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Quantitative analysis versus semiquantitative optical-emission spectrographic analysis of chromium, nickel, zinc, vanadium, and molybdenum in organic-rich Paleozoic marine strata, Western United States

By

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ABSTRACT

Comparison of analytical results between the quantitative method and the semiquantitative six-step optical-emission spectrographic method commonly shows significantly lower values for the semiquantitative method. The lower values are most obvious for splits from the same samples of fine-grained organic-rich rocks where the concentrations of the metals chromium, nickel, zinc, vanadium, and molybdenum are greater than about 200 ppm (parts per million). Samples compared are Paleozoic marine rocks from the Western United States; they include the Permian Phosphoria Formation (Idaho, Montana, Utah, Wyoming), Mississippian Chainman Shale (Nevada and Utah), Mississippian Heath Formation (Montana), Mississippian Doughnut Formation (Utah), Devonian Woodruff Formation (Nevada), and Ordovician Vinini Formation (Nevada).

The semiquantitative method consistently underestimates the concentration of the five metals studied by a factor of 1.7 to 2.7 and, thus, cannot be considered reliable for determining the concentration of metals in these rocks if the reported semiquantitative values exceed about 100 ppm. It is noteworthy that the most comprehensive analytical and statistical studies of metal concentrations in black shales of the United States have used the semiquantitative six-step optical-emission method of analysis.

INTRODUCTION

In our studies of the concentration of metals in fine-grained organic-rich Paleozoic marine rocks during the past 5 years, it was recognized that for the same sample Cr, Ni, Zn, V, and Mo values, which were determined by X-ray fluorescence, colorimetric, and atomic absorption methods, tended to be significantly higher than metal values determined by the semiquantitative optical-emission method.

This report compares quantitative and semiquantitative data for these five elements. All data used in this comparative study were obtained by analysts who were unaware of previous data collected for the same samples by other methods. Most of the data are from laboratories of the U.S. Geological Survey in Denver, but some analyses were done in commercial laboratories.

The samples and elements selected and the results evaluated herein were based solely on availability of samples, ease of acquisition of data, and data already available, none of which were obtained specifically for this report. This report, therefore, only presents the results of a preliminary study.

Five data sets are presented with each representing a suite of samples from either an individual locality, stratigraphic unit, or geographic region. For some data sets, concentrations of organic carbon were available and are included in order to evaluate the effect of organic matter on results obtained by the semiquantitative method.

Results reported for each method were obtained using separate aliquots from each sample which consisted of powdered material (about 90 percent minus 100 mesh). Thus, there may be some minor differences in quantitative values due to inhomogeneity. The quantitative results obtained for aliquots from each of 24 samples using energy-dispersive X-ray fluorescence analysis, wavelength-dispersive X-ray fluorescence analysis, and colorimetric analysis for vanadium are given in table 1. The results generally differed by less than 20 percent from one another for concentrations above 1,000 ppm, although 2 of 16 samples above concentrations of 1,000 ppm differed by 24 and 30 percent (see table 1). Some of these differences may be due to chemical inhomogeneity between the aliquots. Because there are differences of up to 100 percent between the quantitative and semiquantitative methods, differences as much as 20 percent (table 1) determined by the quantitative methods seem relatively unimportant.

The quantitative methods and analysts for each element in each data set are given in the Appendix. For the semiquantitative six-step optical-emission spectrographic method, the visual-plate reader was used, and results are reported as midpoints of geometric intervals using the numbers 1, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, 0.07, etc., and these are referred to as reporting intervals (Myers, Havens, and Dunton, 1961). The precision of a reported value is approximately plus or minus one geometric interval at the 68 percent confidence level or two geometric intervals at the 95 percent confidence level. All semiquantitative analyses were done by several individual analysts in the U.S. Geological Survey Branch of Analytical Laboratories in Denver between 1973 and 1979, and analyses of set 77 were done by a commercial laboratory.

Table 1.--Comparison of quantitative analytical results for different aliquots from the same sample for vanadium using X-ray fluorescence energy-dispersive analysis (XRF-E), X-ray fluorescence wavelength-dispersive analysis (XRF-W) and colorimetric analysis (C)

[Analysts: XRF-E, G. N. Green; XRF-W, H. L. Groves; colorimetric, G. T. Burrow]

Sample No.	Vanadium concentration (ppm) XRF-E	XRF-W	C	Percent difference in methods
NG-12-140-150	3,680		3,700	- 1
Bed 74 CC	2,170		1,900	12
Bed 75 CC	10,500		9,500	10
Carbon seam	9,360		10,000	- 7
E-b-DC	5,240		4,000	24
A-DC	230		300	-30
B-DC	260		400	-47
C-DC	730		1,000	-37
D-DC	860		900	- 5
CS-LS-1/8	7,200	7,500		- 4
77FP-122S	2,550	2,830		-11
UC-5A	2,850	2,830		1
UC-5B	2,430	2,420		1
77FP-117F	390	330		15
77FP-119F	1,150	1,260		-10
77FP-120	410	510		-24
77FP-121	2,450	2,590		- 6
77FP-123F	4,730	4,450		6
77FP-124F	940	1,150		-22
77FP-125FA	1,280	1,670		-30
77FP-126S	2,420	2,360		2
77FP-179	410	570		-39
ES-1	7,390	8,350		-13
ES-2	2,690	3,010		- 1

ANALYSIS OF DATA

Analytical results from the quantitative and semiquantitative methods for each element in each data set are given in tables 1-8 and plotted on figures 1-5. In order to compare the quantitative data (metal X) with the semiquantitative data (metal S) for each element in each sample, the quantitative data are plotted along the ordinate (metal X) and the semiquantitative data are plotted along the abscissa (metal S). For quantitative comparison of the two values, the ratio of "metal X" value to "metal S" value was computed to yield a "prime" value (for example, metal X/metal S = Metal'). This prime value provides an index for comparison of the results obtained by each method. Statistical data relating to each measured and calculated parameter and correlation of parameters are given for each data set. In the statistical tables, mean is arithmetic, deviation is standard deviation, and var refers to variable.

Set 76

Set 76 consists of 66 samples of fine-grained organic-rich marine rocks of the Permian Phosphoria Formation in Idaho, Montana, Utah, and Wyoming for which semiquantitative six-step optical-emission data were reported by Maughan (1976). Subsequently these rocks were quantitatively analyzed by X-ray fluorescence methods using prepared standards. Concentration data for organic carbon, chromium, nickel, and zinc, as well as the values of Metal' (= metal X/metal S), are given in table 2, and univariate statistics and array of number of pairs and correlation coefficients are shown in table 3.

Comparative results of quantitative data (X, plotted along the ordinate) and semiquantitative data (S, plotted along the abscissa) are shown on figure 1 for Cr, Ni, and Zn. Values of CR', NI', and ZN' versus organic-carbon

Table 2.--Set 76 concentration data for metals (ppm) determined by quantitative (metal X) and semiquantitative (metal S) methods, and organic-carbon concentration (weight percent); Metal' numbers refer to calculated value of metal X/metal S

[1.000 entries = no data]

