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Comparative geochemistry of Devonian shale cores from the Appalachian Basin, Mason, Monongalia, and Upshur Counties, West Virginia; Illinois Basin, Tazwell County, Illinois; Clark County, Indiana; and Michigan Basin, Sanilac County, Michigan

By

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Abstract

Core samples from Devonian shales from three localities in West Virginia, and one locality each in Illinois, Indiana and Michigan have been analyzed for major, minor, and trace constituents. As observed previously (Leventhal, 1978, 1979b), the organic C and total S show large variations which seem to be the major control on the trace elements of interest (U, V, Mo, Hg, As, Co, Cu, Zn). The samples from the Illinois and Michigan Basins appear to show the same ranges of chemical compositions and geochemical controls as those from the Appalachian Basin.

Introduction

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

The chemical data presented in this report can be used for resource assessment of such elements as U and V and can be used to recognize possible environmental problems caused by volatile elements such as As or Hg if the shale was processed by heating. This chemical data can also be useful in stratigraphic correlations, geochemical assessment of source rocks, and characterization of depositional environments which may be related to oil and gas potential or resources.

The chemical data and geochemical controls and affinites 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 in particular (Leventhal and Goldhaber, 1978) and major, minor, and trace elements from Perry County, Ky., Jackson and Lincoln Counties, W. Va., and Cattaraugus County, N.Y. (Leventhal 1978) and from Martin County, Ky., Overton County, Tenn., Wise County, Va., and Carroll and Washington Counties, Ohio (Leventhal, 1979b). This paper does not consider organic C and sulfide S relationships (Leventhal, 1979a). The reader is referred to the earlier papers in this series (especially Leventhal 1979b) for a review of the literature. Results of uranium occurrence and sub economic resources will be treated separately (unpub. data, 1977, 1978).

Samples

The core samples (except for Michigan) were obtained as part of the Eastern Gas Shales drilling program. The locations are shown on figure 1 and additional data are given below.

Mason County, W. Va., 38°55′30"N, 82°03′45"W. API number 47-053-20146. Cored depth 2,620-3,406 ft. Stratigraphic units: Ohio, Java, West Falls.

Monongalia County, W. Va., 0.13 mi N of 39°40′N, 3.15 mi. W of 70°55′W. API no. 47-061-20370. Cored depth 7,168-7,520 ft. Stratigraphic units: Mahantango, Marcellus.

Upshur County, W. Va., API no. 47-097-20538. Columbia Gas Co., Goshen Quadrangle, cored Feb. 1978. Our samples are from the interval 3,740 to 4,11 ft.

Clark County, Indiana, 38°33′48"N, 85°46′53"W. 117 ft of core. Our samples range in depth from 145 to 237 ft.

Tazwell County, Ill. 221 ft of core. Our samples range in depth from 979 to 1,129 ft.

Sanilac County, Mich. 43°13′54"N, 82°44′02"W. Interval sampled 832 to 1,461 ft. Stratigraphic units: Sunbury, Bedford ("False Antrim"), Antrim, Traverse. Obtained through cooperation of R. D. Matthews and J. Humphrey, Dow Chemical County (Midland, Mich.).

Three of the cores were examined or described in detail in cooperation with Dave Matthews, Dow Chemical (Sanilac County core) and Roy Kepferle, USGS (Monongalia and Mason County cores). The Sanilac County core consists of the following units: Sunbury Shale 800-963 ft, Berea Sandstone 963 to 1,020, Bedford Shale 1,020 to 1,219 which includes a unit called the "False Antrim" from 1,185 to 1,219, and Traverse Limestone below 1,440. We sampled only one sample each from the sandstone and limestone units. The other samples were

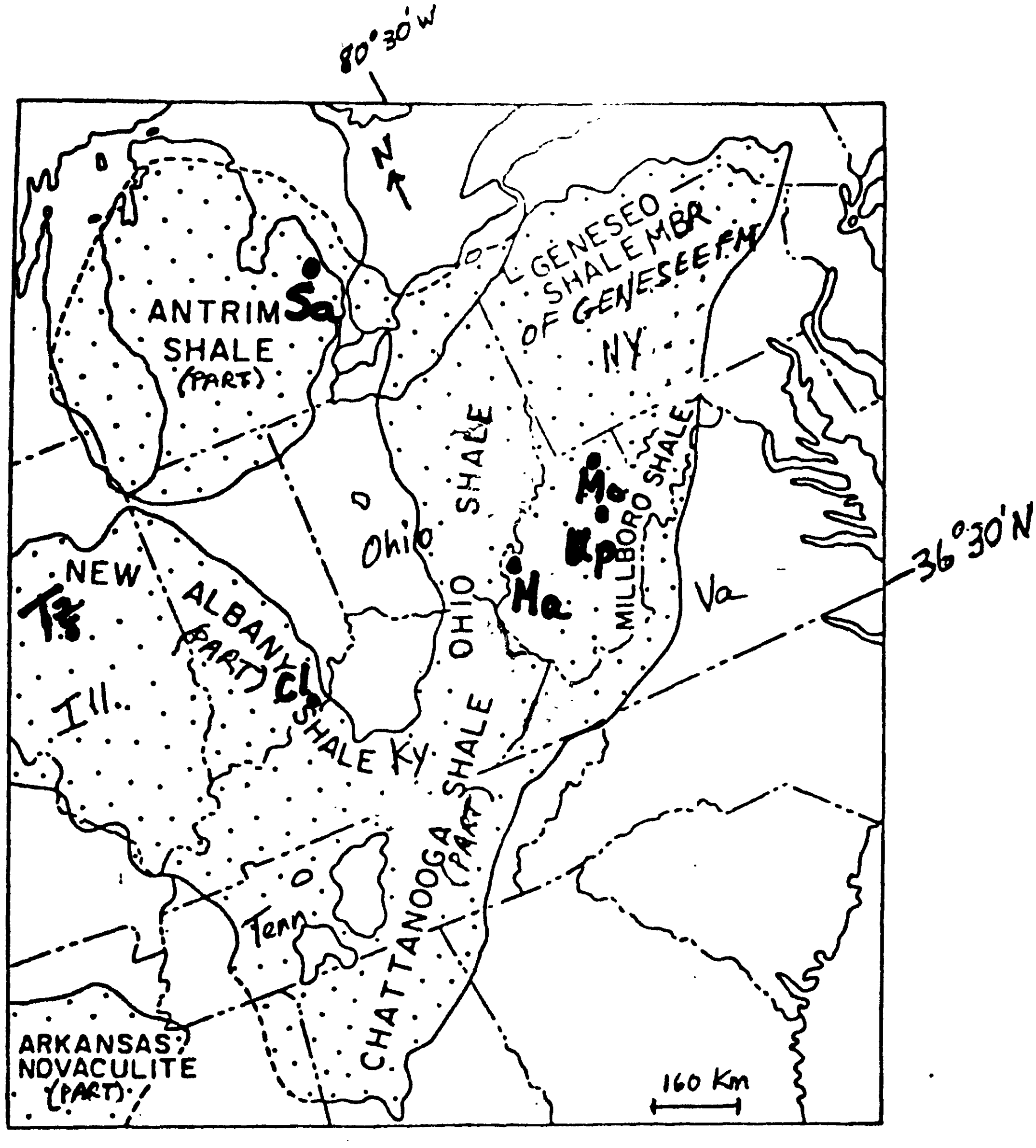


Figure 1.--Map showing core samples localities. The three basins are indicated by the dot pattern, the solid line is the extent of the shale in the basin. Localities abbreviated as follows: Sa, Sanilac County, Michigan; Mo, Monongalia County, West Virginia; Up, Upshur County, West Virginia; Ma, Mason County, West Virginia; Cl, Clark County, Indiana; and Tz, Tazwell County, Illinois. Modified from Leventhal (1979b).

gray to black shales. The Antrim shale sample at 1,431 ft was especially interesting in that it contained a 1 cm thick pyrite layer. This is not a concretion because other cores from the immediate area (within several hundred meters) also show this pyrite-rich zone. A concentration of fossils several inches stratigraphicaly above the pyrite layer occurs. These fossils were identified as crossopterygian scales from a fish that ranges from Devonian to Permian (N. Hotton, III, Smithsonian Institution, written commun., 1978) and as conodonts (Anita Harris, USGS, written commun., 1978). Harris reports that the conodonts are of several types including Ancyrodella rotundiloba alata which have been recognized in the several members of the Genesee Formation of New York and in the Squaw Bay Limestone of Michigan. Another conodont, Palmatolepis transitans is longer ranging and has been reported in the basal portion of the Rhinestreet Member of the West Falls Formation in New York.

The Monongalia County core consists of gray and black shales. Above a depth of 7380 ft the core is Mahantango Shale and below this depth is the Marcellus Shale which is generally higher in uranium (gamma log) and organic matter (color). The Marcellus samples are extremely friable and very black (Munsell color N3) because of burial, heating and the higher organic content. Zones of pyrite, fossils, and vitrinite were encounted throughout the core but were generally not sampled for geochemistry because they represent exceptional conditions (R. C. Kepferle and J. S. Leventhal, unpub. data 1977, 1978).

The Mason County core is more varied in lithology and stratigraphically younger than the Monongalia County core. The lithology includes gray (organic poor) shales, carbonate, and silt zones as well as a black shale. There are numerous thin pyrite rich zones, fossilized burrows and vitrinite layers (R. C. Kepferle and J. S. Leventhal, unpub. data, 1977, 1978). A sample taken at the 2,774 ft depth was divided into two subsamples; both are rich in organic carbon and pyrite, but one contains disseminated pyrite and the other has a visible (1 cm thick) pyrite layer.

Methods and Results

Analytical methods are the same as those described in Leventhal and others (1978) and Leventhal (1979b).

Results of sample analyses are given in tables 1, 2, 3, 4, and 5. The samples are typical of the shales reported earlier. They contain 50-60 percent (range from 41 to 80 percent) SiO_2; 13-19 percent Al_2O_3 (range from 6 to 23 percent); 4-7 percent Fe_2O_3 (range from 3 to 12 percent); and 3-4 percent K_2O. These components (except for Fe_2O_3) and MgO make up quartz and clay minerals. The iron (reported as Fe_2O_3) is present in clays, oxide coatings and pyrite. The CaO found varies from 0.2 to 0.5 percent in most of the Michigan samples and as much as several percent in the Mononogalia, W. Va. and Clark County, Ill. samples. CaO is generally the carbonate mineral phase. Semiquantitative data for elements that show generally constant values are summarized in table 6.

