Geochemical Data from New Albany Shale, Kentucky: A Study in Metal Mobility During Weathering of Black Shales

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Geochemical Data from New Albany Shale, Kentucky: A Study in Weathering of Trace Metals

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Introduction

The data reported in this paper were collected as part of a study to understand the weathering and transport of metals from metalliferous black shale. The black shale targeted in this study is the New Albany Shale, Eastern Kentucky. Our ultimate goal is to apply our findings to predict the geochemical controls on metal mobility in other regions of the United States where metalliferous black shale crop out. These geochemical controls will be discussed in future papers, whereas this paper focuses on presenting the large volume of analytical data, photomicrographs, and element plots produced for this study.

The Upper Devonian New Albany Shale in Eastern Kentucky was chosen for study because anomalous metal concentrations in stream sediments were detected where this shale crops out along the margins of the Central Appalachian Basin (Tuttle and others, 2001). The New Albany shale was deposited in deep (>200 m water depth), anoxic ocean basins where sediment and metals accumulated very slowly (Potter et al., 1980), and, in our study area, is divided into the Huron Member, with the Duffin unit, the Three Lick Bed, and the Cleveland Member (figs. 1 and 2). Our outcrop samples were from the upper Huron Member and core samples through the entire section New Albany section shown in Figure 1 plus the Lower Mississippian (?) Sunbury Shale.

