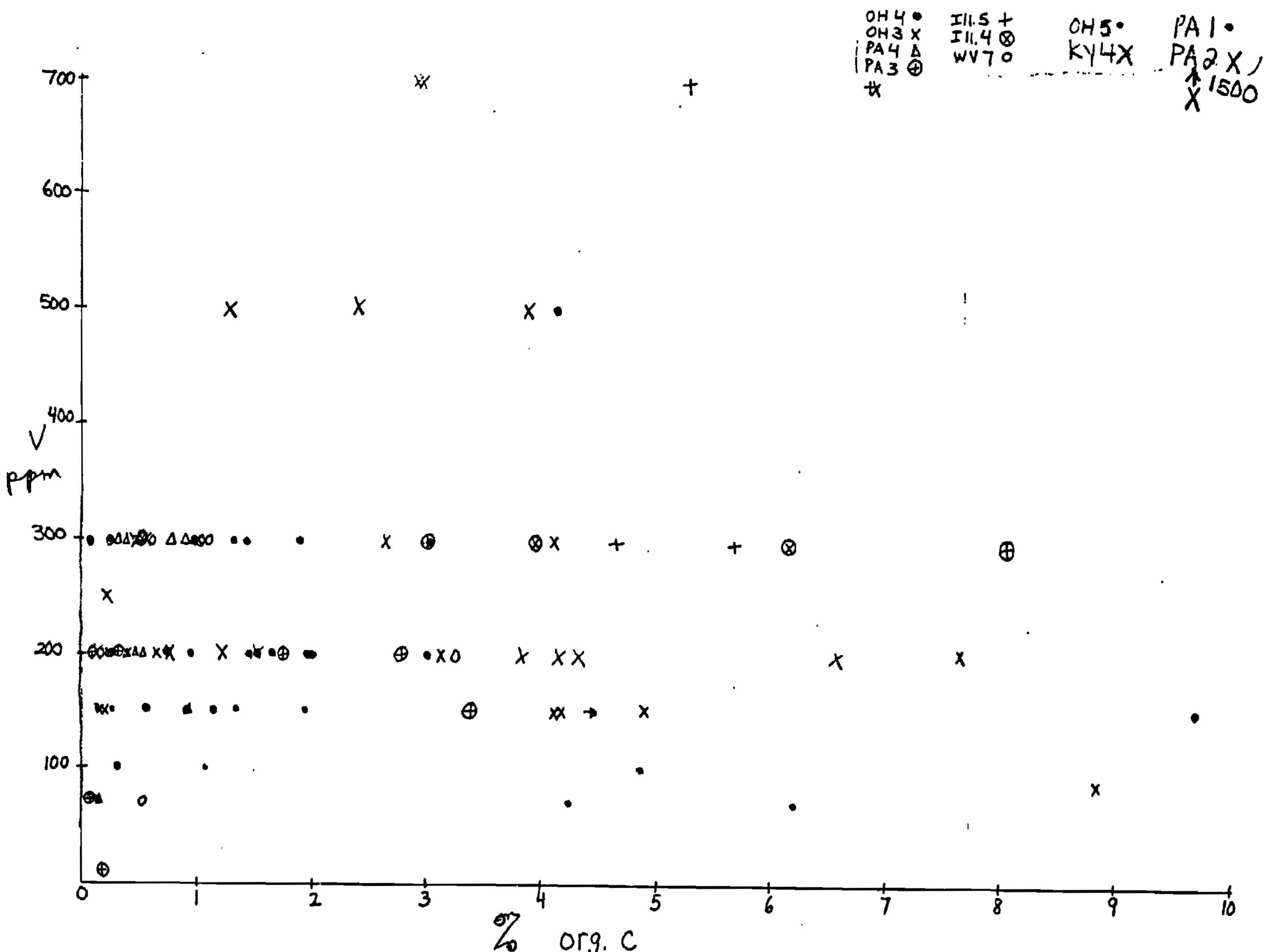


Figure 26.--Plot of organic C vs V.