Number	Carbon	Crx	Crs	Nix	Nis	Znx	Zns	CR'	NI'	ZN'
3272	6.900	2340.000	2000.000	140.000	70.000	580.000	300.000	1.170	2.000	1.933
3273	5.900	2180.000	1500.000	150.000	70.000	730.000	500.000	1.453	2.143	1.460
3534	1.000	1290.000	500.000	480.000	200.000	4340.000	1500.000	2.580	2.400	2.893
3536	1.600	1040.000	700.000	280.000	150.000	2450.000	1500.000	1.486	1.867	1.633
3538	2.100	1120.000	1000.000	180.000	150.000	1270.000	700.000	1.120	1.200	1.814
3539	2.300	1420.000	700.000	250.000	150.000	1800.000	1000.000	2.029	1.667	1.800
3540	2.200	1630.000	1000.000	410.000	200.000	1910.000	1000.000	1.630	2.050	1.910
3541	2.900	2220.000	1500.000	570.000	300.000	2160.000	1500.000	1.480	1.900	1.440
3542	5.000	2550.000	2000.000	460.000	200.000	1650.000	700.000	1.275	2.300	2.357
3545	3.500	2970.000	2000.000	80.000	50.000	260.000	100.000	1.485	1.600	2.600
3546	7.100	2430.000	1500.000	440.000	200.000	3000.000	1500.000	1.620	2.200	2.000
3547	5.200	3390.000	2000.000	410.000	200.000	2690.000	1500.000	1.695	2.050	1.793
3548	2.000	2010.000	1000.000	280.000	150.000	1820.000	1000.000	2.010	1.867	1.820
3555	30.700	18900.000	5000.000	950.000	300.000	240.000	100.000	3.780	3.167	2.400
3725	1.000	2510.000	1500.000	240.000	150.000	930.000	600.000	1.673	1.600	1.550
3726	2.500	2300.000	1500.000	250.000	150.000	1050.000	700.000	1.533	1.667	1.500
3729	3.500	2850.000	2000.000	350.000	200.000	1290.000	700.000	1.425	1.750	1.843
3734	2.700	1670.000	1500.000	150.000	100.000	2580.000	1500.000	1.113	1.500	1.720
3745	0.500	1250.000	1500.000	130.000	150.000	850.000	700.000	0.833	0.867	1.214
3748	1.000	1460.000	1500.000	250.000	150.000	1330.000	700.000	0.973	1.667	1.900
3752	2.700	1.000	1.000	450.000	200.000	5340.000	1500.000	1.000	2.250	3.560
3753	1.400	1460.000	1500.000	270.000	150.000	2850.000	1500.000	0.973	1.800	1.900
3754	0.050	700.000	1000.000	120.000	100.000	1440.000	1000.000	0.700	1.200	1.440
3760	1.700	790.000	1500.000	70.000	70.000	820.000	700.000	0.527	1.000	1.171
3761	1.200	830.000	1000.000	170.000	100.000	1400.000	700.000	0.830	1.700	2.000
3762	2.000	870.000	1000.000	120.000	100.000	960.000	700.000	0.870	1.200	1.371
3763	1.800	830.000	1000.000	90.000	100.000	750.000	700.000	0.830	0.900	1.071
3765	2.100	1080.000	2000.000	190.000	150.000	980.000	700.000	0.540	1.267	1.400
3767	4.000	3180.000	2000.000	450.000	200.000	1930.000	1000.000	1.590	2.250	1.930
3768	6.200	4700.000	3000.000	690.000	300.000	2800.000	1500.000	1.567	2.300	1.867
3769	4.400	3600.000	2000.000	390.000	200.000	1730.000	1000.000	1.800	1.950	1.730
3771	2.200	2970.000	1500.000	400.000	200.000	1780.000	1000.000	1.980	2.000	1.780
3773	6.400	4070.000	3000.000	690.000	300.000	2250.000	1500.000	1.357	2.300	1.500
3774	9.200	4150.000	2000.000	430.000	150.000	1290.000	700.000	2.075	2.867	1.843
3778	8.200	1710.000	1000.000	420.000	150.000	1940.000	1000.000	1.710	2.800	1.940
3779	7.800	2130.000	1000.000	160.000	70.000	260.000	200.000	2.130	2.286	1.300
3780	12.200	2600.000	1500.000	690.000	200.000	3180.000	1500.000	1.733	3.450	2.120
3781	10.800	1.000	1.000	500.000	200.000	2670.000	1500.000	1.000	2.500	1.780
3783	9.100	2970.000	2000.000	190.000	70.000	1160.000	700.000	1.485	2.714	1.657
3784	4.300	2810.000	2000.000	320.000	150.000	2710.000	1500.000	1.405	2.133	1.807
3785	1.500	1590.000	1500.000	140.000	70.000	1400.000	1500.000	1.060	2.000	0.933
3786	2.300	2340.000	1500.000	470.000	150.000	2690.000	1500.000	1.560	3.133	1.793
3799	1.700	960.000	1000.000	160.000	150.000	1470.000	1500.000	0.960	1.067	0.980
3800	1.600	1040.000	1000.000	350.000	200.000	1580.000	1500.000	1.040	1.750	1.053
3801	4.400	2340.000	2000.000	420.000	300.000	1760.000	1500.000	1.170	1.400	1.173
3805	1.200	1630.000	1500.000	70.000	30.000	710.000	1000.000	1.087	2.333	0.710
3878	11.900	4990.000	3000.000	870.000	300.000	4340.000	2000.000	1.663	2.900	2.170
3880	11.600	3270.000	1500.000	1010.000	300.000	10690.000	5000.000	2.180	3.367	2.138
3883	6.700	2300.000	1500.000	220.000	150.000	1980.000	1500.000	1.533	1.467	1.320
3887	6.800	2550.000	1500.000	270.000	150.000	1560.000	1500.000	1.700	1.800	1.040
3889	6.800	1.000	1.000	300.000	150.000	1630.000	1500.000	1.000	2.000	1.087
3910	5.200	4820.000	3000.000	440.000	200.000	2670.000	1500.000	1.607	2.200	1.780
3913	5.300	3180.000	3000.000	410.000	150.000	2670.000	1500.000	1.060	2.733	1.780
3914	2.100	1630.000	1500.000	320.000	100.000	2090.000	1500.000	1.087	3.200	1.393
3917	2.400	1760.000	1000.000	210.000	100.000	1380.000	700.000	1.760	2.100	1.971
3918	0.400	230.000	100.000	100.000	30.000	890.000	700.000	2.300	3.333	1.271
3919	2.600	3020.000	1500.000	220.000	100.000	1560.000	1000.000	2.013	2.200	1.560
3921	1.700	1760.000	1000.000	210.000	100.000	1690.000	1000.000	1.760	2.100	1.690
4018	5.800	1170.000	1500.000	150.000	100.000	870.000	700.000	0.780	1.500	1.243
4022	12.800	2340.000	1500.000	480.000	200.000	1.000	0.000	1.560	2.400	0.000
4023	7.800	1550.000	1000.000	230.000	150.000	1560.000	1500.000	1.550	1.533	1.040
4032	18.900	3310.000	1000.000	450.000	150.000	1310.000	700.000	3.310	3.000	1.871
4033	19.000	3100.000	1500.000	480.000	150.000	1310.000	700.000	2.067	3.200	1.871
4042	21.400	3860.000	1500.000	360.000	150.000	840.000	700.000	2.573	2.400	1.200
4043	18.800	3180.000	1000.000	320.000	150.000	870.000	700.000	3.180	2.133	1.243
3798	12.000	3100.000	1000.000	570.000	150.000	1470.000	700.000	3.100	3.800	2.100

Table 3.--Set 76 data univariate statistics and array of number of pairs and correlation coefficients

Univariate Statistics

Var	Column	Minimum	Maximum	Mean	Deviation
1	Carbon	5.000E-02	3.070E+01	5.758E+00	5.8024E+00
2	Crx	1.000E+00	1.890E+04	2.424E+03	2.3622E+03
3	Crs	1.000E+00	5.000E+03	1.500E+03	8.0126E+02
4	Nix	7.000E+01	1.010E+03	3.408E+02	2.0551E+02
5	Nis	3.000E+01	3.000E+02	1.573E+02	6.7221E+01
6	Znx	1.000E+00	1.069E+04	1.851E+03	1.4800E+03
7	Zns	0.000E+00	5.000E+03	1.091E+03	6.6511E+02
8	CR'	5.270E-01	3.780E+00	1.563E+00	6.5081E-01
9	NI'	8.670E-01	3.800E+00	2.112E+00	6.6373E-01
10	ZN'	0.000E+00	3.560E+00	1.654E+00	5.2017E-01

Array of Number of Pairs and Correlation Coefficients

	1	2	3	4	5	6	7	8	9	10
1	1.00	0.67	0.36	0.56	0.32	-0.01	-0.07	0.68	0.54	0.07
2	66	1.00	0.80	0.57	0.43	-0.05	-0.11	0.59	0.37	0.22
3	66	66	1.00	0.44	0.42	-0.04	-0.04	0.16	0.16	0.10
4	66	66	66	1.00	0.85	0.59	0.48	0.47	0.63	0.40
5	66	66	66	66	1.00	0.49	0.45	0.22	0.20	0.26
6	66	66	66	66	66	1.00	0.91	0.04	0.32	0.46
7	66	66	66	66	66	66	1.00	0.07	0.20	0.14
8	66	66	66	66	66	66	66	1.00	0.60	0.25
9	66	66	66	66	66	66	66	66	1.00	0.32
10	66	66	66	66	66	66	66	66	66	1.00