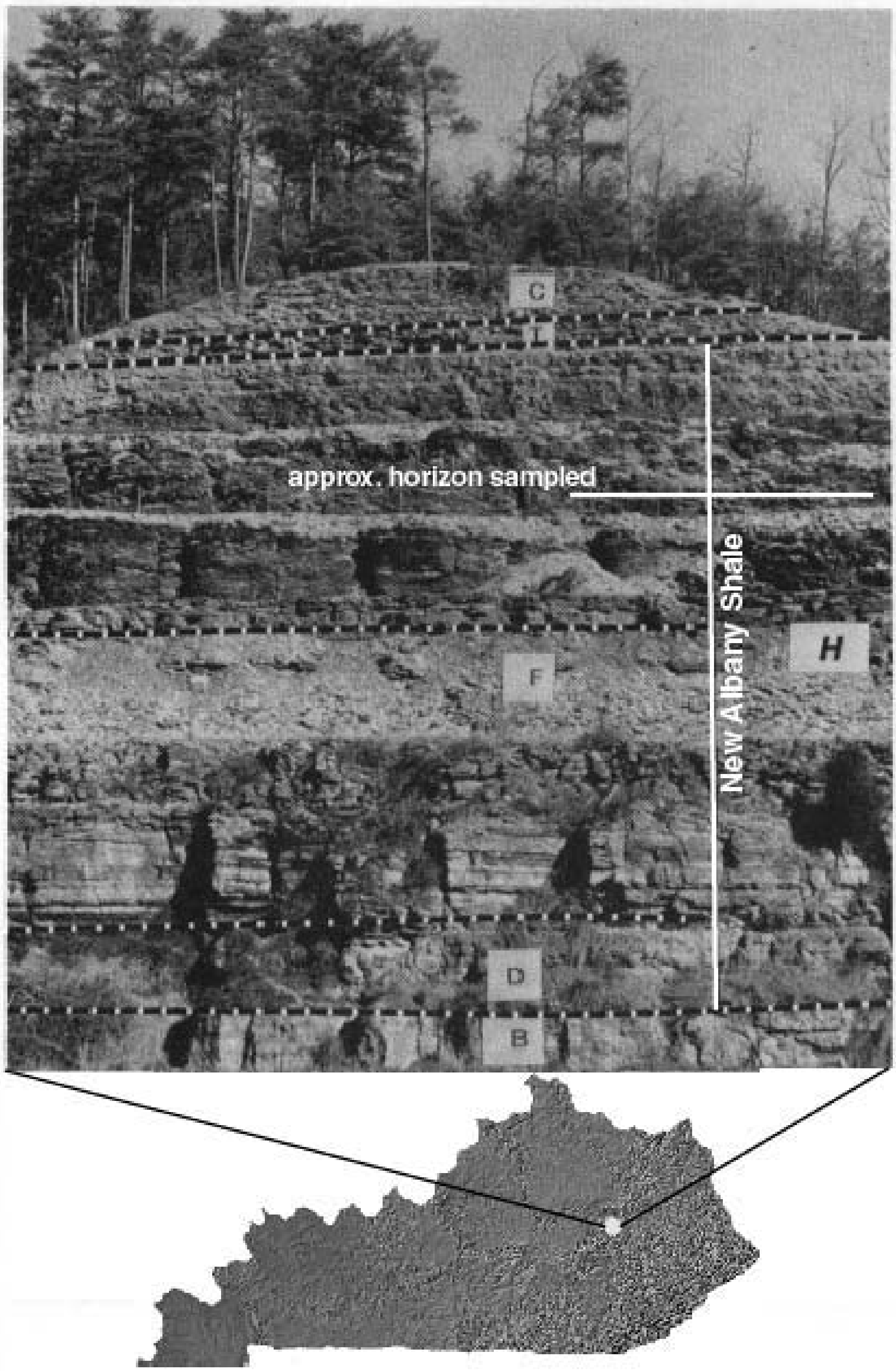

Figure 1. . Map of Kentucky showing the location of our sampling and the stratigraphic column of New Albany Shale at that location. B, Boyle Dolomite; D, Duffin Unit; H, Huron Member; F, Foerstia Zone; T, Threelick Bed; C, Cleveland Member (photograph modified from Pryor and others (1981).

Figure 2. Photo of the transect sampled along the New Albany Shale out crop. White dots show seven of the shale sample locations.

Methods

Sampling Methods

We sampled un-weathered and weathered shale, efflorescent salts and soil along a transect across the Huron Member of the New Albany Shale outcrop just east of Clay City, Kentucky. Un-weathered New Albany Shale and a efflorescent salt were sampled in core from a shallow drill hole near the outcrop (core sampled at the Kentucky Geological Survey's Core Library, Lexington, Kentucky).

The outcrop is located at the following coordinates: latitude 37°52.7400' and longitude 83°57.0717'. Sampling along the outcrop followed a continuous bed from the edge of the outcrop towards the center (fig. 2). Two samples at each transect location (11 locations along a 16.13 m transect) were collected—one of shale with the surface weathering rind, and one of shale several centimeters behind the surface that had no visible oxide staining ("unexposed" shale). In addition, the following were collected from the outcrop: four efflorescent salts midway along the transect where water seepage had occurred, four soil samples at the outer-most end of the transect,[1] and shale fragments, exfoliating from the road bench. These shale samples from the bench are from slightly lower in the Huron section than the transect samples.

Core was provided by the Kentucky State Survey Core Library in Lexington, Kentucky. The drill hole is less than 5 miles from the out crop and is located within the block bounded by the following coordinates: 37°48' and 37°49" latitude and 83°54' and 83°55' longitude. Collection of core began five meters below the surface. Twenty-one samples were collected from a 45.42-meter interval of the core. Most of the shale sampled was pyrite-rich with some shale having massive lenses and nodules of pyrite and others specks of pyrite visible only with a hand lens. A efflorescent salt on a pyrite nodule that formed from sulfide oxidation in humid air also was collected.

All samples were air dried after collecting. One split was kept as collected for analyses by the scanning electron microscope (SEM) and laser ablation induction coupled mass spectrometry (LA-ICP-MS). A split was ground in a ceramic pulverizer to pass –100 mesh. Splits of ground material were made using a Jones splitter—one split was for multi-element analyses and the second split for all other chemical methods.

[1] Although the land surface was sloping at the collection point, we tried to collect soil samples that we believe represent *in situ* soil formation instead of colluvium.

Analytical Methods

The method of analyses for each element or phase analyzed in the sample is listed in Appendix I along with the detection limits for each analysis.

Bulk Chemistry

Bulk chemical parameters were determined on outcrop and core shale, efflorescent salt, and soil samples using analytical methods described in Bullock and others (2002). Multi-element analyses were done using a combination of inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) (elements and detection limits in Appendix I). Samples were prepared for these analyses by first determining moisture content (heating to 107±3°C in a forced air furnace for one hour) and then, because of their high organic-carbon content, ashing the sample (heating to 750°C for 2 hours). The ashed samples were either decomposed using a multi-acid or sodium peroxide sinter decomposition technique, depending on the element being determined (see Appendix I). All analyses on ashed samples are reported on a whole-rock basis.

Mercury, selenium, and total sulfur required separate analyses. Mercury was determined by multi-acid/vanadium pentoxide decomposition and then using a cold vapor-atomic absorption spectrometry (CVAAD). Detection limit for Hg is 0.02 ppm. Selenium analyses used a different multi-acid decomposition and a hydride-generation method for an atomic adsorption spectrophotometer. Detection limit for Se is 0.1 pmm. Total sulfur was determined by combusting the sample and analyzing SO_2 using an infrared absorption detector. Detection limit for S is 0.05 %.

Sulfide Speciation and Sulfur Isotopy

The sulfur in solid sulfide phases (acid-volatile sulfide, S^{2-} and disulfide, S_2^{2-}) was separated in shale samples from the core and along the transect using an analytical scheme modified from Tuttle and others (1986). The ground sample was treated with an acidified chromous chloride solution under an inert atmosphere. The H_2S evolved from the sulfides was collected as Ag_2S, and the amount of sulfide in the sample gravimetrically determined. The detection limit for $S_{sulfide}$ is 0.01% with a five-gram sample. The isotopic composition of the sulfur in the sulfides was analyzed by combusting the Ag_2S in an on-line elemental analyzer coupled to a mass spectrometer (Kester and others, 2001).