Fig 27

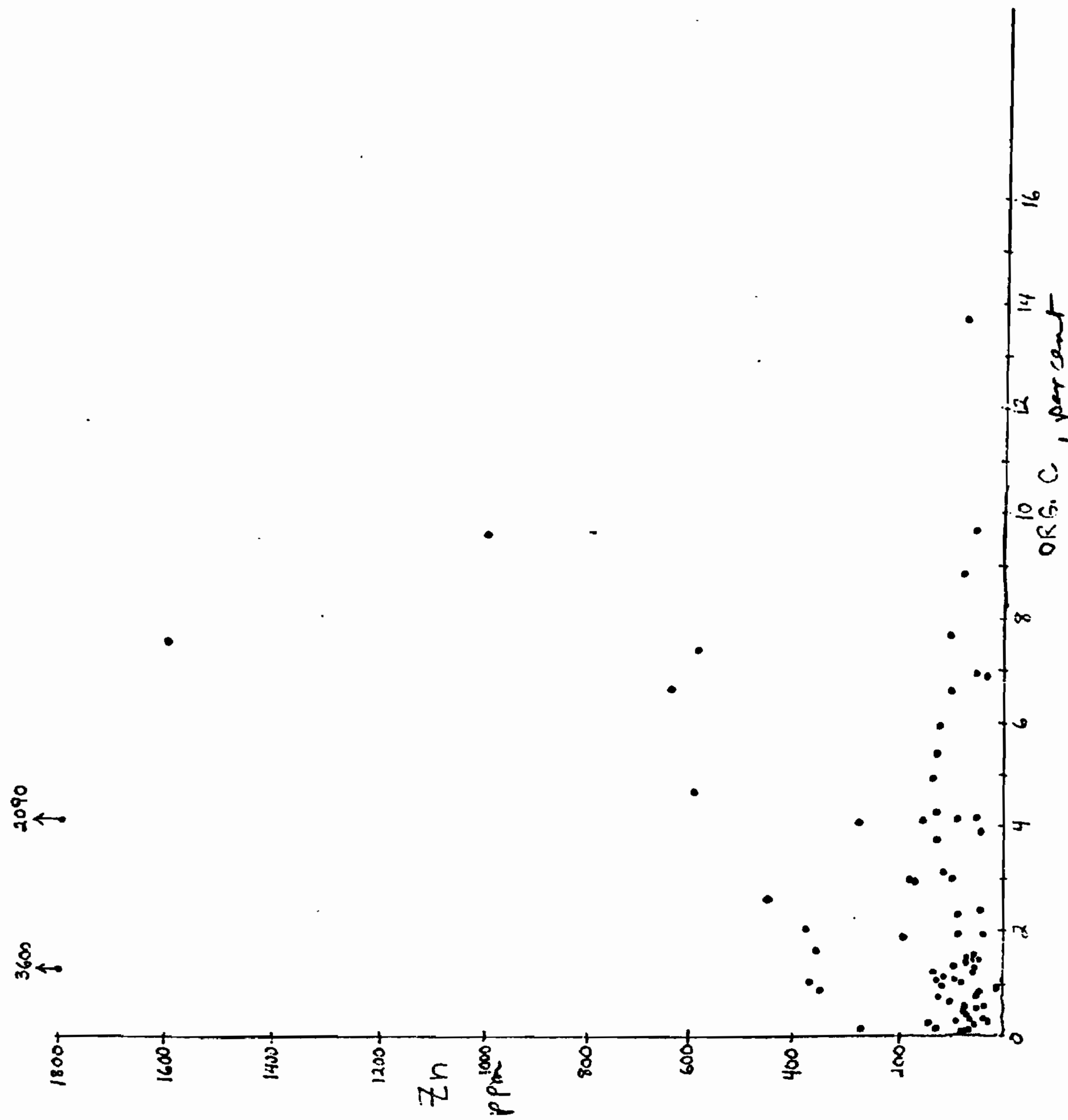


Figure 27.--Plot of organic C vs Zn.