Discussion and conclusions

The trace elements are highly variable in some cores but not in others, for example, V only varies by a factor of 2 in the Mason County, W. Va., Tazwell County, Ill., and Clark County, Ind. cores, but shows several high values that are factors of 3 to 7 greater in the Sanilac and Monongalia cores; the Upshur County core shows distinctly lower values of V. Molybdenum shows a large range of values from <3 ppm (or <10 ppm, depending on analytical technique) to 345 ppm in an organic rich-sulfide rich sample from the

Table 1.--Results of analyses of core samples of Antrim Shale, Sanilac County, Michigan

[* is 6 step spec data, -- is not analyzed]

	Semi-Quantitative						Quantitative													
	percent						parts per million											percent		
Depth, ft	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	V	Mo	Co	Ni	Cu	Zn	Mn	Hg	As	U	Th	S	OrgC	CarbC
832	55	18	3.6	0.2	3.6	0.8	505	57	14	100	38	641	147	0.05	23	9.9	21	0.91	2.9	<0.01
871	54	21	4.8	.1	3.8	.8	185	<3	14	65	32	70	177	.02	16	3.6	18	1.69	.84	<.01
913	56	16	3.6	.2	3.4	.7	195	19	14	55	30	114	117	.03	18	7.6	16	1.44	2.4	<.01
953	58	20	4.4	.2	3.9	.8	284	<3	17	65	30	55	141	.03	25	5.0	14	1.28	.96	<.01
996	81	4	1.4	2.1	.60	.2	<25	<3	3	15	10	22	696	.01	3.9	1.2	5	<.01	.22	.95
1066	59	19	4.6	.3	3.8	.9	185	<3	35	75	25	69	364	.12	46	4.0	19	.09	.42	<.01
1136	62	18	5.1	.3	3.3	.9	160	<3	18	45	30	202	498	.01	16	3.8	17	<.01	.31	.41
1162	54	18	6.8	.5	3.6	.8	155	<3	40	60	42	1390	832	.11	17	3.5	19	<.01	.41	.87
1195	53	23	5.0	.3	4.2	.8	160	<3	20	65	35	78	379	.02	5.2	4.5	19	<.01	.81	.21
1216	51	20	6.8	.4	3.7	.7	140	<3	19	50	38	56	1180	.02	5.1	3.5	16	<.01	.65	1.0
1221	51	19	4.2	.2	3.5	.7	1060	261	48	235	64	1720	114	.08	50	36	--	1.61	8.9	<.01
1266	59	17	4.0	.3	3.7	.6	235	107	14	110	47	40	122	.05	21	25	--	2.00	5.5	<.01
1299	61	14	3.6	.7	3.2	.6	175	69	17	105	42	51	159	.03	23	20	--	1.46	4.7	.14
1320	60	12	3.1	.3	3.0	.5	155	83	21	100	44	186	110	.03	15	23	--	1.51	6.8	.07
1382	45	13	5.1	6.2	3.1	.6	135	9	8	50	36	99	1190	.03	27	18	19	1.19	.96	2.97
1384	56	13	4.5	.4	3.1	.7	180	64	30	140	87	74	159	.06	25	43	--	2.79	10.6	<.01
1418	56	14	4.0	2.0	3.4	.7	160	50	26	95	84	167	309	.05	13	13	16	1.82	6.0	.53
1431	43	12	15	.4	2.8	.5	200*	30*	7*	100*	100*	<300*	100*	--	--	23	--	15.2	6.3	.07
1460	2.6	0.9	6.9	24	0.1	.05	<25	<3	<1	25	7	18	3200	.01	0.7	0.6	2	<.01	.02	12.0

Table 2.--Results of analyses of core samples from Mason County, West Virginia

[--, not analyzed, _ semiquantative data]

	Semi-Quantitative						Quantitative													
	percent						parts per million											percent		
Depth, ft	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	V	Mo	Co	Ni	Cu	Zn	Mn	As	Hg	U	Th	S	OrgC	CarbC
2682	48	16	12	0.3	3.1	0.8	100	7	20	70	9	178	150	24	0.20	3.9	15	11.3	0.89	0.07
2712	54	18	7.2	.6	3.8	.7	180	<3	21	55	36	117	602	--	.02	3.7	14	0.93	0.80	.28
2727	59	13	5.9	.3	2.7	.7	150	70	20	70	70	105	150	29	.19	22.1	22	3.83	5.7	.14
2763	63	13	4.8	.5	2.6	.7	145	40	26	65	42	109	226	--	.03	18	21	2.05	4.8	.20
2774.6	51	18	8.5	.2	3.6	.9	100	20	20	50	50	<300	150	39	.08	5.4	14	6.72	1.5	<.01
2774.7	56	20	6.2	.2	3.9	.8	150	10	20	50	50	<300	150	45	.04	6.6	20	2.70	0.93	<.01
2813	56	12	3.8	1.7	2.4	.8	100	<3	12	30	25	55	394	--	<.01	3.4	11	.96	0.16	.64
2873	57	18	5.4	0.2	4.0	.8	180	<12	23	75	45	197	222	--	.02	5.6	18	1.14	0.13	.07
2930	57	16	5.1	.3	3.2	.7	150	36	25	80	50	129	159	--	.04	16.3	25	2.34	4.1	.07
2980	59	16	5.0	.4	3.4	.7	175	77	29	90	74	62	208	--	.03	23.7	9	2.24	5.8	.14
3080	60	17	5.5	.2	3.4	.8	180	7	53	115	32	76	179	--	.05	6.8	16	2.44	1.8	<.01
3130	60	18	4.6	.9	4.0	.8	75	<3	17	60	37	70	348	--	.03	2.6	13	.07	0.19	.27
3142	41	12	8.3	.8	2.8	.5	160	30	20	70	100	191	200	66	.29	18.4	21	6.02	20.0	.14
3180	54	18	5.2	.4	4.0	.9	165	<3	29	70	20	85	150	--	.03	3.9	15	0.84	0.35	.07
3255	56	17	7.5	1.0	4.0	.7	170	<3	28	45	35	70	700	--	.02	3.3	15	<.01	0.20	.90

Table 3.--Results of analyses of core sample from Monongalia County, West Virginia (MERC)

[--, not analyzed]

	Semi-Quantitative						Quantitative													
	percent						parts per million											percent		
Depth, ft	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	V	Mo	Co	Ni	Cu	Zn	Mn	As	Hg	U	Th	S	OrgC	CarbC
7220	51	17	5.0	8.3	3.9	0.7	175	<10	12	59	26	133	430	--	0.03	3.2	12	0.34	1.2	1.38
7272	57	19	6.7	0.5	4.5	0.8	240	<10	20	98	43	118	200	--	.07	5.0	15	3.1	1.4	.07
7326	56	19	6.2	1.8	4.4	0.8	220	<10	18	72	46	90	305	--	.05	3.6	14	1.3	1.0	.36
7340	57	19	4.8	0.8	3.7	0.7	150	20	15	70	100	107	150	21	.21	11	18	1.9	2.4	<.01
7378	57	17	7.3	1.0	4.0	0.7	535	<10	21	136	109	79	150	--	.08	10	14	4.5	3.0	.15
7410	49	18	6.3	1.6	3.6	0.9	300	70	15	150	200	197	70	51	.26	35	--	5.3	5.3	.22
7431	55	18	6.2	0.8	4.5	0.7	240	15	20	130	75	40	115	--	.09	15	--	4.2	3.8	.03
7453	53	12	3.6	3.2	2.5	0.4	300	100	10	150	150	1080	70	--	.42	62	--	3.8	10.6	.64
7483	47	11	10	2.8	3.1	0.5	1500	345	57	500	252	703	78	--	.25	64	--	9.2	11.3	.42

Table 4.--Results of analyses of core samples from Upshur County, West Virginia

	Semi-Quantitative						Quantitative													
	percent						parts per million											percent		
Depth, ft	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	V	Mo	Co	Ni	Cu	Zn	Mn	Hg	As	U	Th	S	OrgC	CarbC
3740	69	11	3.6	2.3	1.3	0.8	70	<3	15	35	12	62	485	0.02	29	3.9	15	0.47	0.11	0.55
3748	70	12	3.3	2.6	.2	.9	40	<3	14	30	13	69	149	.01	11	3.8	17	<.01	.12	<.01
3770	80	6.5	2.8	.9	.3	.6	35	<3	8	15	30	50	149	<.01	9.3	3.4	14	<.01	.48	<.01
3756	76	7.8	2.4	1.3	1.0	.7	40	<3	11	25	5	47	319	.01	20	3.7	15	.11	.45	.29
3775	80	7.4	3.1	1.0	.5	.6	30	<3	8	15	13	70	208	<.01	6.8	2.7	13	<.01	.53	.11
4111	51	20	7.2	4.4	.2	.9	135	<3	25	65	30	81	204	.05	47	3.7	18	2.51	.74	.05

Table 5.--Results of analysis of core sample from the Illinois Basin, Tazwell County, Illinois

[-- not analyzed]

	Semi-Quantitative						Quantitative													
	percent						parts per million											percent		
Depth, ft	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	V	Mo	Co	Ni	Cu	Zn	Mn	Hg	As	U	Th	S	OrgC	CarbC
979	56	13	4.2	3.9	2.9	0.7	85	<3	18	50	17	58	438	0.01	12	2.6	12	0.52	0.35	1.39
1029	57	18	4.8	5.5	.7	.8	120	9	23	65	30	72	258	.02	21	5.9	13	.66	1.47	.28
1079	58	16	4.3	5.8	.3	.7	160	31	21	70	37	109	197	.04	12	19.0	--	.82	3.19	.14
1129	55	18	5.1	4.7	.7	.7	125	22	25	65	52	73	269	.03	16	6.8	17	1.40	1.99	.22

Clark County, Indiana

	Semi-Quantitative						Quantitative											
	percent						parts per million									percent		
Depth, ft	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	V	Mo	Co	Ni	Cu	Zn	Mn	Hg	U	Th	S	OrgC	CarbC
145	57	9.9	6.3	1.1	2.7	0.6	152	51	31	94	53	93	370	0.10	49	--	3.73	10.7	0.29
195	57	15	5.1	1.9	4.0	0.7	171	<10	20	89	92	269	450	.07	17	--	1.51	4.3	0.91
237	52	13	4.2	4.5	3.8	0.6	171	<10	18	100	115	133	500	.07	11	--	2.01	7.8	1.43

Table 6.--Semiquantitative data

[Average values in ppm, parenthesis indicate one high or low value]

Element	Antrim	Tazwell	Clark	Mason	Monongalia	Upshur
Ba.....	150	200	250	300 (3000)	(500) 1000 (5000)	200
Cr.....	60	70	70	50	90	25 (70)
La.....	50	40	50	40	40	(10) 50 (70)
Pb.....	(10) 40 (70)	25	20	20 (150)	20	(5) 15 (70)
Sr.....	70	70	200	130	150	70
Y......	20	15	30	20	30	20
Zr.....	100	100	150	110	100	(100) 300 (500)

Monongalia County core. Similar large variations are seen for organic carbon, sulfur, and Zn. Nickel, Cu, Co, Hg, U, and As show lesser variations. Manganese shows a range of values that vary only by a factor of 2 or 3 except in the presence of increased carbonate where Mn can show increases by a factor of 5 (see Sanilac County core). The Upshur County core samples show higher SiO_2 and relatively lower Al_2O_3 contents than most shales, indicating a relatively greater quartz content and relatively lesser clay content.