Trace Metals in Pyrite and Pyrite Morphologies

Polished sections of core samples were prepared and photographed. The sections were first examined in detail under the SEM/EDX (JEOL JSM5800LV scanning electron microscope equipped with an Oxford Isis energy dispersive X-ray analyzer) to determine pyrite morphologies (nodules, lenses, framboids, and anhedral grains) and their relative purity with respect to trace metals. Trace metals in these different morphologies were then analyzed by LA-ICP-MS, which is much more sensitive than SEM-EDX. Laser data was collected using a single 25 micron spot and stored as raw counts per second vs time. The USGS sulfide PS-1 (Wilson et al, 2002) was used as a calibration standard. The raw data was subsequently reduced to concentration data using the program GeoPro supplied by Cetac Technologies.[2] Data are reported as parts per million (ppm) in pyrite, and as then averages for different morphologies use to estimate the proportion of each

[2] Use of the tradename Cetac Technologies or any other tradename in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government.

metal in the sample that resides in pyrite.[3] The limit of detection for metals using the LA-ICP-MS is variable and depends on counting statistics. Some values are below the limit of detection as determined by the software, and are noted as < values.

Additional Analyses of Efflorescent Salts

Mineral identification of the efflorescent salts used X-ray diffraction analysis performed with a Siemens D500 diffractometer equipped with a graphite monochromater and using Cu $K\alpha$ radiation. Samples were scanned from 4 to 64° 2Θ using a 0.02° step size at a rate of 2 seconds per step. Samples sufficiently large were ground and analyzed using a packed powder mount. Small samples were prepared by grinding in a few drops of methanol to form a slurry and then transferring the slurry to a glass slide. Some samples were ground and sprinkled on double sticky tape to avoid possible dissolution affects. Detailed observations and analyses of the efflorescent salts used SEM/EDX as described above.

Dissolution and precipitation experiments were run using three of the efflorescent salts from the outcrop. Two splits of each salt were weighted (0.2000 g of salt) and dissolved in 100 mL deionized water. Solids were then filtered off the solutions, dried, and weighed to determine the weight of the salt that dissolved. One solution was acidified with ultra-pure HNO_3, and submitted for analyses using ICP-MS (Lamothe and others, 2002). The second solution was titrated to pH = 7.0 (the approximate pH of most streams in the area) using a standardized sodium hydroxide solution, and allowed to sit for one hour. The precipitate (mostly iron oxyhydroxides plus adsorbed metals) then was

[3] Proportions of the total metal that resides in pyrite were estimated by determining the most abundant morphology in each core sample (massive versus framboid/anhedral grains), determining the average metal content in each pyrite morphology using laser ablation ICP-MS data, calculating the amount of metal in pyrite on a whole rock basis using these averages and whole-rock sulfide data, and dividing that amount by the total amount of metal in the sample.

separated from the solution by filtration, and the filtrate was then acidified and analyzed as above. The difference between the metal concentration in the acidified sample and the titrated sample represent the metals that either adsorbed onto or co-precipitated with the iron oxyhydroxides.

Results

All analytical results are tabulated in the tables in Appendix II, sample photos and SEM photomicrographs are in Appendix III, and graphs of selected element concentrations are plotted along the outcrop transect in Appendix IV. The interpretation of these results is forthcoming in two papers presently in preparation. The first addresses the role of soluble salts in the mobility of trace metals during weathering of the New Albany and expands on preliminary findings presented in Tuttle and others (2001). The second is a comprehensive paper that focuses on the geochemical controls that affect weathering and transport of trace metals from metalliferous black shale to the environment.

Bulk Chemistry, Sulfide Data, and Sulfur Isotopy

The bulk chemistry of New Albany core samples, including the sulfide and sulfur isotope data, are tabulated in Table AII-1 (Appendix II) and those for shale along the outcrop transect in Table AII-2. Descriptive statistics for selected elements in these samples are given in Tables 1 and 2. Core statistics are further split into the two dominant pyrite morphologies within the shale—massive pyrite (nodules and lenses) and framboidal/anhedral grain pyrite. Outcrop statistics are split by soil, efflorescent salt, bench shale, and transect shale, with the latter being further split by surface weathered shale and “unexposed” shale.

Selected metal concentrations in surface and “unexposed” shale along the transect are shown in distance plots in Appendix IV. Also included on these plots are average concentrations of metals in Huron shale from the core, in soils at the end of the transect, and in efflorescent salts that formed along the transect.