Fig 28

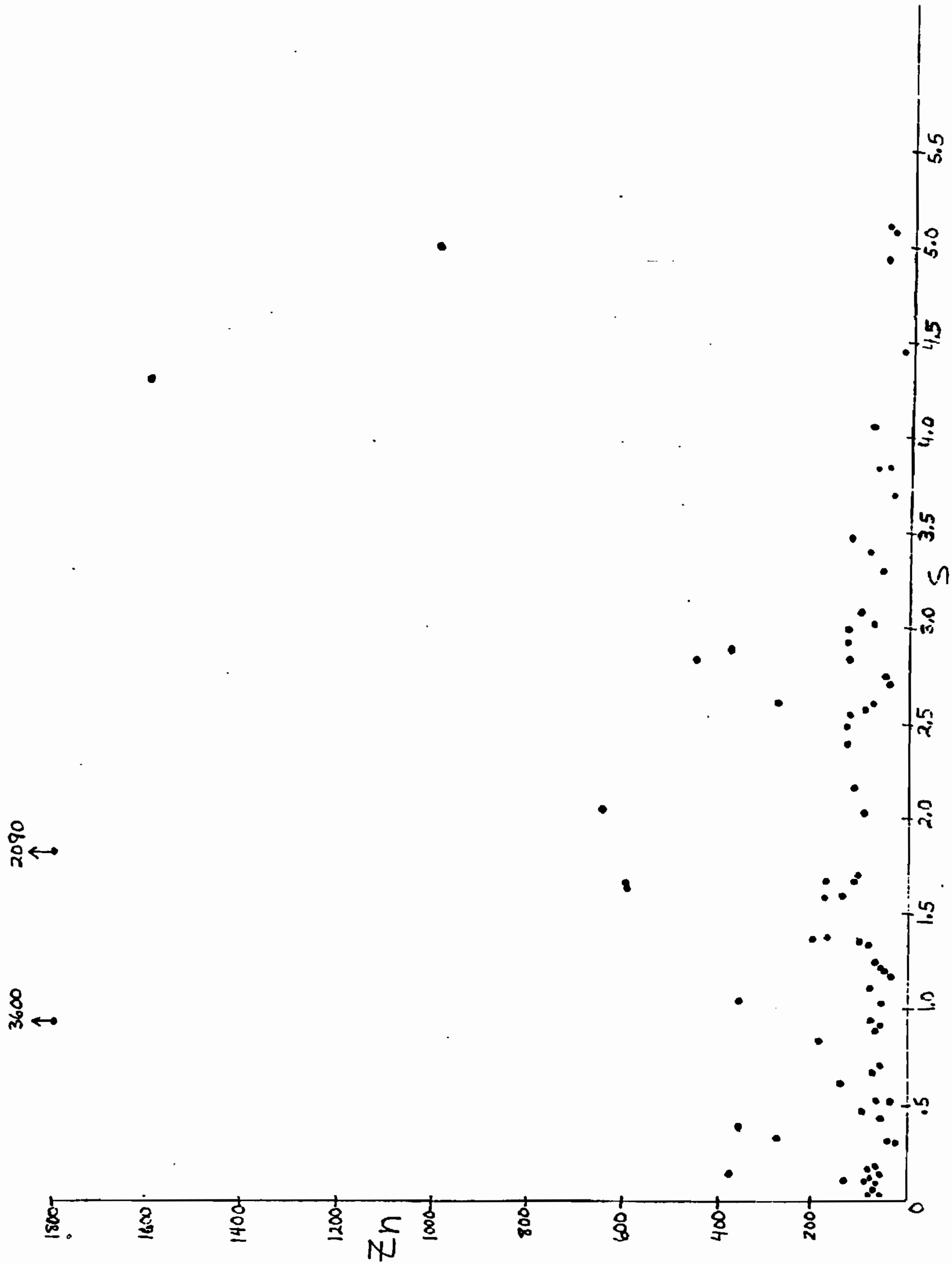


Figure 28.--Plot of sulfur vs Zn.