The results of the chemical analyses can be used for mineralogical information. K_2O and Al_2O_3 are good indices of the total clay content, whereas SiO_2 represents quartz plus clay; CaO is related to carbonate: and Fe_2O_3 above 3-4 percent is present as pyrite, the residual 3-4 percent or less being in clays or oxides (fig. 2).

Down-hole plots

Down-hole plots for three cores are shown in figures 3, 4, and 5.

The Sanilac County core from the Michigan Basin shows the same general trends as observed for core samples from the Appalachian Basin (Leventhal, 1978, 1979b). The organic rich samples of the Antrim Shale (below 1219 ft) show much higher molybdenum and uranium contents than the overlying "False Antrim" which looks very similar in hand specimen. Other trace elements such as Co, Ni, and Cu also show somewhat higher values in the Antrim. Zn, V, As, and Hg show some erratic high values but they are not easily attributable to stratigraphy, or organic carbon or sulfur content. The high Mn contents are generally associated with higher carbonate contents. Another interesting transition can be seen for the samples at 1382 ft (a carbonate rich shale) and 1384 ft (an organic rich shale). The 1384 sample shows higher levels of V, Mo, Co, Ni, Cu, Hg, and U which are generally associated with increases in organic content. The Mn value is much greater for carbonate rich sample

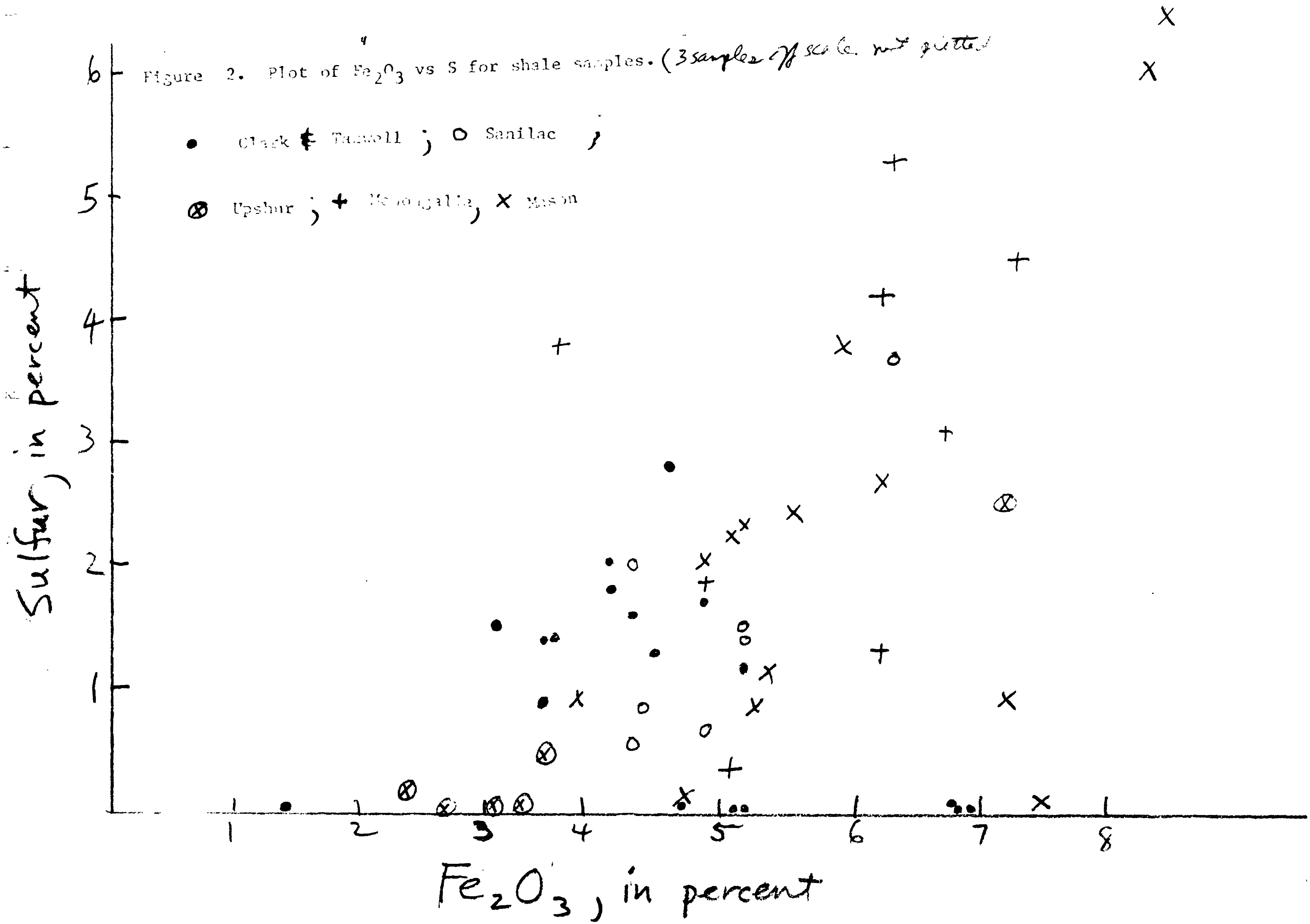


Figure 2. Plot of Fe_2O_3 vs S for shale samples. (3 samples off scale not plotted)

Figure 3. Down-hole plot for Sanilac County, Michigan showing variation (not to scale) of content of elements and other constituents of shales. Increase in content is to the right. Constituents showing similar patterns are nested together.

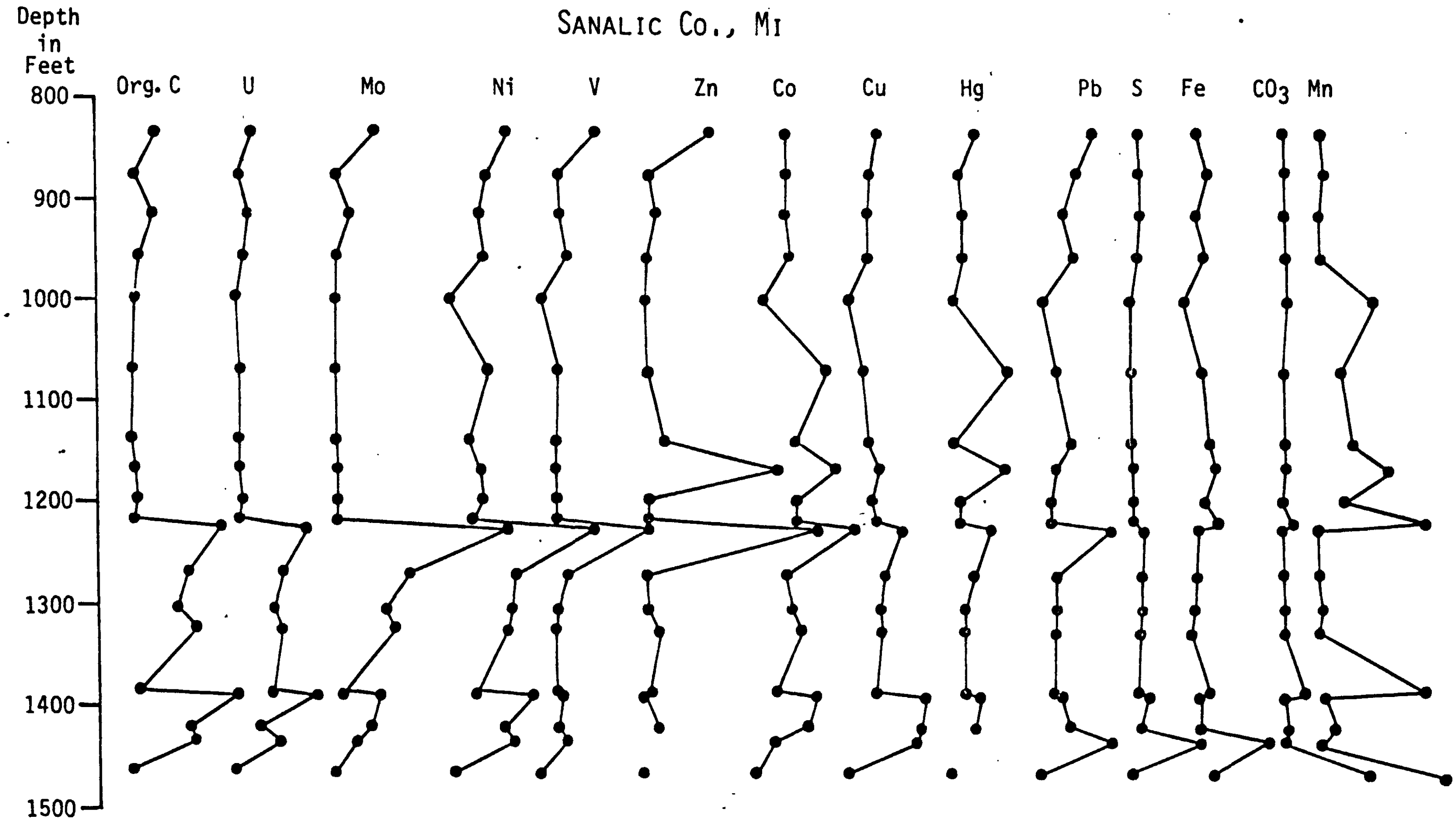


Figure 4. Down hole plot for Mason County, West Virginia showing variation (not to scale) of content of elements and other constituents of shales. Increase in content is to the right. Constituents showing similar patterns are nested together.