Trace Metals in Pyrite and Pyrite Morphologies

The LA-ICP-MS data on trace element concentrations in pyrite from core samples is tabulated in Table AII-3 (Appendix II). Photos of the sections showing the spots analyzed are in Figures AIII-1 through AIII-2 (Appendix III) and photomicrographs of sulfides in Figure AIII-3. Descriptive statistics for these analyses are given in Table 3 and are split according to whether the morphology is massive (nodules and lenses) or framboidal/anhedral grains. These morphology averages are used to calculate the percentage of the metal that resides in pyrite for core and outcrop shale samples (Table AII-1).

Table 1. Mean and range of selected elements and $\delta^{34}S_{sulfide}$ for shale in core (n = 20), Huron shale in core (equivalent to outcrop samples) (n = 8), core containing massive pyrite (lenses or nodules) (n = 7), and pyritic shale (contains framboids or anhedral grains of pyrite) (n = 13). Means are geometric except for $\delta^{34}S_{sulfide}$, which is arithmetic.

Element/Parameter		All Shale	Huron Shale	Shale w/Massive Py.	Shale w/ Framboid or Grains
As ppm	m•••	75	64	195	44
	range	11 to 2570	25 to 255	37 to 2570	11 to 385
Cd ppm	m•••	1.2	0.48	.96	1.3
	range	0.12 to 26	0.12 to 3.0	.26 to 22	0.12 to 26
Co ppm	m•••	16	20	18	14
	range	3.1 to 44	13 to 44	11 to 44	3.1 to 26
Cr ppm	m•••	79	77	67	86
	range	16 to 190	53 to 140	16 to 130	32 to 190
Cu ppm	m•••	135	105	86	165
	range	25 to 1230	25 to 1230	25 to 260	28 to 1230
Fe_2O_3 %	m•••	10	9.5	26	6.0
	range	2.1 to 51	4.6 to 26	17 to 51	2.1 to 15
Hg ppm	m•••	0.14	0.10	0.14	0.13
	range	0.04 to .43	0.05 to .26	0.04 to .41	0.04 to .43
Mn ppm	m•••	275	200	305	265
	range	87 to 2760	34 to 385	87 to 2500	130 to 2760
Mo ppm	m•••	81	88	95	74
	range	36 to 495	48 to 360	3.6 to 360	6.0 to 495
Ni ppm	m•••	155	115	97	215
	range	34 to 425	34 to 385	34 to 210	98 to 425
Pb ppm	m•••	29	19	39	25
	range	1.9 to 430	11 to 45	14 to 210	1.9 to 430
S_{total} %	m•••	4.7	4.6	15	2.5
	range	0.52 to 29	1.6 to 15	9.5 to 29	0.52 to 9.5
Sb ppm	m•••	6.3	5.2	6.8	6.0
	range	1.1 to 23	3.2 to 9.0	1.9 to 21	1.1 to 23
Se ppm	m•••	5.1	3.8	3.2	6.6
	range	0.32 to 30	2.0 to 18	0.32 to 29	1.4 to 30
$S_{sulfide}$ %	m•••	3.6	3.6	14	1.8
	range	0.62 to 28	1.1 to 14	8.8 to 28	0.62 to 5.8
$\delta^{34}S_{sulfide}$ ‰	m•••	-18.0	-17.2	-13.7	-20.3
	range	-33.6 to +4.6	-23.7 to +4.6	-33.6 to +4.6	-29.6 to –3.8
Tl ppm	m•••	3.7	4.9	3.7	3.6
	range	0.28 to 11	1.7 to 7.3	0.28 to 7.9	0.39 to 11
U ppm	m•••	26	27	20	29
	range	4.0 to 110	18 to 55	4.0 to 85	4.1 to 110
V ppm	m•••	255	210	120	355
	range	38 to 870	54 to 870	38 to 215	88 to 870
Zn ppm	m•••	225	100	200	235
	range	35-3550	35 to 660	70 to 2940	35 to 3550

Table 2. Descriptive statistics (mean and range) of selected elements and $\delta^{34}S$ values for surface shale (n = 11) and unexposed shale samples (n = 10) in the outcrop, soil (n = 4), and efflorescent salts (n = 4). Based on distributions, means are geometric, except for $\delta^{34}S$. $\delta^{34}S$ ‰ are on sulfides in shale and for sulfates in soil and efflorescent salts.