Fig 29

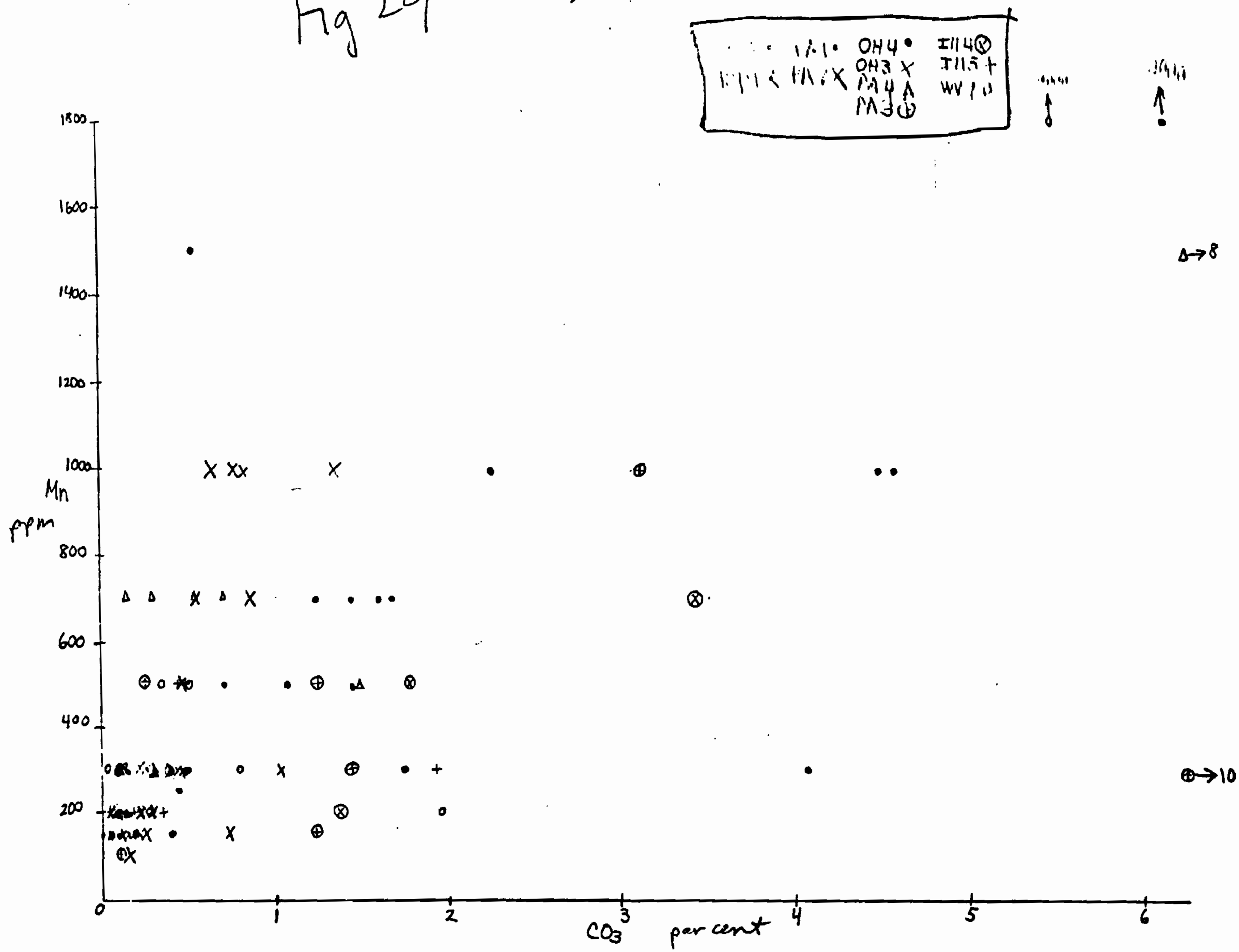


Figure 29.--Plot of carbonate C vs Mn

high Mn (one was low CO_3) and one high CO_3 (with only 200 ppm Mn) samples.

These samples with high Mn and CO_3 are also generally low (usually <.5, often <.2%) in organic C;' perhaps the less reducing conditions would render Mn less mobile or provide an environment which is more favorable for carbonate formation.

Conclusions

The geochemical results reported here and in previous reports can be used in several ways. The major parameter of interest is organic carbon, which actually represents organic matter (which includes nitrogen, oxygen and hydrogen). This organic matter itself is the source for gas and oil. The organic matter requires burial, heat, and time for production of oil and gas and suitable pathways (porosity, permeability, fractures) to a reservoir in order for a resource to form which would be considered economically useful today. In the future, the organic rich shale may be economic as a source for oil and gas by near surface mining and retorting or by in-situ generation of oil and gas.