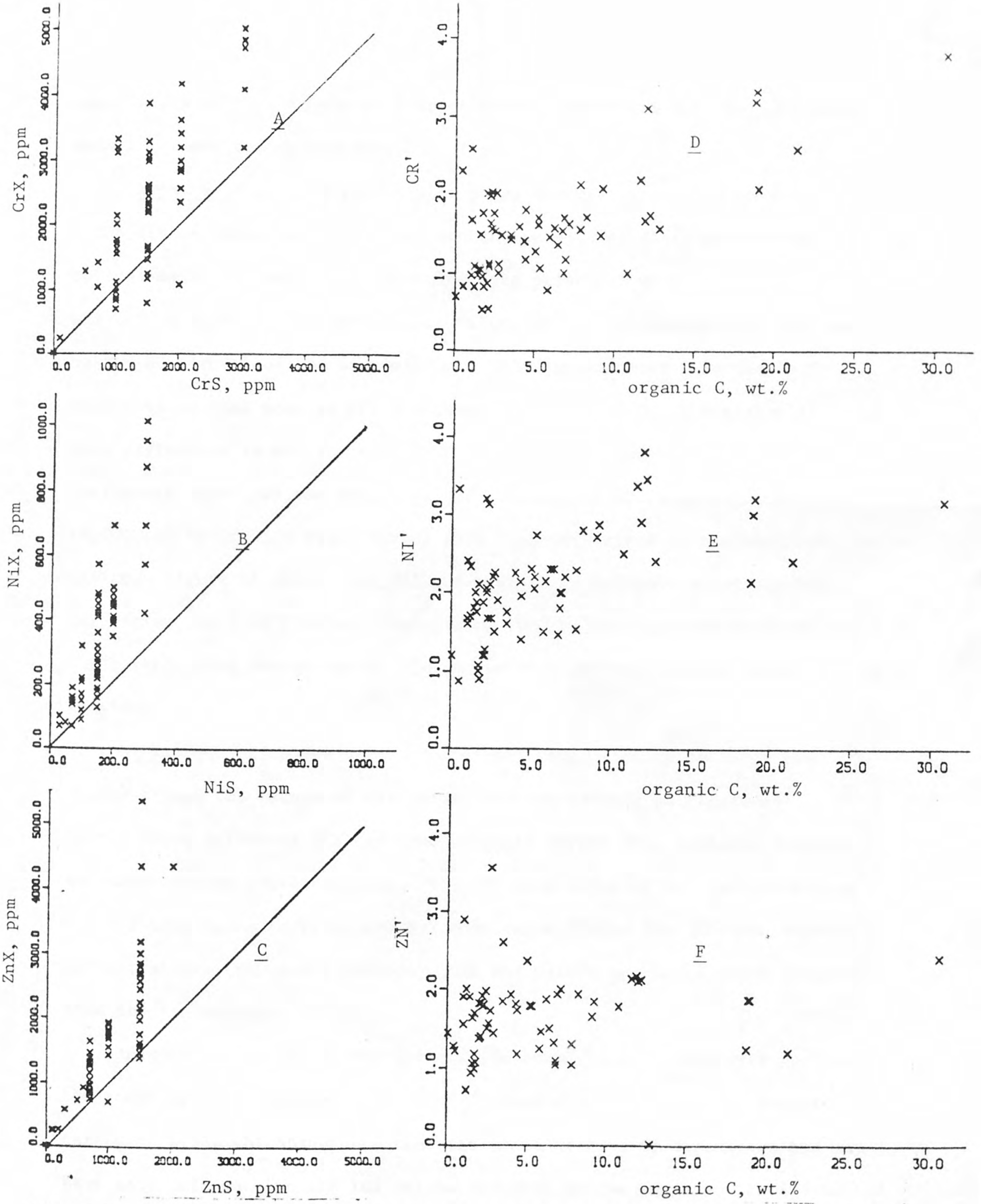

Figure 1.--Graphic illustration of set 76 data showing plots of: A, CrX versus CrS; B, NiX versus NiS; C, ZnX versus ZnS; D, CR' versus organic C; E, NI' versus organic C; F, ZN' versus organic C; Metal' = metal X/metal S.

content are plotted in figure 1 to determine whether or not the semiquantitative data are lower due to the presence of organic carbon.

Chromium--Figure 1A graphically shows concentration data obtained by X-ray fluorescence analysis (CrX) and the results of semiquantitative optical-emission analysis (CrS). One data point for which CrX is 18,000 ppm and CrS is 5,000 ppm is not shown. Values of CrX are higher than CrS for nearly 80 percent of the samples. The CR' mean value of 1.56 (table 3) demonstrates that most of the quantitative-method values are higher although this difference is within only two reporting intervals at the 95 percent confidence level for the semiquantitative method. The sample containing 18,000 ppm CR' is 3.6 times higher than that determined by the semiquantitative method. Figure 1D shows that CR' and organic carbon have a correlation coefficient of 0.68 (table 3) indicating that underestimates obtained by the semiquantitative method may be due to the influence of organic carbon in the samples.

Nickel--Quantitative values for nickel range from 70 to 1,010 ppm (table 2) and the values of NiX versus NiS are plotted on figure 1B. Quantitative values of NiX are significantly larger than semiquantitative values at higher concentrations. The NI' mean value of 2.1 indicates that the NiX mean value is twice the NiS mean value (table 3). For the highest concentrations (900 and 1,000 ppm), the NiX values are three times greater than the NiS values.

Agreement between the two methods, however, is generally very good in the range of 70 to 150 ppm. Correlation coefficient of NI' with organic carbon is 0.54, which suggests that the concentration of organic carbon may have some influence on the low values obtained by the semiquantitative method.

Zinc--Data for ZnX versus ZnS are plotted on figure 1C. One ZnX value of 10,000 ppm and ZnS value of 5,000 ppm is not shown on the figure (see table 2). The ZnX mean value for this data set is about 1.8 times greater than the ZnS value (table 3), which is within only two reporting intervals or the 95 percent confidence level of the semiquantitative method. Agreement between the two analytical methods is better below about 2,000 ppm Zn. Figure 1F shows that the ZN' value cannot be considered a simple function of the organic-carbon concentration in the samples because the correlation coefficient is only 0.07 for these two parameters.

Set 77

Samples in Set 77 are from the Meade Peak Member of the Phosphoria Formation at the Mabie Canyon Mine about 30 km northeast of Soda Springs in southeastern Idaho (Desborough, 1977). The semiquantitative analyses were done by a commercial laboratory, and the data are given in table 4.

Chromium--The range of chromium concentration is 2,500 to 4,000 ppm, and the data are plotted on figure 2A. The CrX mean is more than twice the CrS mean, and the CR' mean value is 2.9 (table 4) demonstrating that the quantitative results are much higher than the semiquantitative results. There is little apparent correlation between the CR' values and organic-carbon concentration.

Nickel--Concentration of nickel is 300 to 600 ppm and the NiX and NiS values are plotted on figure 2B. The NiX mean value is twice that of NiS, as shown on table 4. However, all the semiquantitative values are within two reporting intervals for the method (for example, 150, 200, 300, 500 ppm). There is no apparent correlation of NI' with organic-carbon concentration (table 4, fig. 2E).