Element/parameter	Surface Shale	Unexposed Shale	Soil	Efflorescent Salts
As ppm m••• range	44 32 to 63	47 36 to 58	51 43 to 57	51 18 to77
Cd ppm m••• range	0.15 0.06 to .75	0.14 0.06 to .78	0.15 0.07 to .27	1.6 0.74 to 4.6
Co ppm m••• range	9.7 5.2 to 42	8.9 4.9 to 31	5.6 5.1 to 5.9	54 36 to 89
Cr ppm m••• range	78 62 to 96	66 59 to 71	120 104 to135	54 49 to 60
Cu ppm m••• range	32 2.1 to 125	15 1.2 to 100	54 43 to 63	150 79 to 240
Fe_2O_3 % m••• range	6.0 4.3 to 7.5	5.8 3.8 to 8.7	7.7 6.0 to 9.0	11 7.2 to 15
Hg ppm m••• range	0.06 0.04 to .07	0.06 0.04 to .08	0.06 0.05 to .07	0.04 0.02 to .05
Mn ppm m••• range	56 34 to 230	51 32 to 165	50 44 to 54	310 220 to 440
Mo ppm m••• range	60 40 to 77	60 43 to 97	97 86 to 110	27 15 to 40
Ni ppm m••• range	38 19 to 155	33 15 to 97	15 12 to 18	190 110 to 325
Pb ppm m••• range	16 11 to 21	17 14 to 20	23 21 to 28	2.1 0.39 to 9.8
S_{total} % mean range	1.3 0.33 to 4.4	1.3 0.46 to 4.5	0.14 0.08 to .33	12 9.0 to 15
$S_{sulfide}$ % mean range	0.24 0.45 to 1.5	0.36 0.070 to 2.7	0.011 0.003 to .024	nd
$\delta^{34}S_{sulfide}$ ‰ m••• range	-20.0 -22.0 to –17.1	-18.2 -20.4 to –16.1	nd	nd
$S_{sulfate}$ % mean range	nd	nd		
$\delta^{34}S_{sulfate}$ ‰ m••• range	nd	nd	-13.6 -14.7 to –12.6	-11.9 -18.1 to –6.5
Sb ppm m••• range	3.3 2.3 to4.2	3.4 2.9 to 4.3	6.5 5.6 to 7.4	0.84 0.21 to 2.0
Se ppm m••• range	1.4 0.25 to 2.2	1.7 1.4 to 2.3	3.9 3.3 to 4.5	0.55 0.29 to .92
Tl ppm m••• range	3.5 2.2-5.6	3.4 2.7 to 5.1	7.1 4.5 to 10	0.75 0.27 to 1.7
U ppm m••• range	17 11 to 28	15 12 to 21	23 20 to 24	37 19 to 65
V ppm m•••	205	195	460	55

	range	150 to 260	155 to 325	395 to 525	17 to 140
Zn ppm	m•••	26	19	35	295
	range	9 to 105	2.4 to 63	27 to 39	160 to 1030

Table 3. Descriptive statistics (geometric mean and range) of selected metals in massive pyrite (lenses and nodules) (n = 75) and in framboid/anhedral grains of pyrite (n = 64).

Element		Massive Pyrite	Framboids or anhedral grains
As ppm	m•••	420	475
	range	27 to 1810	74 to 3080
Cd ppm	m•••	0.37	1.2
	range	0.07 to 2.2	0.10 to 8.7
Co ppm	m•••	0.83	27
	range	0.06 to 18	0.73 to 280
Cr ppm	m•••	50	66
	range	24 to 115	24 to 215
Cu ppm	m•••	13	515
	range	0.59 to 1420	46 to 3130
Fe %	mean	40	38
	range	30 to 49	27 to 53
Hg ppm	m•••	0.71	0.98
	range	0.07 to 2.0	0.05 to 5.0
Mo ppm	m•••	48	87
	range	0.07 to 135	1.8 to 575
Ni ppm	m•••	13	400
	range	0.10 to 375	13 to 1690
Pb ppm	m•••	7.0	200
	range	0.06 to 390	15 to 1170
Sb ppm	m•••	26	62
	range	2.6 to 105	10 to 290
Se ppm	m•••	2.5	23
	range	0.07 to 135	0.50 to 165
Tl ppm	m•••	3.1	14
	range	0.22 to 18	0.44 to 93
V ppm	m•••	2.8	15
	range	0.07 to 59	0.08 to 310
Zn ppm	m•••	3.3	60
	range	0.07 to 71	0.50 to 495

Bulk Chemistry and Mineralogy of Efflorescent Salts

The chemistry of the salt collected on massive pyrite in the core (represents salt formed by pyrite oxidation in the presence of humidity) is in Table AII-1 (Appendix II), and that of salt collected on the out crop is in Table AII-3. The mineralogy of the core salt was determined to be szomolnokite ($FeSO_4 \cdot H_2O$) based on bulk chemistry. The outcrop salts were found to be a complex mixture of iron/aluminum-sulfate salts (see Table AII-4 for EDX chemical and XRD mineralogical data and Figure AIII-3 for SEM photomicrographs of the minerals). The average of metal content in outcrop salts (recognizing that the average represents a suite of different iron/aluminum-sulfate salts) is in Table 2.