MASON CO., W. VA.

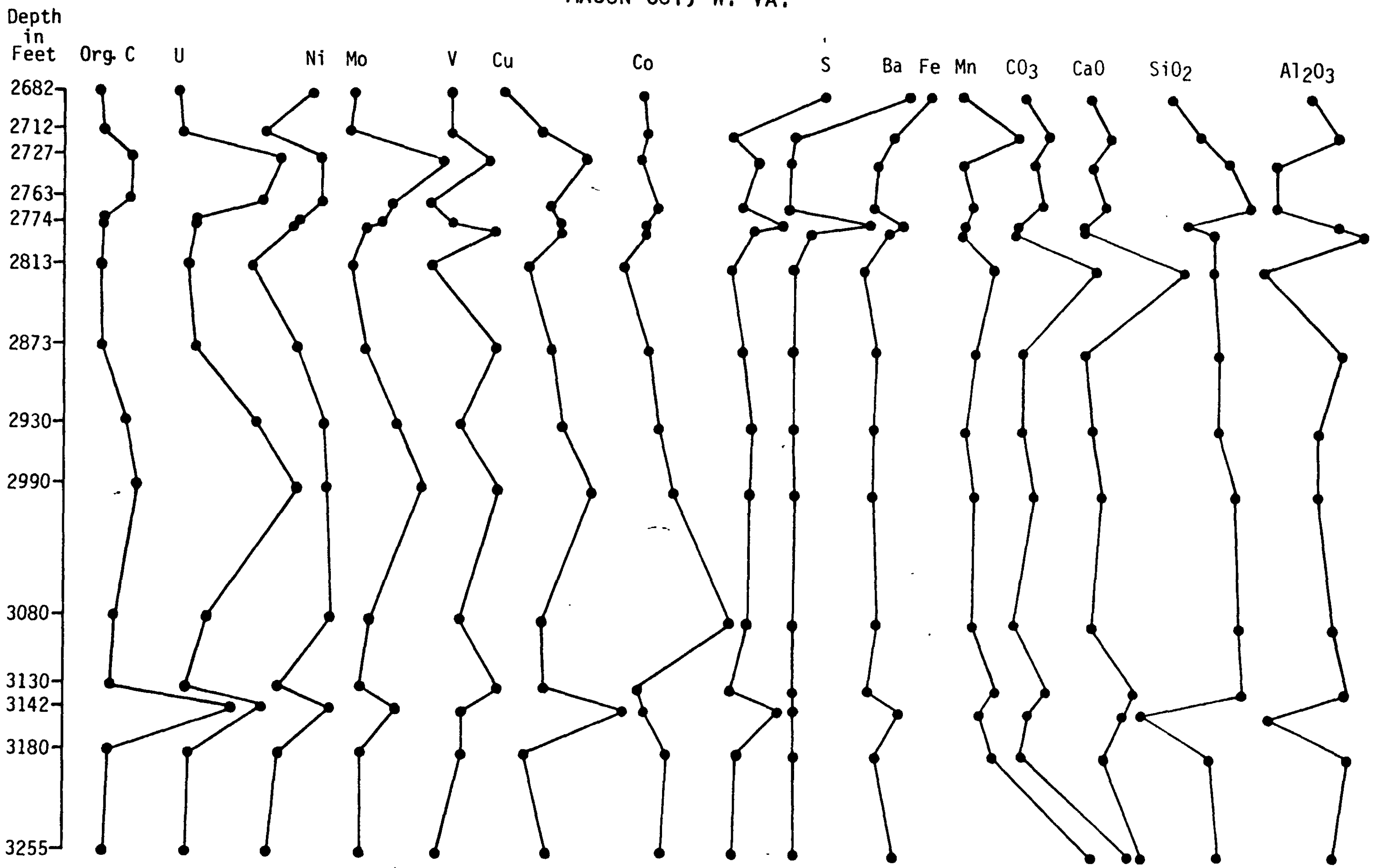
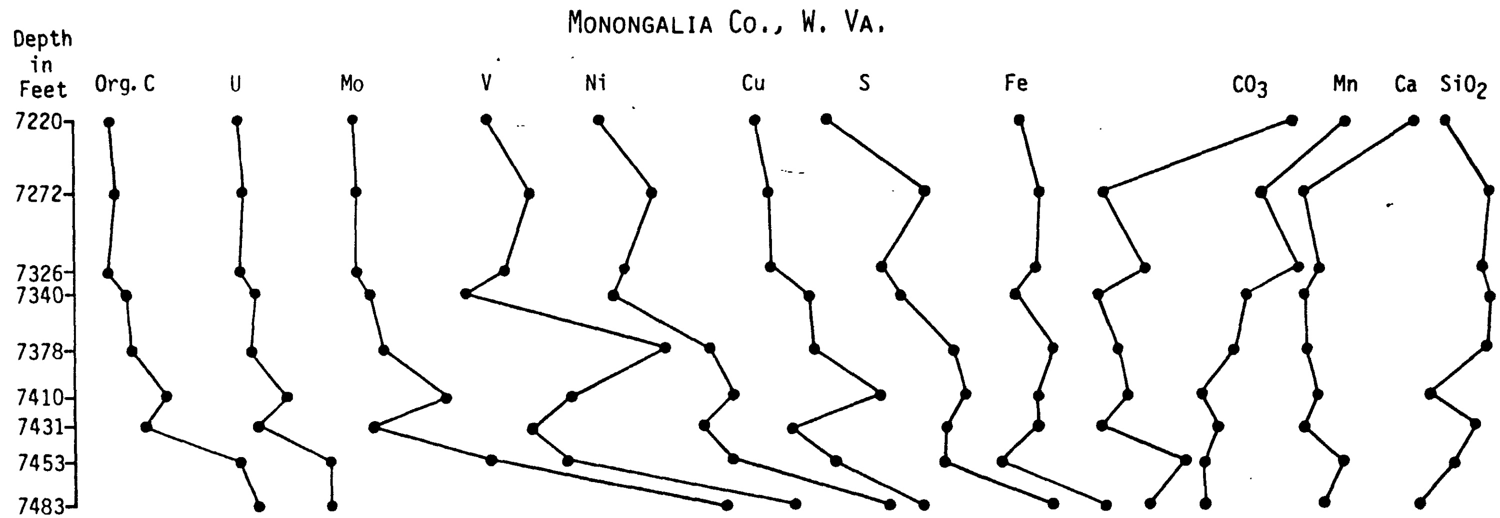


Figure 5. Down hole plot for Monongalia County, West Virginia showing variation (not to scale) of content of elements and other constituents of shales. Increase in content is to the right. Constituents showing similar patterns are nested together.



1382. Zn and As show only small changes and are not organically controlled but may be related to sulfide content which is similar for these two samples. There are several samples that do not follow the organic-sulfur control of trace elements. In particular the samples at 1066 and 1162 are anomalous in that they both have low contents of S and organic C, but high contents of Hg, and Zn or As.

The Mason County core shows less variation in chemical composition. The down-hole plot shows a good covariance between organic carbon, U, Ni, and Mo. V, Cu, and Co do not follow the organic carbon as well. In the Mason County core the sample at 3142 has very high S and organic C, but not nearly as much U or Mo in comparison to sample 2930, for example. Fe and S show similar behavior as do Mn, CaO, and CO_3.

Pyrite grain size

The sample at 2774 ft from Mason County was subdivided to see if a pyrite layer showed a different trace element pattern than disseminated (fine grained) pyrite in an adjacent sample. The comparison of 2774.6 and 2774.7 shows rather similar trace element contents despite the fact that 2774.6 has a considerably higher sulfide content (Table 2).

Two elements of particular interest are Hg and As which are strongly associated with sulfide. The Hg content of the sample which includes the sulfide layer (2774.6) has twice as much Hg as the sample with disseminated sulfide. Molybdenum is also enriched in the former sample. The As content, however is slightly lower in the sample with the pyrite layer, as is the V. Tentative conclusions are that the physical size of the sulfide is not as important a factor as the actual amount of sulfide. However, it is important to note that this particular sample is not as enriched in certain trace elements (except Hg and As) (for example) the sample at 2980 is. The 2980 sample has similar amount of sulfide but has much more Mo, Ni, and U and somewhat more V and Cu, which may be associated with the much higher organic C content. It is also possible that the fine grained sulfide is syngenetic, whereas the pyrite layer is early diagenetic and thus the environment which controlled the available trace elements may have been somewhat different (J. S. Leventhal and M. B. Goldhaber, unpub. data, 1980).

Maturity and trace elements

The Mononogalia County core is a good example of samples that are overmature and have already sourced oil and gas due to burial and heat. The samples from 7400 ft and below are very black in color and friable. They are very different from samples of similar major element composition in that they are not physically coherent, that is, they are falling apart. This is due the destruction the organic matter. The samples now contain 4 to 11 percent organic carbon, however they may have contained 30 to 50 percent more than this prior to heating. A sample with 10 weight percent organic carbon actually contains approximately 14 percent organic matter (C, H, O, N) and by volume this is 30-40 percent of the rock. Because this organic matter is dispersed throughout the rock, such as coating clay minerals, the destruction the organic matter also destroys the bulk fabric of the rock.

In view of this physical change in the rock properties, the high temperature history, and loss of volatile organics the question of what happens to the trace elements which were originally associated with the organic content is important. The down-hole plot (fig. 5) shows rather similar organic carbon-U-Mo relations to those observed in other samples. Vanadium, Ni, and Cu seem to be related to organic carbon and Fe and S. Even volatile Hg is not markedly different. Calcium oxide, CO_3, and MnO are interrelated as has been seen before. In summary, the trace element patterns do not seem to be greatly different in this rock that has experienced a severe thermal history. The absolute amounts of trace elements and their abundance relative to organic carbon and sulfur is within the range of previously analyzed samples (Leventhal, 1979b).