Organic matter is also important because it is the major control for the occurrence of sulfides. This was accomplished through microbial reduction of sulfate utilizing organic matter as an energy source at the time of deposition of the shale. Together the organic matter and sulfide account for the unusual enrichment of trace elements found in the shale.

The chemical data show organic carbon contents that vary from several tenths of a percent to several percent in most cores and some show high values between 5 and 10 percent. Sulfur contents are about half of the organic carbon content.

Stratigraphy is usually defined on the basis of color, which is related to organic carbon, and geophysical gamma log, which is related to uranium (and its daughters). We have removed the organic C and S and found that the major elements (e.g. Al_2O_3 and SiO_2) also show stratigraphic effects. This is expected and related to source-area quartz and allochthonous clay precursors and also later depositional-diagenesis clays and silica.

Generally these carbon- and sulfur-content variations are also reflected in the trace elements U, Mo, V, Ni, As, Hg, Pb, and Zn which were usually measured. Iron often is often noticeably higher in the high-sulfur samples.

The carbon content of the shales is the master variable which can be used to interpret the history of the sedimentary rocks. The organic carbon content (and its dependents, sulfur and trace elements) can be used to interpret following variables: environment of deposition (including Eh of water column), distance from source (position in basin), and sedimentation rate.

The organic carbon content reflects what is remaining from the original primary biological input after microbial recycling and oxidation. These factors may be more or less effective, depending mainly on the Eh of the water column and the sedimentation rate. If the water column contains little or no oxygen, the primary organic matter content will be affected less because the usual catabolic biological (micro organisms) processes are greatly slowed. The presence of H_2S in the water column is the extreme (as it has zero oxygen) and constitutes reducing conditions.. A rapid sedimentation rate will bury the organic matter, also achieving low levels of oxygen (and microbial activity) and relatively more preservation. These two oxygen-deficient environments can be differentiated using carbon/sulfur ratio plots (Leventhal, 1979) or histograms or sulfur isotopes (Claypool and others, 1980) as well as the usual indicators such as type of or lack of fossils or laminated sediments. Later, this discussion will consider the use of trace elements specifically associated with sulfides.

Figure 30 shows a plot of carbon and sulfur data for normal (oxygen-containing) water column and an H_2S-containing water column (Black Sea) from recent sediments. Line A is the linear-least-squares fit for oxic water environments and line B for the euxinic Black Sea. The dashed line separates the two environments rather well. The H_2S environment shows higher S contents (or S/C ratios) and an intercept on the S axis for the linear-least-squares fit of the data.

Figure 31 shows the C and S for the shales in this report. The same dashed line is shown on this figure and may be interpreted in the same way. Thus these shales may be interpreted to have been deposited under conditions involving variously oxygenated and H_2S- containing water columns. This varying depositional environment is not unexpected and is related to depth (whether it is above or below the ~100 m mixed oxygenated zone) or mixing patterns of the entire Appalachian Devonian Sea. The restricted environment may have been well isolated from the open ocean. In addition, the 10-30^o S geographic location would not allow for wide scale replenishment of oxygen from sinking of cold, polar water masses such as occurs today. This latter factor may be the explanation for the continuous low to zero oxygen conditions during the deposition of these shales.

The sedimentation rate can be examined by using the organic content. Samples richer in organic matter must have experienced less dilution by mineral matter (assuming the depositional environment to be the same) and thus represent a slower sedimentation rate.