Dissolution and Precipitation Experiments

The composition of easily dissolved salts and the composition of the iron oxyhyroxides that precipitate when the salt solutions are titrated to pH 7 are in Table AII-5. The dissolution solutions give us an idea of the relative amount of metals that can be flushed from the outcrop during a precipitation event (obviously, exact metal concentration in the weathering solution will depend on the ratio of salt to rain). Most of the metals are nearly quantitatively removed from solutions that are titrated to pH of 7 (table 3). The precipitation data are used to assess the amount of metals that either co-precipitate with or adsorb on to the iron oxyhydroxides that form when the acidic weathering solution mixes with local stream water (most streams in area are pH 7-8). Comparing the dissolution and precipitation data gives us some idea not only about the behavior of metals (removed with iron oxyhydroxides or remained in solution) during this weathering process, but also illustrates how most metals actually are enriched in the oxyhydroxides relative to salt (generally around 3x enrichment).

Summary

The data presented herein provides a comprehensive description of the chemistry of both un-weathered and weathered New Albany Shale at our sample locations, soils derived from these shales, and salts that form as weathering solutions percolate through the shale and then evaporate. In addition, the mineralogy of these salts is described and trace-metal behavior during salt dissolution/iron oxyhydroxide precipitation briefly discussed.

The weathering profiles associated with the New Albany Shale out crop are represented by the lateral and inward trends in metal concentrations. Using sequential metal extractions, we are planning a future to further investigate the residence of trace metals in weathered and un-weathered shale and to investigate in greater detail the changes that occur along the weathering profiles on the out crop. Together with the data presented in the paper, the new extraction data will help predict weathering of trace metals in black shale in other regions and under different climatic regimes.

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Appendix I

The method of decomposition of whole-rock samples, method of analyses, and detection limits for ICP/AES and ICP/MS analyses are given in Table I-1. The detection limits of elements analyzed in the dissolution/precipitation solutions are in Table I-2 (note that limit of detection is for element in solution and is not calculated on a solid weight basis).

Table I-1. Decomposition method, instrument method, and detection limits for most bulk chemical analyses

Element	Decomposition	Method	Reported As	Detection Limit
Al	Sinter	ICP-AES	Al2O3, %	0.02
Ca	Sinter	ICP-AES	CaO, %	0.02
Fe	Sinter	ICP-AES	Fe2O3, %	0.02
Mg	Sinter	ICP-AES	MgO, %	0.02
P	Sinter	ICP-AES	P2O5, %	0.02
K	Sinter	ICP-AES	K2O, %	0.02
Si	Sinter	ICP-AES	SiO2, %	0.02
Ti	Sinter	ICP-AES	TiO2	0.02
Ba	Sinter	ICP-AES	Ba, ppm	2
B	Sinter	ICP-AES	B, ppm	20
Zr	Sinter	ICP-AES	Zr, ppm	5
Na	Multi-acid	ICP-AES	Na2O	0.01
Co	Multi-acid	ICP-AES	Co, ppm	2
Cr	Multi-acid	ICP-AES	Cr, ppm	2
Cu	Multi-acid	ICP-AES	Cu, ppm	2
Li	Multi-acid	ICP-AES	Li, ppm	4
Mn	Multi-acid	ICP-AES	Mn, ppm	2
Ni	Multi-acid	ICP-AES	Ni, ppm	4
Sc	Multi-acid	ICP-AES	Sc, ppm	4
Sr	Multi-acid	ICP-AES	Sr, ppm	1
Th	Multi-acid	ICP-AES	Th, ppm	8
V	Multi-acid	ICP-AES	V, ppm	2
Y	Multi-acid	ICP-AES	Y, ppm	1
Zn	Multi-acid	ICP-AES	Zn, ppm	4
As	Multi-acid	ICP-MS	As, ppm	0.2
Cd	Multi-acid	ICP-MS	Cd, ppm	0.1
Cs	Multi-acid	ICP-MS	Cs, ppm	0.1
Ga	Multi-acid	ICP-MS	Ga, ppm	0.1
Ge	Multi-acid	ICP-MS	Ge, ppm	0.1
Mo	Multi-acid	ICP-MS	Mo, ppm	0.2
Nb	Multi-acid	ICP-MS	Nb, ppm	0.1
Pb	Multi-acid	ICP-MS	Pb, ppm	0.5
Rb	Multi-acid	ICP-MS	Rb, ppm	0.1
Sb	Multi-acid	ICP-MS	Sb, ppm	0.1
Te	Multi-acid	ICP-MS	Te, ppm	0.1
Tl	Multi-acid	ICP-MS	Tl, ppm	0.1
U	Multi-acid	ICP-MS	U, ppm	0.1

Table I-2. Detection limits for elements analyzed in dissolution/precipitation solutions.