The samples at 7453 and 7483 have very similar (high) amounts of organic carbon, however the sample at 7483 has approximately 2 1/2 times as much sulfur as 7453. The 7483 sample also shows much higher amounts of Mo, V, Ni, and Cu, but rather similar amounts of Zn and U. These trace element changes may be a result of the increased sulfide content or may reflect the drastic change in conditions from the depositional environment at 7495 ft where the top Onondaga Limestone is encountered.

Some of the Monongalia samples showed 1 ppm Ag (7340, 7378, 7410, 7453) and one sample showed 5 ppm Ag (7483) by semiquantitative spectroscopy. These Ag values may be typical of the sulfide-organic rich Marcellus shale unit.

Samples from Upshur County, W. VA, as mentioned earlier, are relatively richer in quartz and poorer in clay, they are also not very organic rich and show lower amounts of trace elements, except sample from 4111 which has 2.5 percent S and somewhat more organic carbon, As, Hg, Ni, Co and V than the other samples.

Samples from Clark County, Ind., have high amounts of organic matter, but only one sample (145) shows high U and Mo. Only one sample (195) shows moderately high Zn. However, all the samples show high Hg.

Tazwell County, Ill. samples are similar to others showing increased V, Mo, Zn, Hg and U in the sample with the highest organic carbon. The Mn content is related to the CO_3 content (Fig 15, p 30)

Figures 6 thru 14 show plots of trace elements vs organic carbon or sulfur. From inspecting these figures it may be seen that there are no

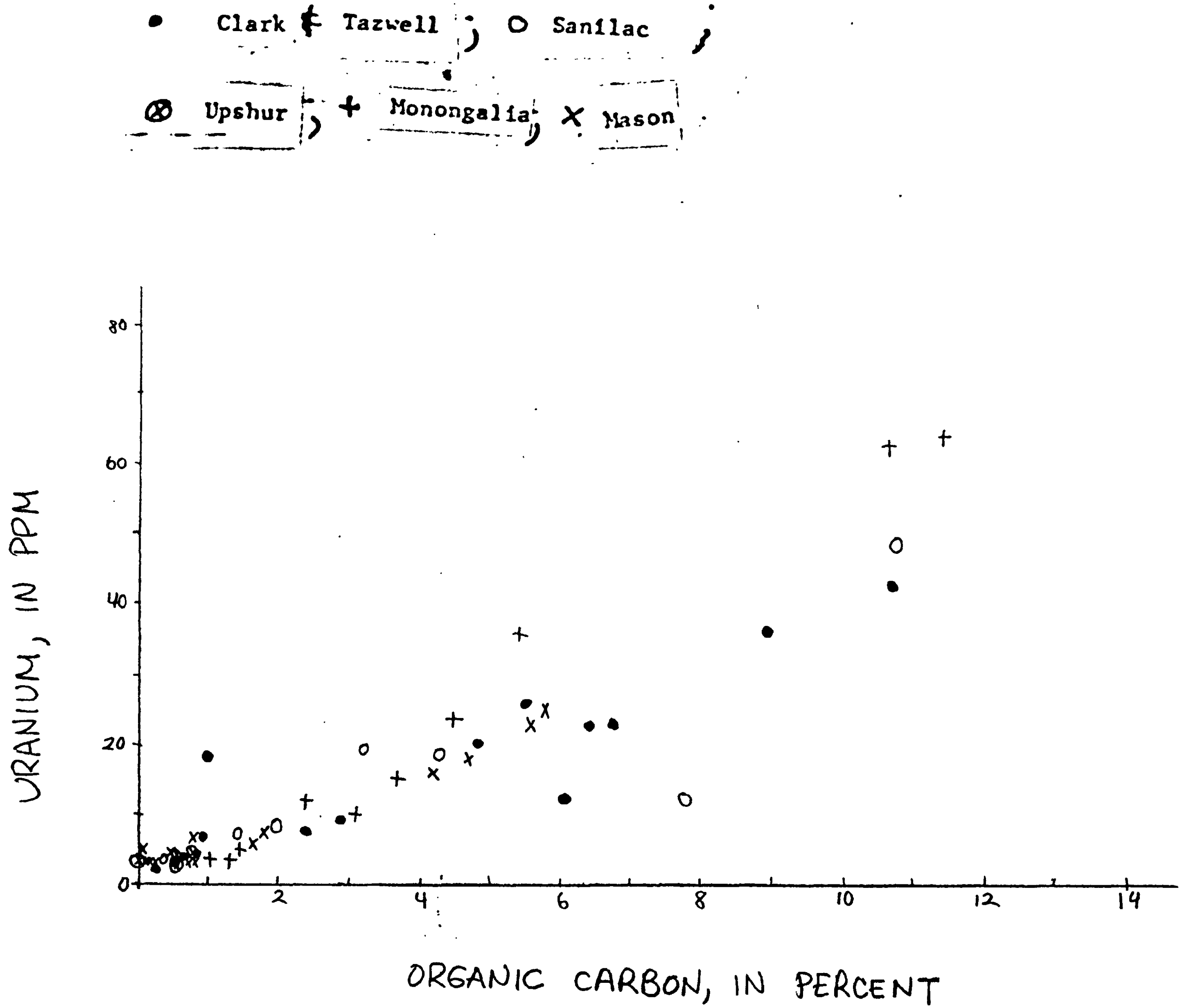


Figure 6.--Organic carbon vs uranium for 6 cores (Mason 3142 ?, scale ?)

Figure 7

Figure 7. Organic carbon vs molybdenum for 6 cores. (Mason 3142 off scale)

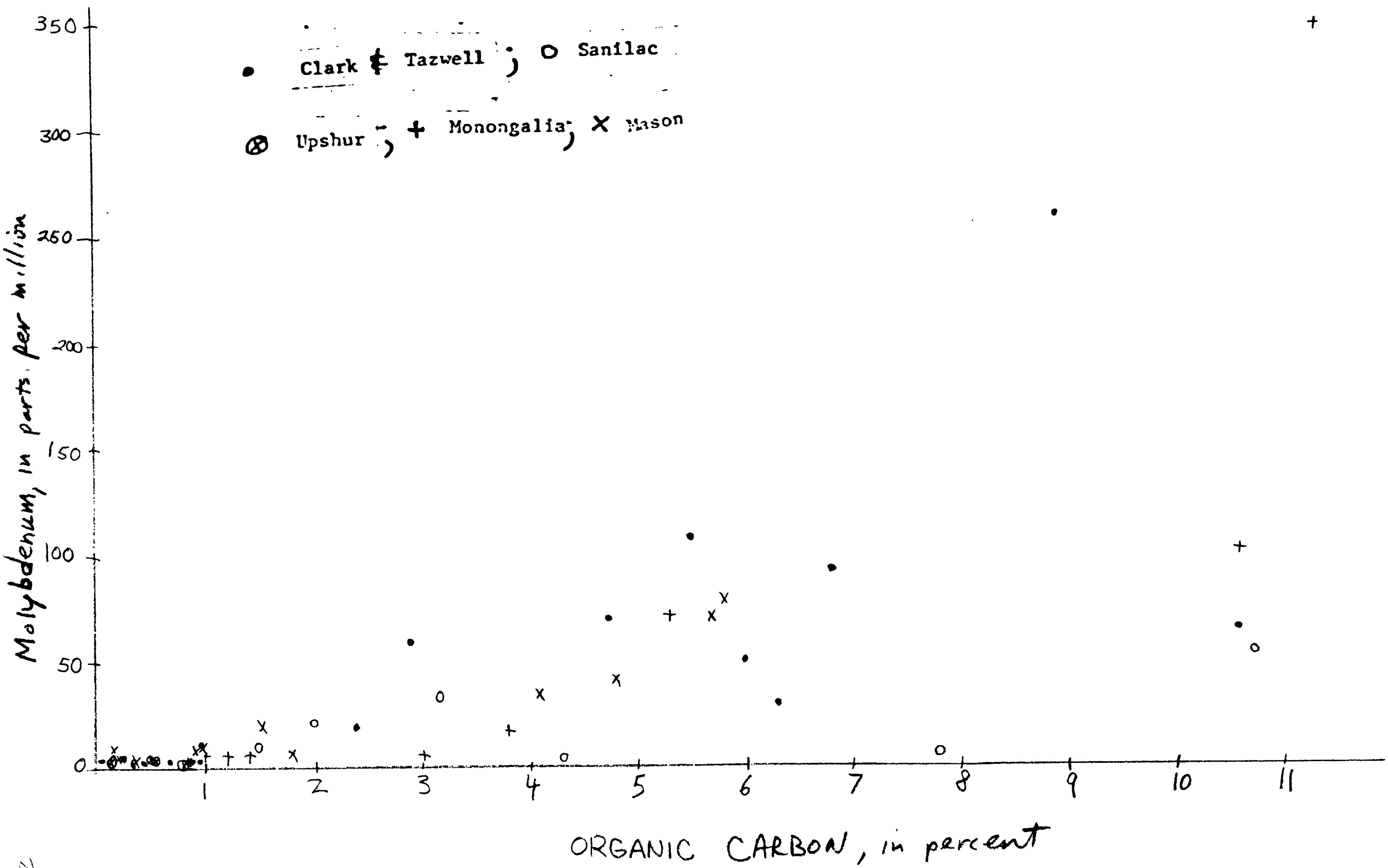


Fig. 8

Figure 8. Organic carbon vs vanadium for 6 cores. (Mason 31K2 off scale)