The type of organic matter can be used to give an idea of the location in

Fig 30

o Black Sea
• normal marine

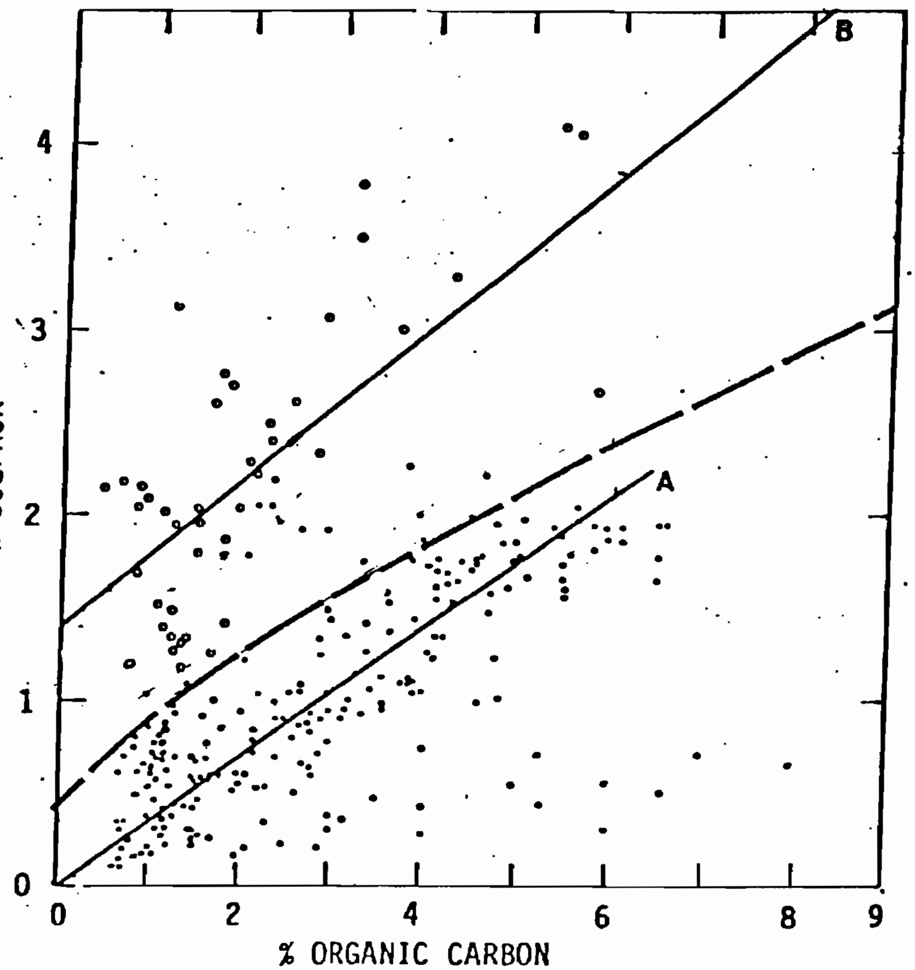


Figure 30.--Plot of carbon and sulfur for modern marine and Black Sea samples.