Element	Detection Limit
Li ug/L	0.1
Be ug/L	0.05
Na mg/L	0.01
Mg mg/L	0.01
Al ug/L	0.1
Si mg/L	0.2
P mg/L	0.01
SO4 mg/L	2
K mg/L	0.03
Ca mg/L	0.05
Sc ug/L	0.1
Ti ug/L	0.1
V ug/L	0.1
Cr ug/L	1
Mn ug/L	0.01
Fe ug/L	50
Co ug/L	0.02
Ni ug/L	0.1
Cu ug/L	0.5
Zn ug/L	0.5
Ga ug/L	0.02
Ge ug/L	0.02
As ug/L	1
Se ug/L	1
Rb ug/L	0.01
Sr ug/L	0.5
Y ug/L	0.01

Element	Detection Limit
Zr ug/L	0.05
Nb ug/L	0.02
Mo ug/L	0.2
Cd ug/L	0.02
Sb ug/L	0.1
Cs ug/L	0.01
Ba ug/L	0.1
La ug/L	0.01
Ce ug/L	0.01
Pr ug/L	0.01
Nd ug/L	0.01
Sm ug/L	0.01
Eu ug/L	0.005
Tb ug/L	0.005
Gd ug/L	0.005
Dy ug/L	0.005
Ho ug/L	0.005
Er ug/L	0.005
Tm ug/L	0.005
Yb ug/L	0.005
Lu ug/L	0.1
Ta ug/L	0.02
Tl ug/L	0.05
Pb ug/L	0.05
Bi ug/L	0.005
Th ug/L	0.005
U ug/L	0.005

Appendix II

The chemical and isotopic data are tabulated in this appendix. Bulk chemical, sulfide, and sulfur isotopic data for the shale and salt samples in the core are in Table II-1. Also included in Table II are the estimated percentages of selected metals that reside in the pyrite (see method of calculation in text. Bulk chemical and sulfide data for the surface, exposed, and bench shale; efflorescent salts, and soils from the out crop are in Table II-2. Laser Ablation ICP-MS data on metal concentrations in pyrite are in Table II-3. Semi-quantitative EDX data from the SEM analyses of efflorescent salts are in Table II-4. Chemical composition of efflorescent salts on a dry weight basis determined from dissolution experiment and, in parenthesis, the percentage of metal removed from solution when titrated to pH = 7, are in Table II-5.

Table II-1. Bulk chemical, sulfide, and sulfur isotopic data for samples in D8 Core.

Field No.	Sample Description
01KY-47	Vert. py. vein in dk. grayish brn sh.-Sunbury
01KY-48	Dark brn. pyritic sh.
01KY-49	Pyrite nodules and banding in dk. brn. sh.
01KY-50	Very dk. brn. pyritic sh.
01KY-51	White weathering salts on pyrite in shale
01KY-45	Brec.? pyritized med. gry. material in v drk brn py. sh. (top Cleveland)
01KY-46	Dk. brn. pyritic sh.
01KY-52	Med. dk. brn. pyritic sh.
01KY-53	Med. gry. lense of material variably sulfidized
01KY-54	Pyritized lense in med. gry. brn. lam. sh.
01KY-55	Med. brn. pyritic sh. (near bottom of Cleveland)
01KY-57	Med. gry. br. sh.
01KY-58	Med. gry. br. sh. near top of Huron
01KY-59	Med dk. br. sh. middle of Huron
01KY-60	Dk. gry. br. py. Huron sh.
01KY-61	Py. nodule in v. dk. brn Huron sh.
01KY-62	Med gry. pyritic bands & nodules in dk. brn. Huron sh.
01KY-63	Med. dk. brn. pyritic Huron sh.
01KY-64	Med. brn. py. Huron sh.
01KY-65	Med brnish gry. Hur/Duf mudstone/sh.
01KY-66	Sulfidized nodule in Hur/Duf med. brnish gry.calcareous mudstone

Field No.	Type of Sample	Depth (ft)	Depth (m)	Formation
01KY-47	Shale w/massive	24.85	7.57	Sunbury
01KY-48	Shale	25.65	7.82	Sunbury
01KY-49	Shale w/massive	27.15	8.28	Sunbury
01KY-50	Shale	27.25	8.31	Sunbury
01KY-51	Salts	36.3	11.06	Cleveland
01KY-45	Shale w/massive	30.35	9.25	Cleveland
01KY-46	Shale	30.45	9.28	Cleveland
01KY-52	Shale	37.45	11.41	Cleveland
01KY-53	Shale	37.55	11.45	Cleveland
01KY-54	Shale w/massive	65.45	19.95	Cleveland
01KY-55	Shale	65.65	20.01	Cleveland
01KY-57	Shale	74.75	22.78	Huron
01KY-58	Shale	87.05	26.53	Huron
01KY-59	Shale	107.05	32.63	Huron
01KY-60	Shale	127.05	38.72	Huron
01KY-61	Shale w/massive	109.65	33.42	Huron
01KY-62	Shale w/massive	144.35	44.00	Huron
01KY-63	Shale	143.55	43.75	Huron
01KY-64	Shale	158.85	48.42	Huron
01KY-65	Shale	163.35	49.79	Huron/Duf
01KY-66	Shale w/massive	173.85	52.99	Huron/Duf