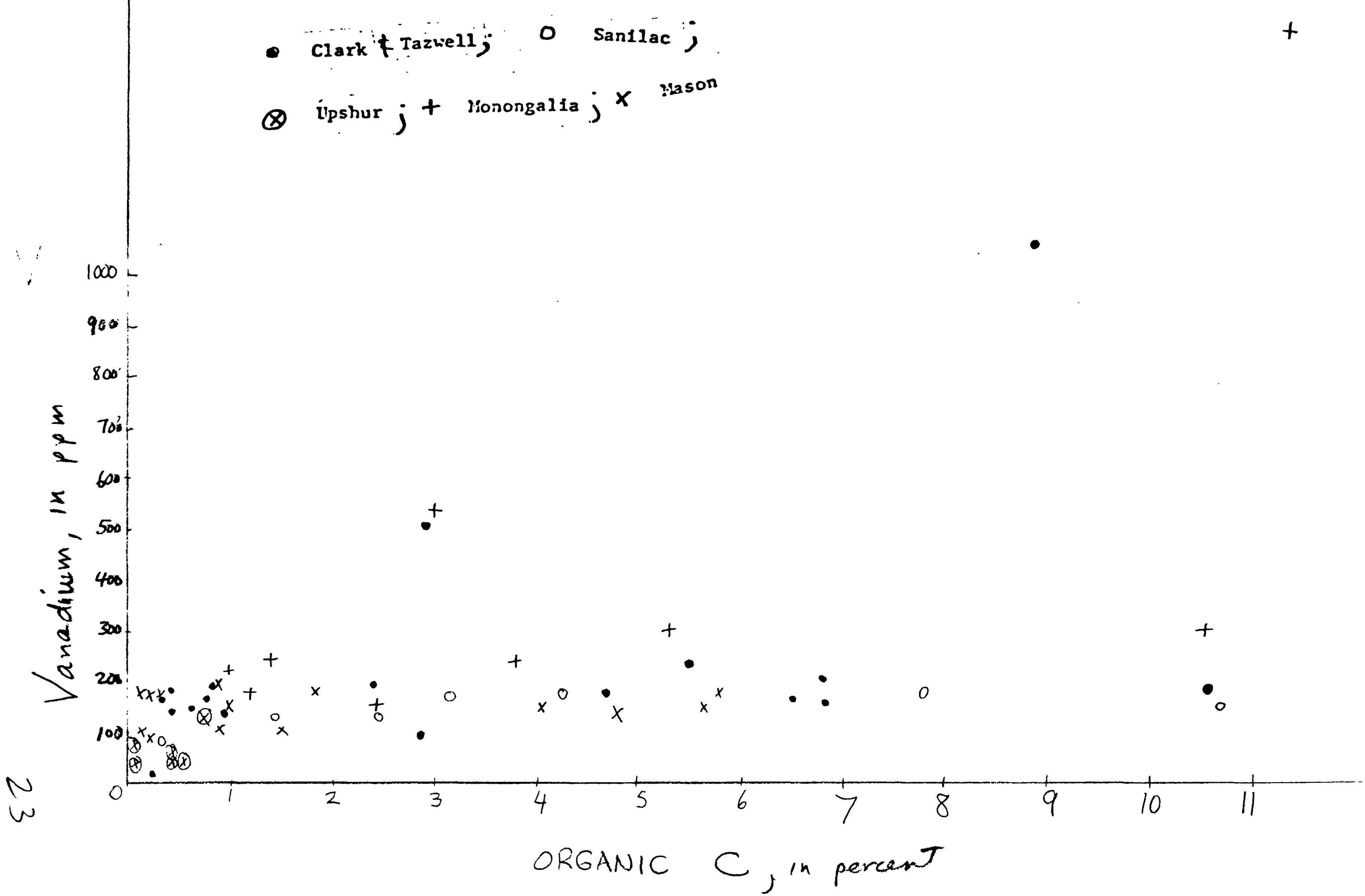


Fig. 9

Figure 9. Organic carbon vs nickel for 6 cores. (Mason 3142 c/o ...)

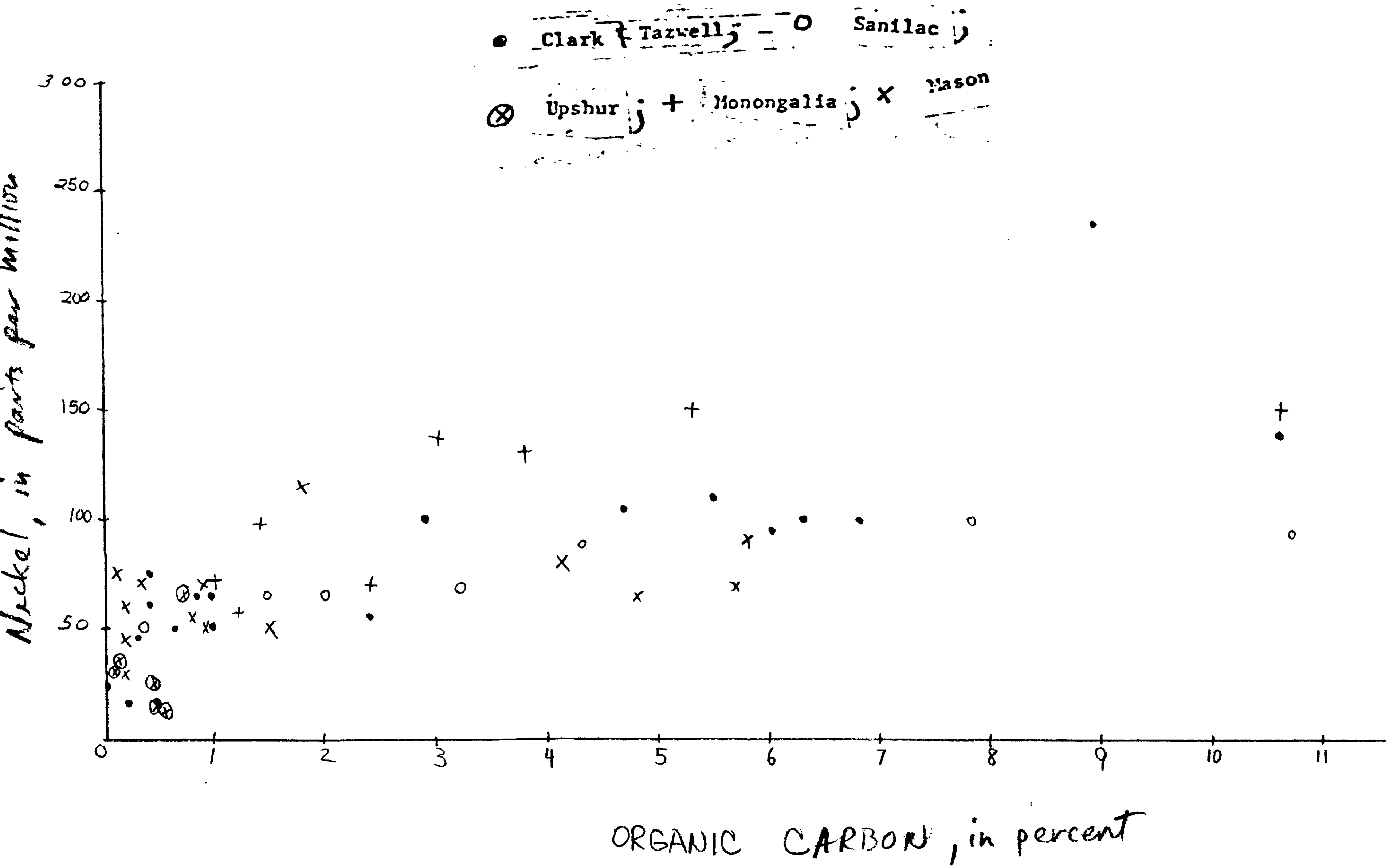
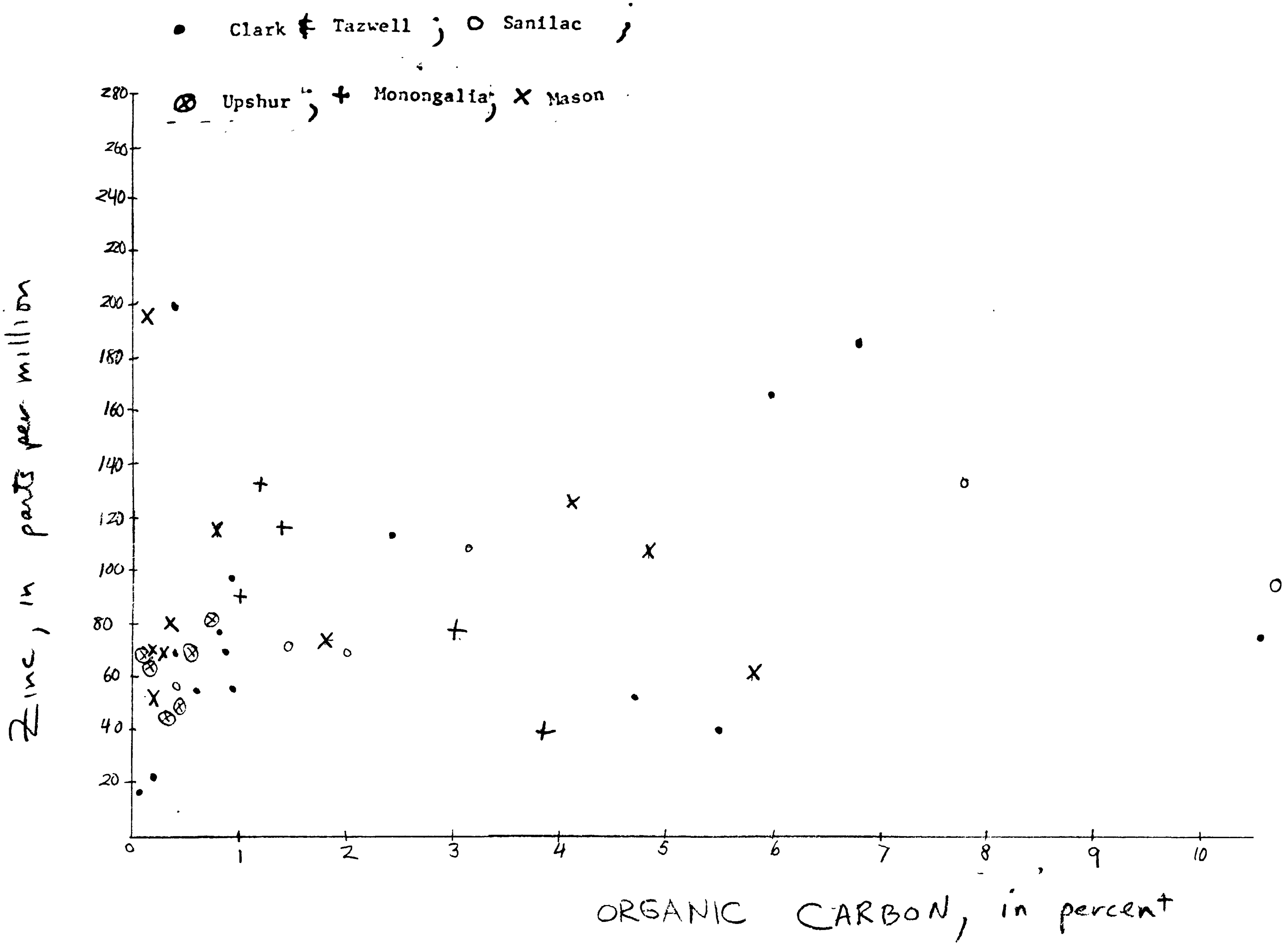