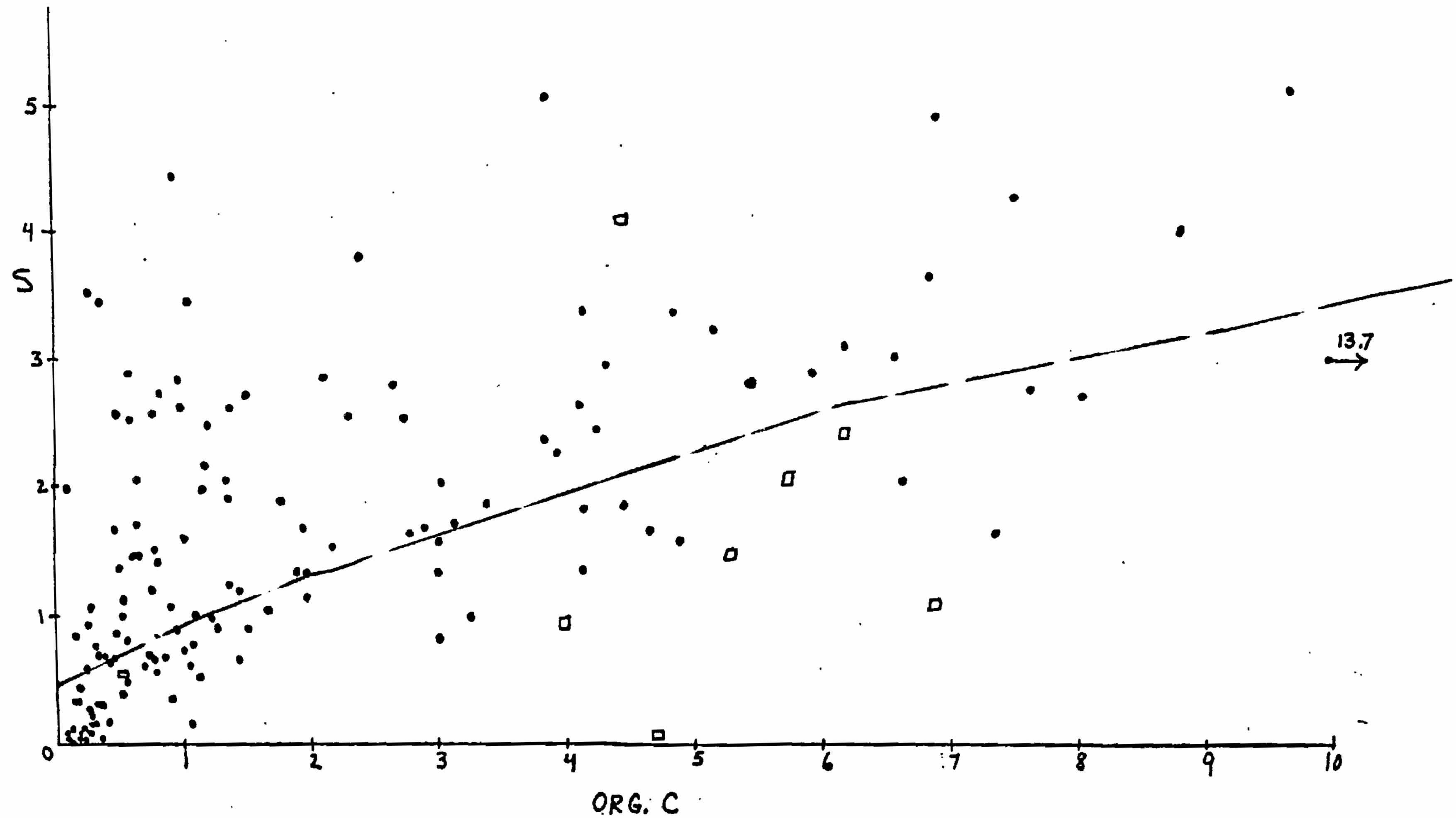


Figure 31.--Plot of carbon and sulfur for Devonian shales.

the basin. Samples with a larger proportion of terrestrial-source material are presumed to be closer to shore (again, all other things being equal). This organic type can be recognized by kerogen typing, either visual (Bostick, unpub. data) or molecular (Leventhal, 1978) or chemical (Claypool, unpub. data). This nearness-to-shore parameter may be supported by clay type (Hosterman, 1980) and major, minor, or trace-element geochemistry.

The above uses of organic carbon are more complex as many of the above parameters can vary at the same time within a single core, for example as the water depth, oxygen level in the water, and position in the basin change. In order to understand these changes, each stratigraphic unit should be considered separately at each core locality where it is present. This will be done for the entire set of samples already reported on (Leventhal, 1978, 1979, 1980) as well as these discussed here.

Certain exceptions need to be noted: in particular, some few samples have high organic contents but low metal contents. This case is probably an example of high biological productivity, coupled with high preservation (perhaps by burial) and normal sedimentation rates. The high organic content and high metal content is more usual for these samples and probably represents low sedimentation rates occurring beneath an oxygen-depleted or H_2S-containing water column. In this case the long time at the sediment-water interface allows enrichment with trace elements. Augmenting this could be the presence of an H_2S layer which would scavenge elements at the interface of the H_2S- and oxygen-bearing waters. Uranium, in particular, has been associated with terrestrial-type organic matter. Thus samples high in organic matter and uranium can indicate a terrestrial source and nearer-to-shore environment; samples with high sulfide, As, and Hg indicate a H_2S-containing water column;

and samples high in organic but low in metals indicate high preservation of marine organic matter by rapid burial. Figure 32 shows these complex relations in a schematic form.

A further way to examine data is to use metal/organic (or sulfide) ratios (Leventhal, 1979). This parameter could indicate any of the above-described parameters of water column, position in the sedimentary basin, and availability of metals. It is likely that much of the metal input to the basin was by weathering of volcanic ash. Episodes of volcanism are recorded in the samples, but their importance as a source of trace elements has not been emphasized. In particular the sediments stratigraphically above an ash bed are often enriched in trace elements and uranium (Leventhal and Kepferle, unpub. data). This is particularly true in the Marcellus Shale (above the Tioga ash bed), the Rhinestreet Shale above the Belpre ash bed, and the Gassaway (member of the Chattanooga Shale) above the Center Hill ash bed (fig. 2).