Table 4.--Set 77 concentration and statistical data for metals (ppm) determined by quantitative (metal X) and semiquantitative (metal S) methods, and organic-carbon concentration (weight percent); Metal' numbers refer to calculated value of metal X/metal S

Number	Carbon	Crx	Crs	Nix	Nis	Znx	Zns	CR'	NI'	ZN'
e1	4.100	4000.000	700.000	300.000	150.000	1300.000	700.000	5.714	2.000	1.857
e2	4.100	3600.000	1000.000	400.000	150.000	1300.000	500.000	3.600	2.667	2.600
e3	3.500	2500.000	1000.000	300.000	200.000	900.000	500.000	2.500	1.500	1.800
e4	4.200	3800.000	1500.000	400.000	200.000	900.000	500.000	2.533	2.000	1.800
e5	1.900	2600.000	700.000	400.000	200.000	900.000	500.000	3.714	2.000	1.800
c1	5.000	2800.000	1500.000	500.000	200.000	1600.000	1000.000	1.867	2.500	1.600
c2	7.500	4000.000	1500.000	600.000	300.000	1900.000	700.000	2.667	2.000	2.714
c3	6.800	3600.000	1500.000	600.000	300.000	2000.000	1000.000	2.400	2.000	2.000
c4	4.100	2900.000	1500.000	600.000	300.000	1900.000	1000.000	1.933	2.000	1.900
c5	5.900	3000.000	1500.000	500.000	300.000	1400.000	700.000	2.000	1.667	2.000

Univariate Statistics

Var	Column	Minimum	Maximum	Mean	Deviation	Valid
1	Carbon	1.900E+00	7.500E+00	4.710E+00	1.6462E+00	10
2	Crx	2.500E+03	4.000E+03	3.280E+03	5.8080E+02	10
3	Crs	7.000E+02	1.500E+03	1.240E+03	3.5024E+02	10
4	Nix	3.000E+02	6.000E+02	4.600E+02	1.1738E+02	10
5	Nis	1.500E+02	3.000E+02	2.300E+02	6.3246E+01	10
6	Znx	9.000E+02	2.000E+03	1.410E+03	4.3063E+02	10
7	Zns	5.000E+02	1.000E+03	7.100E+02	2.1833E+02	10
8	CR'	1.867E+00	5.714E+00	2.893E+00	1.1777E+00	10
9	NI'	1.500E+00	2.667E+00	2.033E+00	3.4069E-01	10
10	ZN'	1.600E+00	2.714E+00	2.007E+00	3.6205E-01	10

Array of Number of Pairs and Correlation Coefficients

	1	2	3	4	5	6	7	8	9	10
1	1.00	0.51	0.70	0.68	0.65	0.75	0.48	-0.36	-0.01	0.48
2	10	1.00	0.11	0.10	-0.04	0.28	-0.03	0.42	0.26	0.54
3	10	10	1.00	0.77	0.72	0.59	0.56	-0.83	0.00	0.08
4	10	10	10	1.00	0.85	0.87	0.71	-0.62	0.13	0.30
5	10	10	10	10	1.00	0.68	0.54	-0.65	-0.40	0.18
6	10	10	10	10	10	1.00	0.84	-0.32	0.21	0.34
7	10	10	10	10	10	10	1.00	-0.39	0.17	-0.21
8	10	10	10	10	10	10	10	1.00	0.13	0.09
9	10	10	10	10	10	10	10	10	1.00	0.27
10	10	10	10	10	10	10	10	10	10	1.00

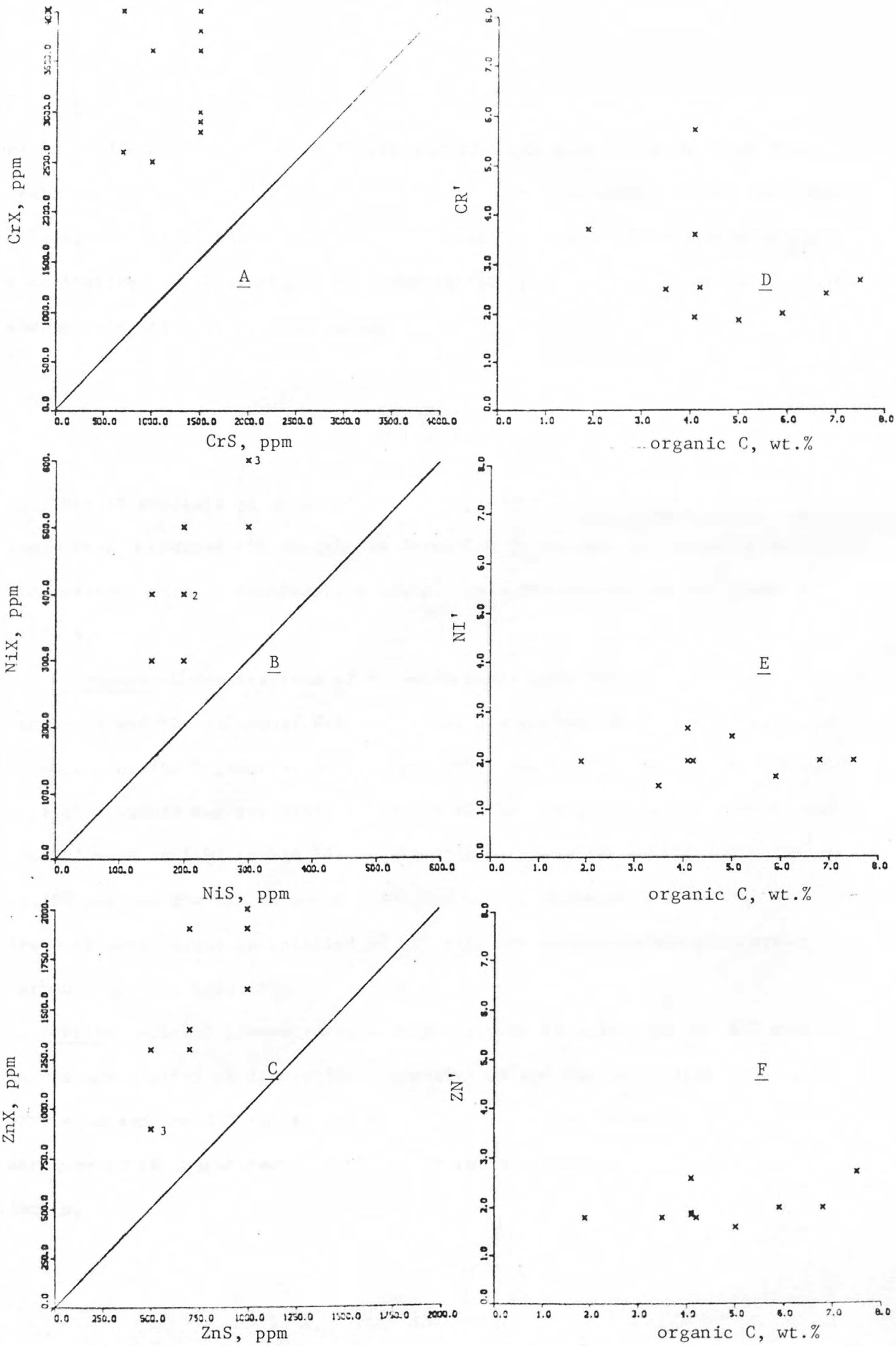

Figure 2.--Data set 77 plots of metal X (ppm) versus metal S (ppm), and Metal' versus organic C (weight percent).

Zinc--Concentrations of zinc range from 900 to 2,000 ppm and the values of ZnX and ZnS are plotted on figure 2C. The ZnX mean value is twice ZnS (table 4). The ZnX values are systematically and distinctly higher than ZnS values, but all of the ZnS values are within two reporting intervals of the quantitative results. Figure 2F shows little apparent correlation of ZN' with the concentration of organic carbon.

Set 78

Set 78 consists of 31 samples that represent each lithologic unit in the Meade Peak Member of the Phosphoria Formation in an adit at Pritchard Creek in the Caribou Range of southeastern Idaho. Data and statistics are given in table 5.

Chromium--Concentrations of chromium range from 100 to 11,700 ppm (table 5) and the values of CrX versus CrS are plotted on figure 3A with the exception of the highest value (11,700 ppm). Differences in CrX and CrS are generally within two reporting intervals of the semiquantitative method, and the CR' mean is 1.97 (table 5). A significant exception is the CrX value of 11,700 ppm and the CrS value of 1,500 ppm with a difference factor of 7.8. There is no apparent correlation of CR' with the concentration of organic carbon (fig. 3D, table 5).