Figure 10. Organic carbon vs zinc for 6 cores. (4 samples off scale)



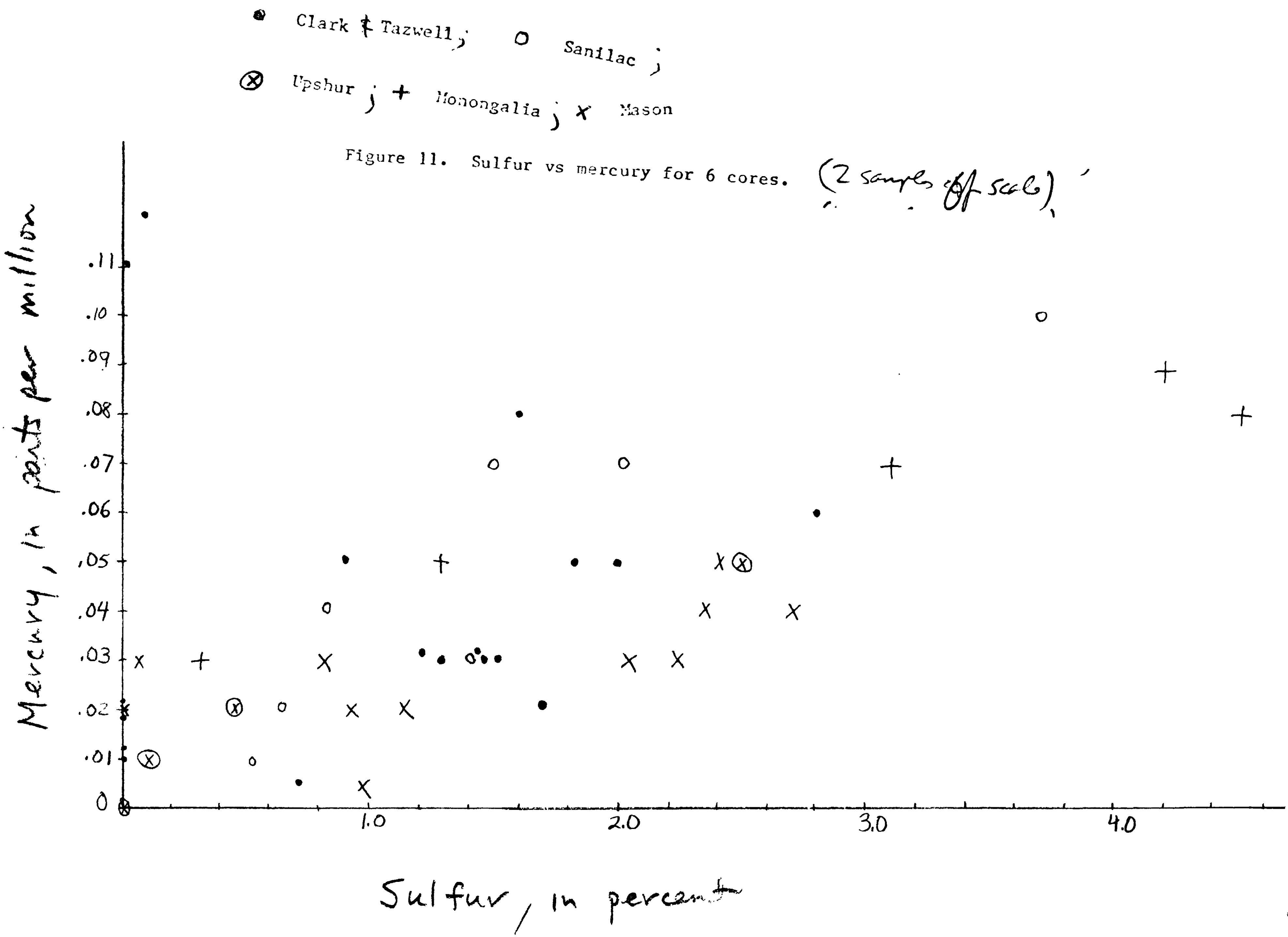


Figure 11. Sulfur vs mercury for 6 cores. (2 samples off scale)

Figure 12. Sulfur vs arsenic for 4 cores. (1 sample off scale)

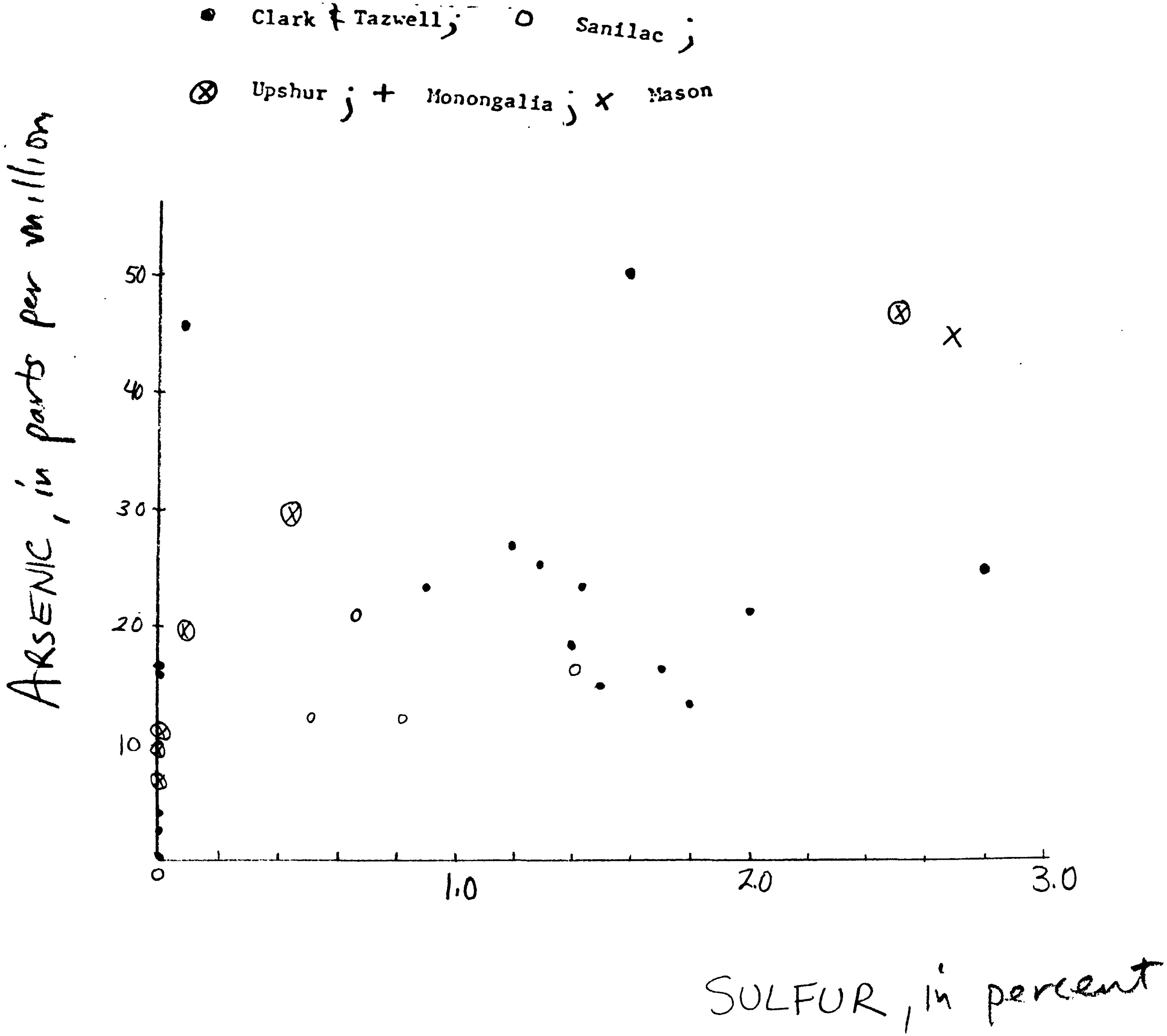


Figure 13. Sulfur vs nickel for 6 cores. (Antrim- 1431 off scale)