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Fig 32

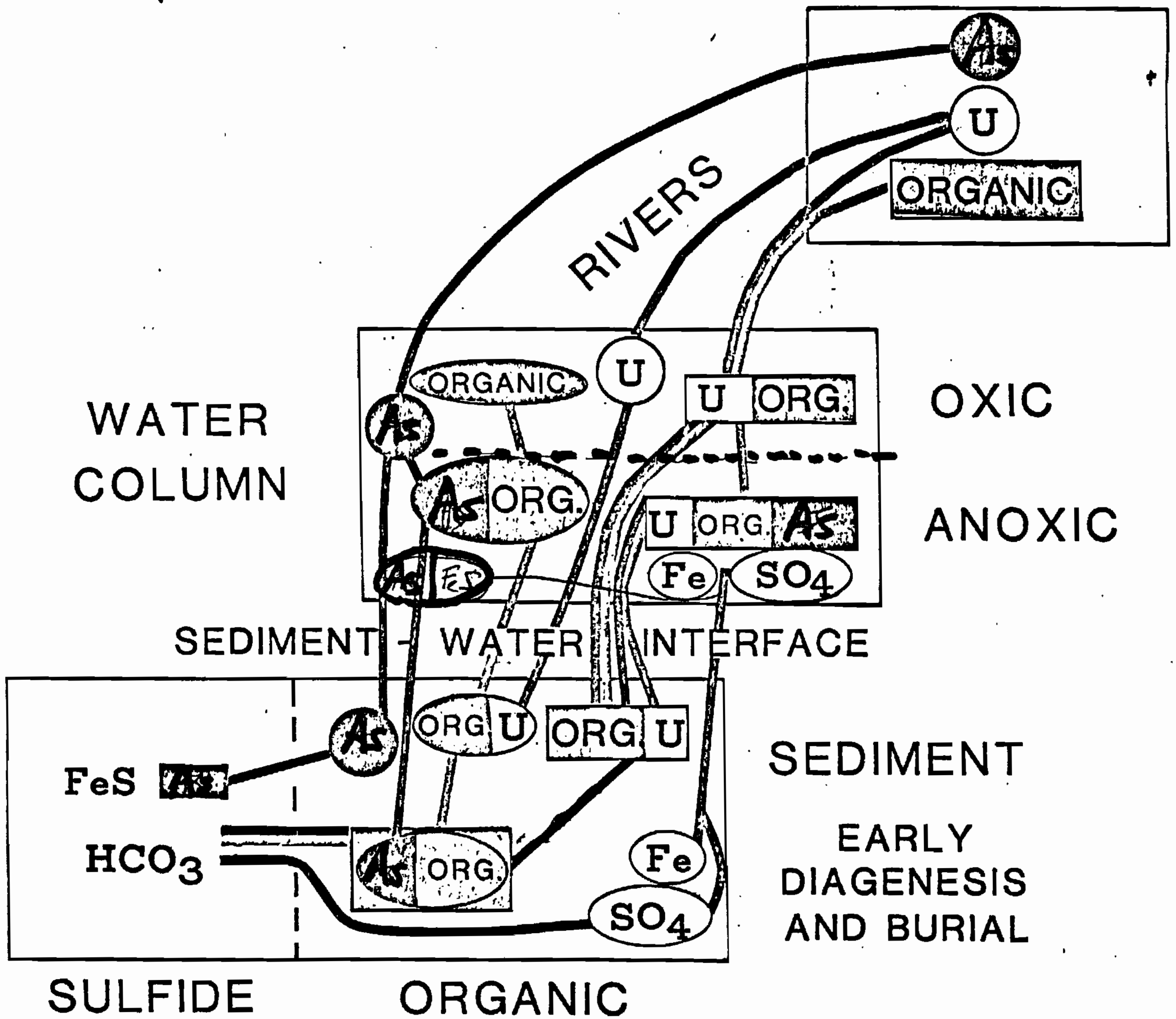

Figure 32.--Schematic for U and As syngenesis and early diagenesis.

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