Nickel--Nickel concentrations range from 20 to 1,380 ppm and NiX and NiS values are plotted on figure 3B. Agreement of the two analytical methods is very good and the NiS values are within one reporting interval of the results obtained by the quantitative method. There is no correlation with organic carbon.

Table 5.--Set 78 concentration and statistical data for metals (ppm) determined by quantitative (metal X) and semiquantitative (metal S) methods, and organic-carbon concentration (weight percent); Metal' numbers refer to calculated value of metal X/metal S

Number	Carbon	Crx	Crs	Nix	Nis	Mox	Mos	CR'	NI'	MO'
d	7.000	1200.000	500.000	280.000	200.000	280.000	100.000	2.400	1.400	2.800
e	4.100	1100.000	300.000	90.000	100.000	190.000	50.000	3.667	0.900	3.800
f	2.000	300.000	150.000	20.000	30.000	20.000	15.000	2.000	0.667	1.333
g	2.400	100.000	150.000	20.000	30.000	25.000	15.000	0.667	0.667	1.667
h	4.100	600.000	200.000	130.000	150.000	10.000	30.000	3.000	0.867	0.333
j	5.600	200.000	700.000	200.000	150.000	25.000	70.000	0.286	1.333	0.357
k	5.500	1400.000	700.000	320.000	200.000	30.000	50.000	2.000	1.600	0.600
l	4.400	500.000	150.000	120.000	70.000	40.000	30.000	3.333	1.714	1.333
m	5.200	400.000	700.000	200.000	150.000	25.000	30.000	0.571	1.333	0.833
n	5.900	700.000	1000.000	210.000	200.000	25.000	50.000	0.700	1.050	0.500
p	14.000	6700.000	3000.000	700.000	500.000	210.000	100.000	2.233	1.400	2.100
q	5.500	300.000	500.000	100.000	70.000	10.000	15.000	0.600	1.429	0.667
r	11.000	1000.000	1500.000	310.000	300.000	100.000	100.000	0.667	1.033	1.000
s	9.200	2000.000	1000.000	340.000	200.000	60.000	50.000	2.000	1.700	1.200
t	9.800	2100.000	1500.000	360.000	300.000	40.000	70.000	1.400	1.200	0.571
u	21.700	6400.000	3000.000	1380.000	1500.000	870.000	700.000	2.133	0.920	1.243
v	9.300	1500.000	1000.000	400.000	300.000	200.000	150.000	1.500	1.333	1.333
w	22.800	6900.000	3000.000	1100.000	700.000	370.000	200.000	2.300	1.571	1.850
x	3.700	300.000	150.000	30.000	30.000	40.000	15.000	2.000	1.000	2.667
y	2.500	100.000	150.000	30.000	30.000	28.000	15.000	0.667	1.000	1.867
z	9.800	11700.000	1500.000	340.000	300.000	660.000	100.000	7.800	1.133	6.600
aa	7.600	500.000	300.000	80.000	70.000	10.000	20.000	1.667	1.143	0.500
bb	17.900	3600.000	3000.000	920.000	700.000	370.000	150.000	1.200	1.314	2.467
cc	4.100	800.000	100.000	30.000	30.000	20.000	10.000	8.000	1.000	2.000
dd	8.300	4800.000	1500.000	380.000	300.000	170.000	70.000	3.200	1.267	2.429
ee	7.700	100.000	700.000	780.000	500.000	40.000	150.000	0.143	1.560	0.267
ff	10.500	2000.000	1500.000	450.000	500.000	230.000	150.000	1.333	0.900	1.533
gg	3.400	100.000	300.000	160.000	100.000	120.000	70.000	0.333	1.600	1.714
hh	1.300	500.000	1000.000	20.000	20.000	20.000	15.000	0.500	1.000	1.333
jj	3.600	1000.000	1000.000	100.000	100.000	10.000	30.000	1.000	1.000	0.333
kk	1.900	1200.000	700.000	40.000	50.000	45.000	15.000	1.714	0.800	3.000

Univariate Statistics

Var	Column	Minimum	Maximum	Mean	Deviation	Valid
1	Carbon	1.300E+00	2.280E+01	7.477E+00	5.4354E+00	31
2	Crx	1.000E+02	1.170E+04	1.939E+03	2.6789E+03	31
3	Crs	1.000E+02	3.000E+03	9.984E+02	9.0797E+02	31
4	Nix	2.000E+01	1.380E+03	3.110E+02	3.3799E+02	31
5	Nis	2.000E+01	1.500E+03	2.542E+02	3.0036E+02	31
6	Mox	1.000E+01	8.700E+02	1.385E+02	1.9953E+02	31
7	Mos	1.000E+01	7.000E+02	8.500E+01	1.2534E+02	31
8	CR'	1.430E-01	8.000E+00	1.968E+00	1.8462E+00	31
9	NI'	6.670E-01	1.714E+00	1.188E+00	2.9753E-01	31
10	MO'	2.670E-01	6.600E+00	1.620E+00	1.2881E+00	31

Array of Number of Pairs and Correlation Coefficients

	1	2	3	4	5	6	7	8	9	10
1	1.00	0.68	0.90	0.93	0.88	0.73	0.74	0.06	0.27	0.08
2	31	1.00	0.72	0.61	0.58	0.81	0.48	0.51	0.11	0.61
3	31	31	1.00	0.86	0.82	0.68	0.64	-0.02	0.17	0.13
4	31	31	31	1.00	0.95	0.73	0.83	-0.04	0.30	0.01
5	31	31	31	31	1.00	0.81	0.94	-0.01	0.10	0.01
6	31	31	31	31	31	1.00	0.82	0.35	-0.00	0.52
7	31	31	31	31	31	31	1.00	-0.01	0.01	0.00
8	31	31	31	31	31	31	31	1.00	-0.09	0.64
9	31	31	31	31	31	31	31	31	1.00	-0.15
10	31	31	31	31	31	31	31	31	31	1.00