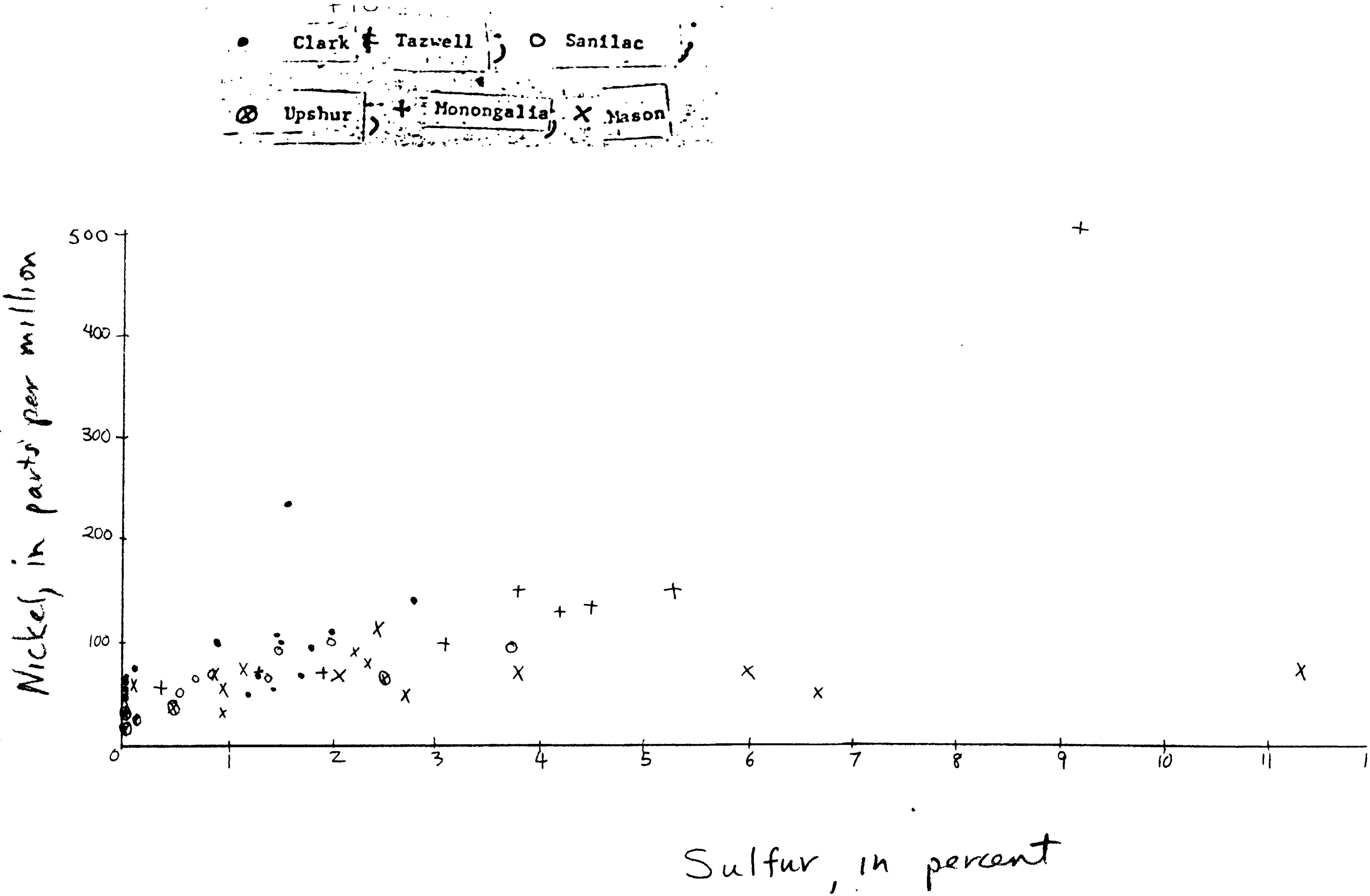


Figure 14. Sulfur vs zinc for 6 cores. (2 samples not plotted)

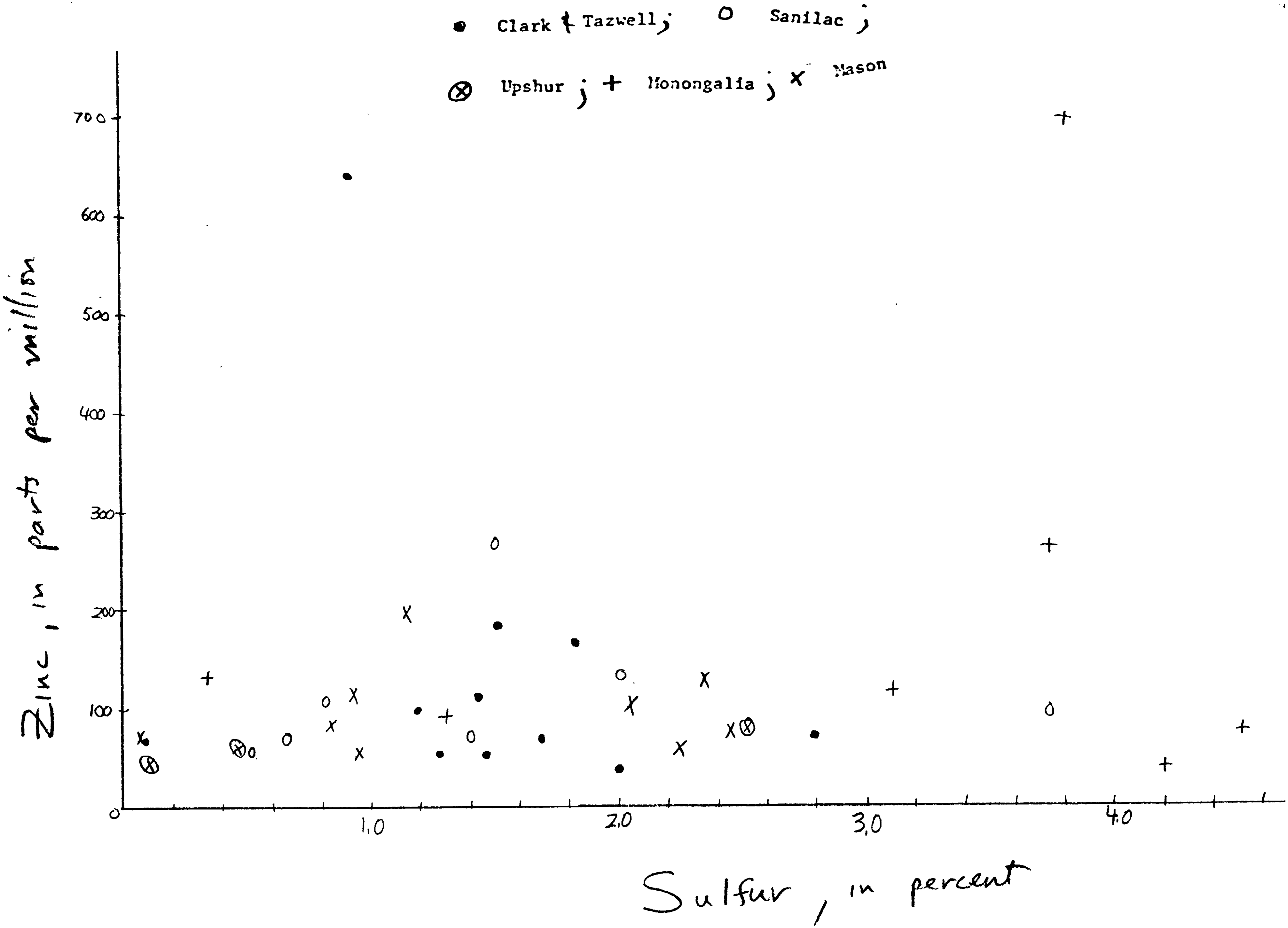
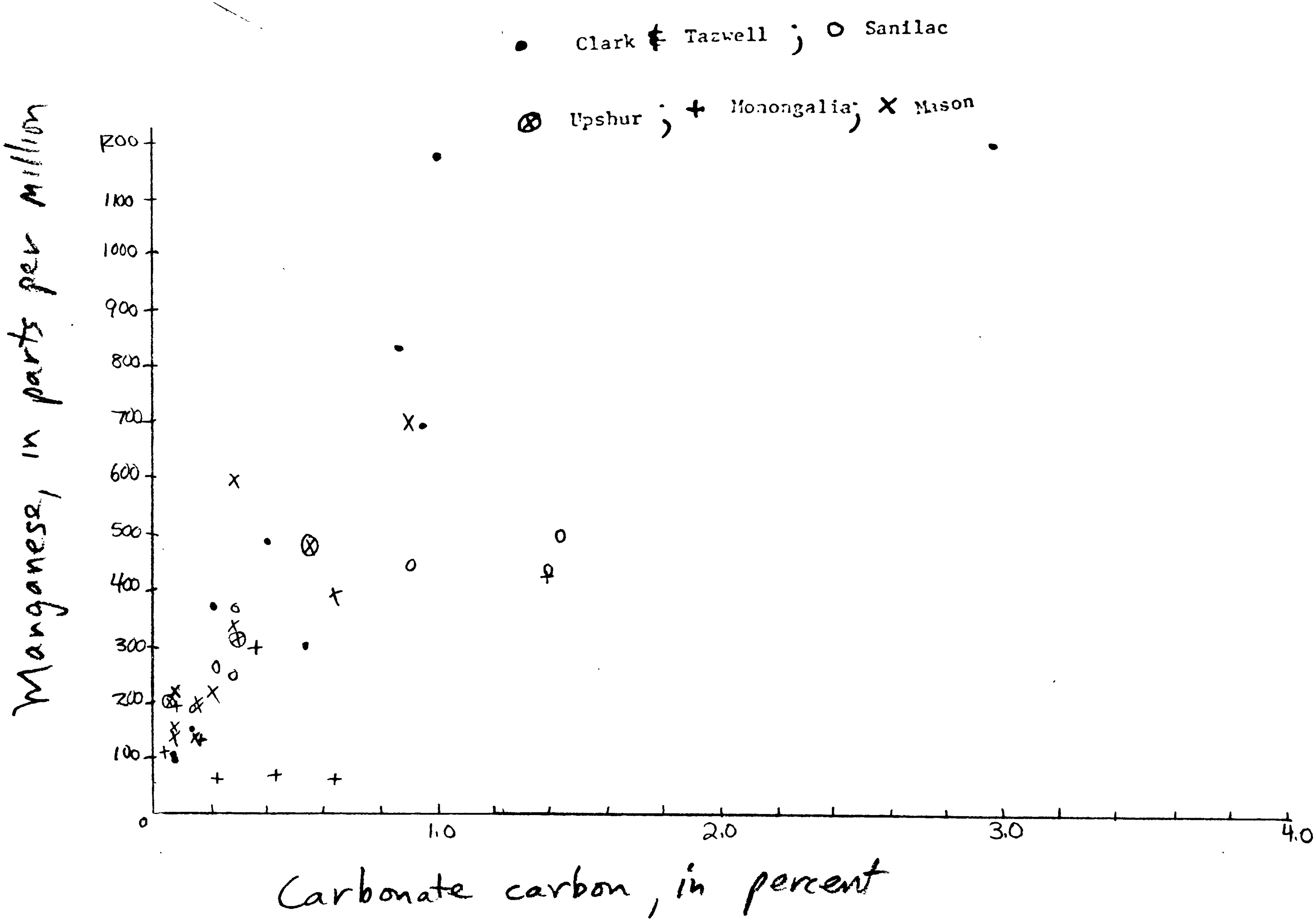


Figure 15. Carbonate carbon vs manganese for 6 cores.



striking differences due to the geographic sedimentary basin; it is not clear however whether or not this is necessarily due to a water connection between the Appalachian, Illinois, and Michigan Basins. It may be that depositional processes are similar and this overrides any difference in source rock chemistry. It is also not obvious that the deep burial and heating with resulting oil and gas generation in one of the cores has caused large changes in the trace elements, even volatile elements (such as Hg) are not apparently affected. This may be because the volatile elements (Hg, As, S) are in the pyrite which is not greatly affected by heating in a non-oxidizing environment.

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