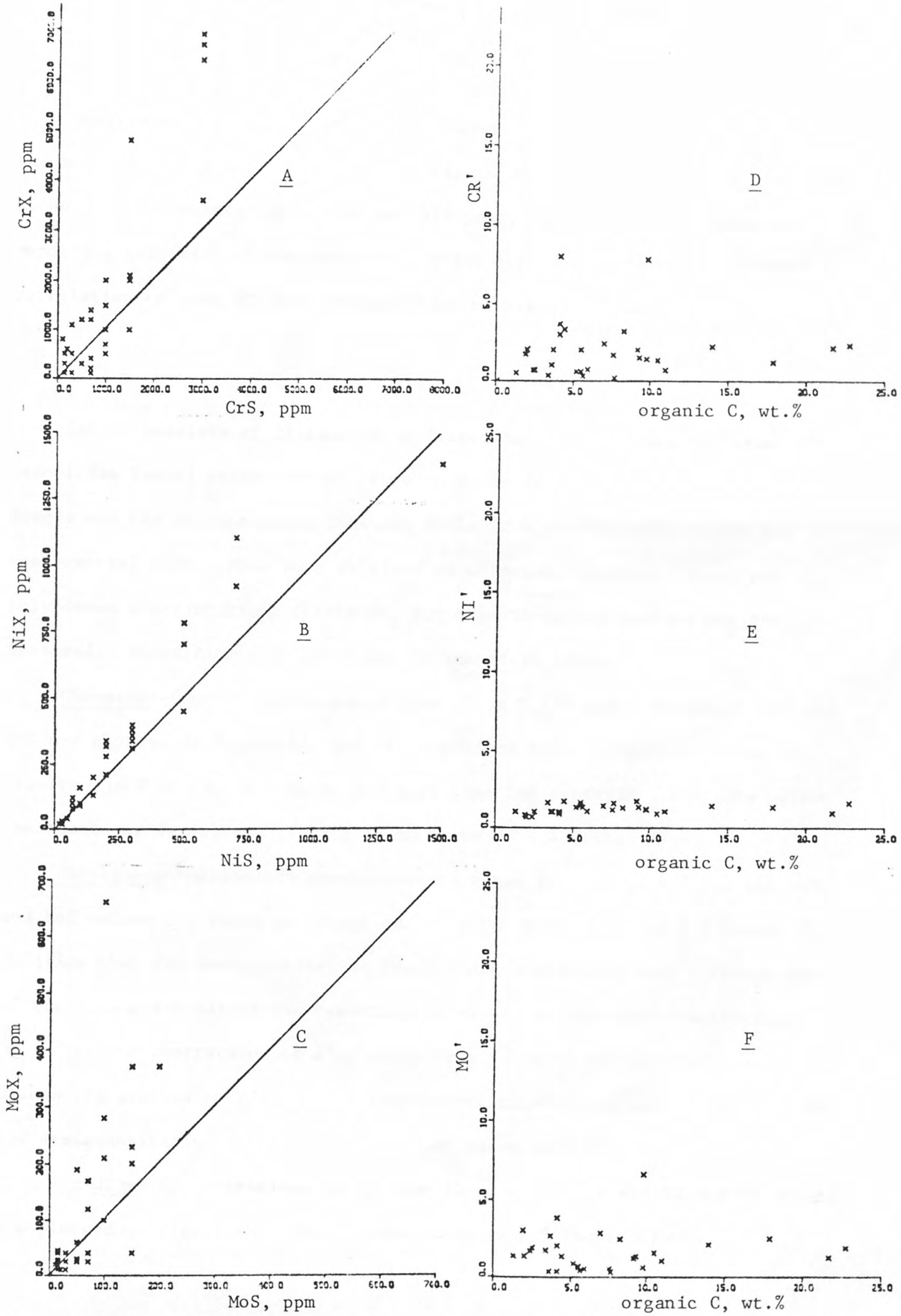

Figure 3.--Data set 78 plots of metal X (ppm) versus metal S (ppm), and Metal' versus organic C (weight percent).

Molybdenum--Concentrations of molybdenum range from 10 to 870 ppm and the MoX and MoS values are plotted on figure 3C. The MO' mean value is 1.62. Except for two points (MoX = 660 and 870 ppm), all values are within two reporting intervals of the semiquantitative method. There is no apparent correlation between MO' and concentration of organic carbon

Set 79

Set 79 consists of 31 samples of Paleozoic marine strata including the Ordovician Vinini Formation and Devonian Woodruff Formation from east-central Nevada and the Mississippian Chainman Shale from southeastern Nevada and west-central Utah. Data were obtained on chromium, vanadium, zinc, and molybdenum concentrations (table 6), but organic-carbon content was not measured. Univariate statistics are presented in table 7.

Chromium--Concentrations range from 35 to 1,150 ppm. Values of CrX and CrS are plotted on figure 4A, and it is obvious that the semiquantitative results for 9 of the 14 samples are more than two reporting intervals below the quantitative values. The CR' mean value is 9.4 (table 7).

Molybdenum--Molybdenum concentrations range from 15 to 435 ppm and MoX and MoS values are shown on figure 4B. The MO' mean value of 2.2 (table 7) verifies that the semiquantitative results are distinctly low, although most of the values are within two reporting intervals of the quantitative results.

Zinc--Concentrations of zinc range from 90 to 10,200 ppm and ZnX and ZnS values are plotted on figure 4C. They record significant underestimation by the semiquantitative method. The ZN' mean value is 2.2 (table 7).

Vanadium--Concentrations range from 75 to 4,735 ppm and VX and VS values are plotted on figure 4D. The V' mean value is 2.5 (table 7).

Table 6.--Set 79 concentration data for metals (ppm) determined by quantitative (metal X) and semiquantitative (metal S) methods

[1.000 entries = no data, or element is below detection limit]

Number	Vx	Vs	Znx	Zns	Mox	Mos	Crx	Crs	V'	ZN'	MO'	CR'
73FP-410	815.000	1000.000	1.000	1.000	75.000	70.000	1.000	1.000	0.815	1.000	1.071	1.000
73-411S	375.000	700.000	1.000	1.000	85.000	70.000	1.000	1.000	0.536	1.000	1.214	1.000
73-413S	4240.000	5000.000	5750.000	2000.000	277.000	150.000	1.000	1.000	0.848	2.875	1.847	1.000
75-485S	271.000	96.000	1.000	1.000	1.000	1.000	1.000	1.000	2.823	1.000	1.000	1.000
75-487S	340.000	190.000	1.000	1.000	1.000	1.000	1.000	1.000	1.789	1.000	1.000	1.000
75-488S	1842.000	550.000	422.000	290.000	25.000	10.000	1.000	1.000	3.349	1.455	2.500	1.000
75-489S	166.000	190.000	1.000	1.000	1.000	1.000	1.000	1.000	0.874	1.000	1.000	1.000
75-490S	106.000	110.000	1.000	1.000	1.000	1.000	1.000	1.000	0.964	1.000	1.000	1.000
75-491S	1710.000	900.000	695.000	800.000	24.000	30.000	1.000	1.000	1.900	0.869	0.800	1.000
75-494S	277.000	170.000	89.000	93.000	1.000	1.000	1.000	1.000	1.629	0.957	1.000	1.000
76-131S	270.000	200.000	1.000	1.000	1.000	1.000	35.000	30.000	1.350	1.000	1.000	1.167
76-132S	4562.000	3000.000	10262.000	3000.000	143.000	30.000	1.000	1.000	1.521	3.421	4.767	1.000
76-129S	165.000	70.000	1.000	1.000	1.000	1.000	151.000	100.000	2.357	1.000	1.000	1.510
76-130S	110.000	30.000	1.000	1.000	1.000	1.000	93.000	70.000	3.667	1.000	1.000	1.329
76-134S	75.000	20.000	1.000	1.000	1.000	1.000	1.000	1.000	3.750	1.000	1.000	1.000
76-135S	253.000	150.000	1.000	1.000	1.000	1.000	1.000	1.000	1.687	1.000	1.000	1.000
77-122S	2553.000	1500.000	4175.000	2000.000	252.000	100.000	523.000	30.000	1.702	2.087	2.520	17.433
UC-5A	2846.000	3000.000	3519.000	1000.000	57.000	20.000	536.000	50.000	0.949	3.519	2.850	10.720
UC-5B	2427.000	2000.000	2882.000	1000.000	49.000	15.000	592.000	50.000	1.213	2.882	3.267	11.840
77-117F	390.000	150.000	1.000	1.000	1.000	1.000	59.000	50.000	2.600	1.000	1.000	1.180
77-119F	1148.000	500.000	1.000	1.000	1.000	1.000	257.000	50.000	2.296	1.000	1.000	5.140
77-120	412.000	150.000	1.000	1.000	58.000	20.000	44.000	15.000	2.747	1.000	2.900	2.933
77-121	2446.000	1000.000	1.000	1.000	435.000	150.000	638.000	50.000	2.446	1.000	2.900	12.760
77-123F	4735.000	1500.000	2718.000	1000.000	69.000	20.000	1150.000	50.000	3.157	2.718	3.450	23.000
77-124F	938.000	500.000	1.000	1.000	108.000	50.000	274.000	20.000	1.876	1.000	2.160	13.700
77-125FA	1276.000	500.000	1.000	1.000	18.000	10.000	301.000	15.000	2.552	1.000	1.800	20.067
77-126S	2423.000	1000.000	1.000	1.000	31.000	15.000	578.000	70.000	2.423	1.000	2.067	8.257
77-179	406.000	20.000	1.000	1.000	1.000	1.000	1.000	1.000	20.300	1.000	1.000	1.000
73-737S	2830.000	2000.000	1916.000	1500.000	20.000	50.000	1.000	1.000	1.415	1.277	0.400	1.000
73-738S	1226.000	1500.000	1000.000	1000.000	15.000	30.000	1.000	1.000	0.817	1.000	0.500	1.000
73-891S	4236.000	1500.000	1542.000	1500.000	1.000	1.000	1.000	1.000	2.824	1.028	1.000	1.000

Table 7.--Set 79 univariate statistics

Var	Column	Minimum	Maximum	Mean	Deviation
1	Vx	75	4,735	1,388	1,405
2	Vs	20	5,000	923	1,141
3	Znx	89	10,262	3,039	2,960
4	Zns	90	3,000	1,244	834
5	Mox	15	435	102	115
6	Mos	10	150	49	45
7	Crx	35	1,150	373	315
8	Crs	15	100	46	23
9	V'	0.54	20.3	2.5	3.5
10	ZN'	0.87	3.5	2.2	1.0
11	MO'	0.40	4.8	2.2	1.2
12	CR'	1.2	23.0	9.4	7.5

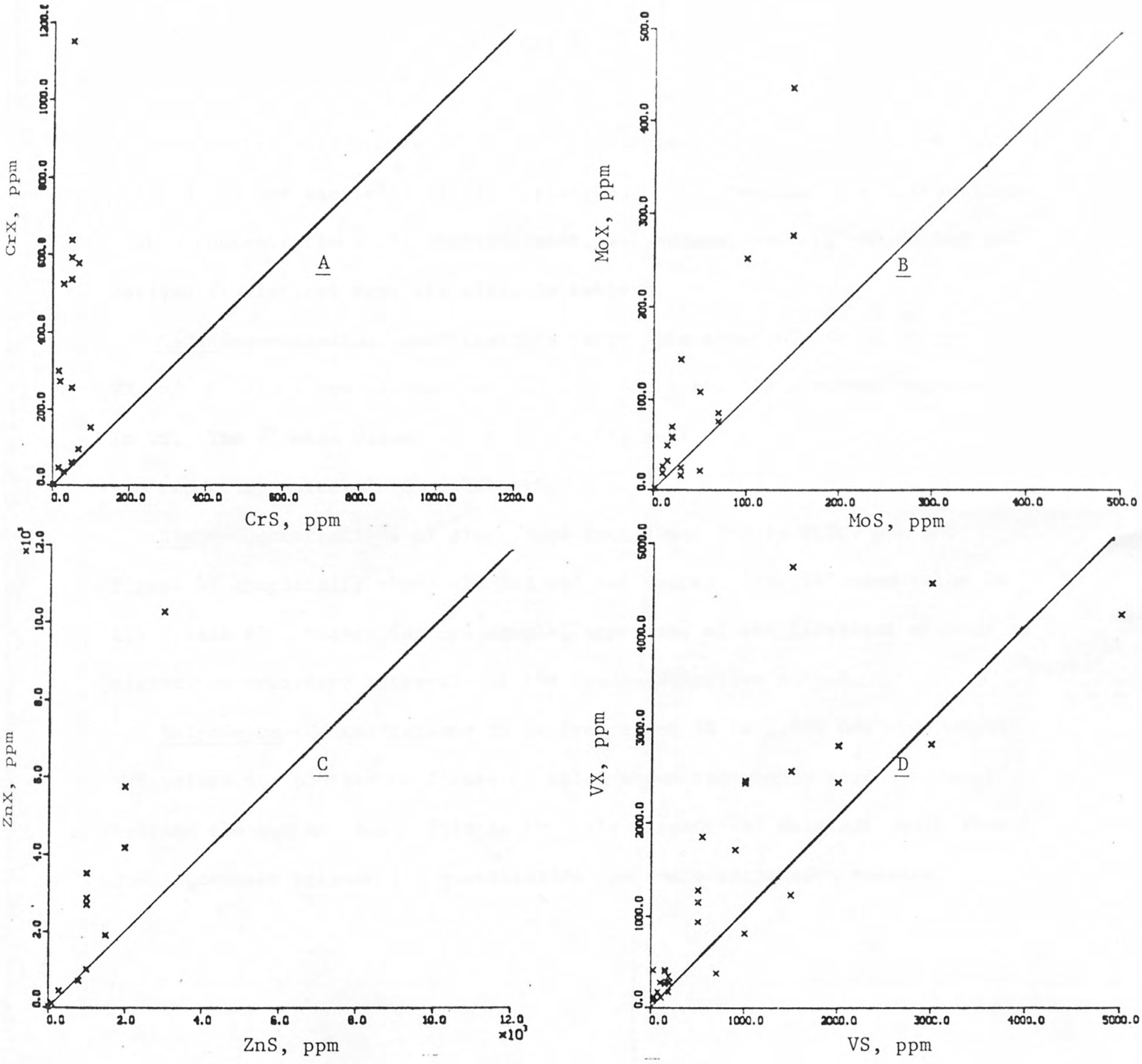

Figure 4.--Data set 79 plots of metal X (ppm) versus metal S (ppm).

Set 80

Set 80 has only six samples of Mississippian Heath Formation from central Montana and one sample of Mississippian Doughnut Formation from northeastern Utah. Concentrations of vanadium, zinc, molybdenum, and organic carbon and derived statistical data are given in table 8.

Vanadium--Vanadium concentrations range from about 650 to 5,300 ppm and VX and VS values are plotted on figure 5A which reveals a strong negative bias in VS. The V' mean value is 1.6 (table 8); most of the VS values are within two reporting intervals for the method.

Zinc--Concentrations of zinc range from about 980 to 9,300 ppm and figure 5B graphically shows the ZnX and ZnS values. The ZN' mean value is 1.5 (table 8). Except for one sample, agreement of the different methods is within two reporting intervals of the semiquantitative method.

Molybdenum--Concentrations range from about 30 to 1,800 ppm and MoX and MoS values are plotted on figure 4C which shows remarkably good agreement between the two methods. This is the only element and data set which show good agreement between the quantitative and semiquantitative results.

Table 8.--Set 80 concentration and statistical data for metals (ppm) determined by quantitative (metal X) and semiquantitative (metal S) methods, and organic-carbon concentration (weight percent)

Number	Carbon	Vx	Vs	Znx	Zns	Mox	Mos	V'	ZN'	Mo'
63925	22.000	1671.000	1500.000	2531.000	1500.000	122.000	150.000	1.114	1.687	0.813
63939	24.700	5341.000	2000.000	1141.000	1500.000	441.000	500.000	2.670	0.761	0.882
63941	14.300	1862.000	1000.000	979.000	1000.000	118.000	100.000	1.862	0.979	1.180
64146	5.400	654.000	1000.000	1205.000	1500.000	34.000	70.000	0.654	0.803	0.486
64208	15.700	3067.000	2000.000	2605.000	1500.000	430.000	500.000	1.533	1.737	0.860
64210	11.400	4011.000	2000.000	9327.000	3000.000	1808.000	1500.000	2.005	3.109	1.205

Univariate Statistics

Var	Column	Minimum	Maximum	Mean	Deviation	Valid
1	Carbon	5.400000	24.70000	15.58333	7.030624	6
2	Vx	654.0000	5341.000	2767.667	1717.441	6
3	Vs	1000.000	2000.000	1583.333	491.5960	6
4	Znx	979.0000	9327.000	2964.667	3198.805	6
5	Zns	1000.000	3000.000	1666.667	683.1301	6
6	Mox	34.00000	1808.000	492.1667	667.0593	6
7	Mos	70.00000	1500.000	470.0000	540.7402	6
8	V'	0.654000	2.670000	1.639667	0.707634	6
9	ZN'	0.761000	3.109000	1.512667	0.892460	6
10	MO'	0.486000	1.205000	0.904333	0.265406	6

Array of Number of Pairs and Correlation Coefficients

	1	2	3	4	5	6	7	8	9	10
1	1.00	0.56	0.48	-0.23	-0.23	-0.14	-0.08	0.57	-0.14	0.20
2	6	1.00	0.85	0.33	0.40	0.56	0.62	0.91	0.25	0.46
3	6	6	1.00	0.50	0.55	0.62	0.70	0.59	0.53	0.29
4	6	6	6	1.00	0.96	0.96	0.93	0.18	0.96	0.52
5	6	6	6	6	1.00	0.95	0.94	0.18	0.87	0.35
6	6	6	6	6	6	1.00	0.99	0.42	0.87	0.59
7	6	6	6	6	6	6	1.00	0.46	0.85	0.56
8	6	6	6	6	6	6	6	1.00	0.09	0.65
9	6	6	6	6	6	6	6	6	1.00	0.52
10	6	6	6	6	6	6	6	6	6	1.00

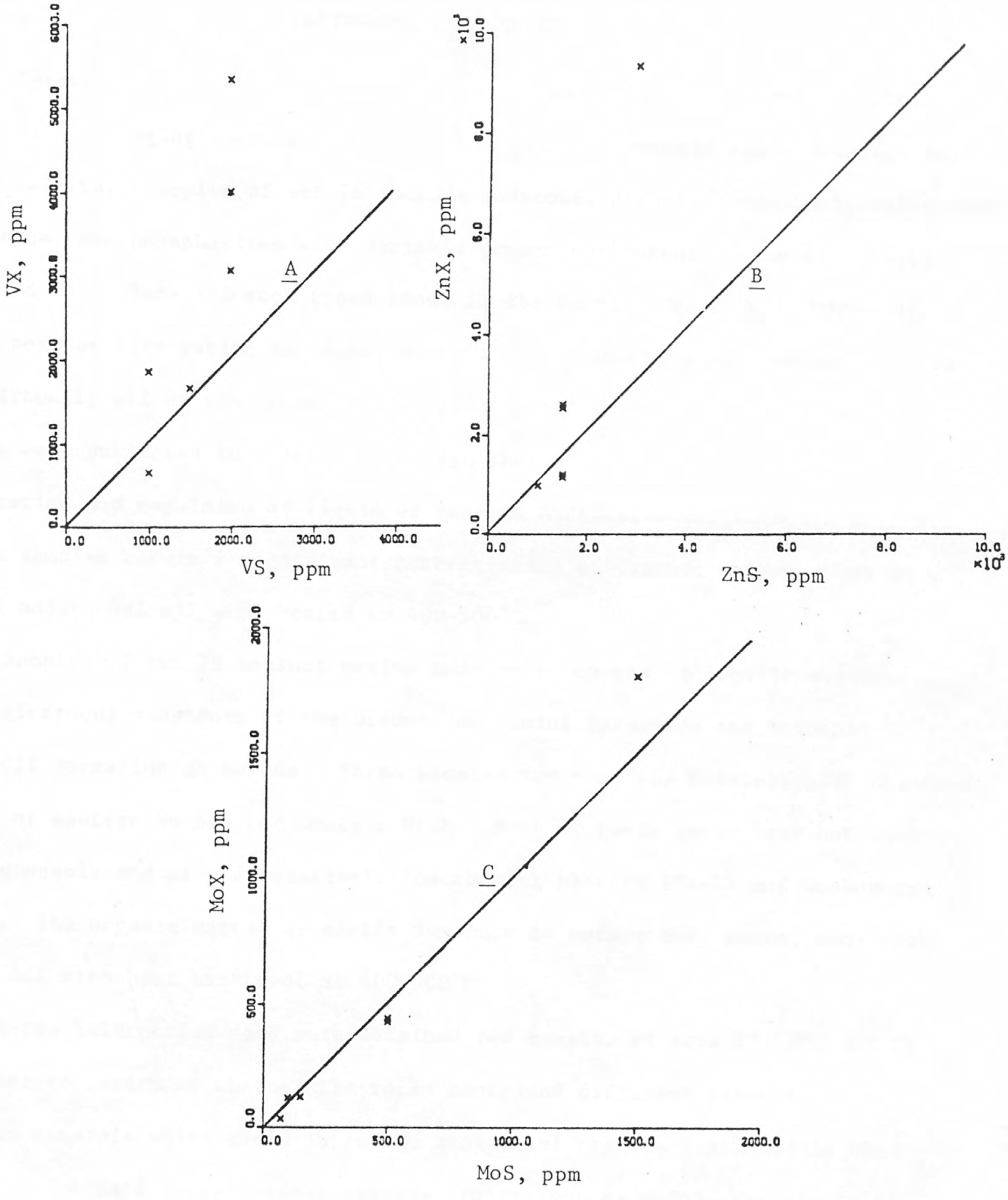

Figure 5.--Data set 80 plots of metal X (ppm) versus metal S (ppm).

LITHOLOGY OF SAMPLES

Samples of sets 76 and 77 are dominantly marine mudstones and phosphorites with widely ranging phosphate content; some samples contain minor dolomite and (or) calcite. Samples of set 78 include mudstone, dolomitic mudstone, calcareous mudstone, and phosphorites with variable phosphate content. Samples of sets 76, 77, and 78 include all rock types known in the Permian Meade Peak Member of the Phosphoria Formation in Idaho, Montana, Utah, and Wyoming. Organic matter in virtually all of the Meade Peak samples is thermochemically supermature. The rocks were subjected to a relatively high thermal history which caused petroleum generation and expulsion of liquid or gaseous hydrocarbons. Although most of these samples retain a significant concentration of organic carbon, they do not yield additional oil when heated to 400-500°C.

Samples of set 79 include marine mudstones, cherts, dolomitic mudstones, and calcareous mudstones of the Ordovician Vinini Formation and Devonian Woodruff Formation in Nevada. Three samples are from the Mississippian Chainman Shale of eastern Nevada and western Utah. Most of these rocks have not been buried deeply and have a relatively low thermal history (Poole and Desborough, 1980). The organic matter is mostly immature to mature and, hence, many rocks yield oil with heat treatment at 400-500°C.

X-ray diffraction data were obtained for samples of sets 77, 78, and 79 in order to determine whether the rocks contained different proportions of certain minerals which could influence analytical results evaluated in this report. The data reveal widely varying proportions of major minerals in the samples and, therefore, rock constituents do not seem to have an important influence on the semiquantitative results. It is also noteworthy that there is no difference in metal content determined by the semiquantitative method in organic-rich samples regardless of organic maturity.

SUMMARY

Evaluation of quantitative versus semiquantitative results for chromium, nickel, zinc, molybdenum, and vanadium concentrations in fine-grained organic-rich Paleozoic marine strata in the Western United States shows that the concentration of these metals as determined by the semiquantitative method, is systematically biased toward lower concentrations. Table 9 summarizes amount of bias for all the data presented. The amount of negative bias of the semiquantitative method ranges from a factor of about 1.7 for molybdenum to 2.7 for chromium. Negative bias of the semiquantitative data is consistent for 15 out of 16 groups of data. There is no systematic relation between the amount of negative bias of semiquantitative results and concentration of organic carbon, and thus, it is presumed that organic-carbon content of the samples did not substantially influence the semiquantitative results.

In view of these results, it is suspected that data presented by Vine and Tourtelot (1970) for metals in black shales of the United States may represent an underestimation for some metals when they occur in relatively high concentrations.

ACKNOWLEDGMENTS

We thank Steve D. Ludington for helpful suggestions concerning computer handling and graphics for the data presented; we greatly appreciate advice on the text provided by Jon J. Connor, Joel S. Leventhal, David A. Lindsey, and James L. Seeley.

Table 9.--Values of grand mean, $\overline{X}'$, of all data sets for CR', NI', ZN', MO', and V'

[$\overline{X}' = \text{sum}(\overline{x}' \times n_{set})/N$; N = number of samples in all sets]

	CR'	NI'	ZN'	MO'	V'
$\overline{X}'$	2.71	1.84	1.75	1.72	2.39
N	118	107	93	54	36

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APPENDIX

Quantitative analytical methods used to determine each element in each data set, and the analysts.

Element(s)	Method	Analyst
	Set 76	
Cr, Ni, Zn	wavelength-dispersive X-ray fluorescence	H. Leon Groves
	Set 77	
Cr, Ni	wavelength-dispersive X-ray fluorescence	H. Leon Groves
Zn	atomic absorption (*in* Desborough, 1977)	Lorraine M. Lee and Claude Huffman, Jr.
	Set 78	
Cr	wavelength-dispersive X-ray fluorescence	H. Leon Groves
Ni	atomic absorption	James G. Crock
Mo	energy-dispersive X-ray fluorescence	Gregory N. Green
	Set 79	
Cr	wavelength-dispersive X-ray fluorescence	H. Leon Groves
V, Zn, Mo	energy-dispersive X-ray fluorescence	Gregory N. Green
	Set 80	
V, Zn, Mo	energy-dispersive X-ray fluorescence	Gregory N. Green