Field No.	% Ash	% Moisture	Na2O %	Co ppm	%Co in pyrite	Cr ppm
01KY-47	89.4	1.5	0.14	15	1.5	79
01KY-48	80.3	1.6	0.26	22	3.9	84
01KY-49	74.8	1.3	0.22	22	0.37	99
01KY-50	74.2	7.3	0.27	22	4.8	88
01KY-51	86.6	0.8	0.11	8.7		78
01KY-45	84.9	1.1	0.23	11	2.5	130
01KY-46	79.7	1.2	0.43	10	2.8	190
01KY-52	78.8	1.3	0.34	10	9.6	175
01KY-53	96.8	0.4	0.13	3.1	7.5	58
01KY-54	76.4	0.4	0.21	17	2.3	110
01KY-55	86.6	1.3	0.37	18	4.0	86
01KY-57	88.5	1.3	0.43	13	3.1	110
01KY-58	91.8	1.3	0.39	20	4.0	72
01KY-59	91.2	0.3	0.47	19	3.0	53
01KY-60	88.8	1.0	0.46	26	3.7	62
01KY-61	86.9	1.0	0.39	18	0.83	76
01KY-62	87.8	1.0	0.39	19	1.1	65
01KY-63	81.9	0.9	0.33	44	7.5	71
01KY-64	72.4	0.9	0.32	13	7.1	140
01KY-65	98	0.7	0.36	10	2.8	32
01KY-66	97.9	0.2	0.06	19	0.75	16

Field No.	%Cr in pyrite	Cu ppm	%Cu in pyrite	Li ppm	Mn ppm	Ni ppm
01KY-47	18	91	3.8	17	455	175
01KY-48	3.3	230	7.3	35	150	410
01KY-49	5.4	370	0.35	27	130	425
01KY-50	3.8	350	6.0	31	150	415
01KY-51		300		<4.0	28	120
01KY-45	14	260	1.6	16	87	175
01KY-46	0.46	275	2.0	30	150	185
01KY-52	1.8	355	5.4	29	155	225
01KY-53	1.3	28	16	11	2760	<4.0
01KY-54	23	68	9.1	8.0	260	210
01KY-55	2.7	180	7.9	30	260	175
01KY-57	1.2	115	7.1	46	160	145
01KY-58	3.6	73	22	34	195	140
01KY-59	3.4	65	17	27	155	98
01KY-60	5.0	76	25	26	265	105
01KY-61	13	105	2.3	21	215	90
01KY-62	20	25	13	20	205	34
01KY-63	15	96	68	48	225	120
01KY-64	2.1	1230	1.5	34	220	385
01KY-65	2.9	78	7.4	16	2140	<4.0
01KY-66	60	2.0	115	<4.0	2500	35

Field No.	%Ni in pyrite	Sc ppm	Sr ppm	Th ppm	V ppm	%V in pyrite
01KY-47	2.0	10	240	<8.0	215	0.37
01KY-48	3.2	14	100	11	635	0.26
01KY-49	0.31	11	230	12	515	0.06
01KY-50	3.9	12	270	12	530	0.13
01KY-51		<4.0	265	<8.0	18	
01KY-45	2.4	7.0	205	<8.0	215	0.45
01KY-46	2.2	14	360	13	455	0.04
01KY-52	6.6	12	460	15	715	0.09
01KY-53	88	8.5	1220	21	310	0.05
01KY-54	3.0	6.2	545	8.6	38	3.7
01KY-55	6.2	14	640	17	460	0.10
01KY-57	4.3	17	705	12	870	0.03
01KY-58	9.0	14	245	<8.0	205	0.26
01KY-59	8.7	12	89	8.0	220	0.17
01KY-60	14	13	85	14	155	0.41
01KY-61	2.7	12	145	<8.0	180	0.30
01KY-62	10	6.3	99	13	54	1.34
01KY-63	42	10	125	15	175	1.24
01KY-64	3.7	14	59	5.6	355	0.17
01KY-65	110	8.0	165	9.6	88	0.22
01KY-66	6.6	6.9	190	<8.0	1.0	37

Field No.	Y ppm	Zn ppm	%Zn in pyrite	Al2O3%	CaO%	Fe2O3%	K2O%
01KY-47	80	540	0.17	6.8	4.8	27	1.9
01KY-48	53	415	0.46	13	0.30	8.1	3.6
01KY-49	45	3550	0.01	9.9	0.34	15	2.7
01KY-50	49	385	0.62	11	0.32	9.2	3.0
01KY-51	<1.0	50		2.9	0.10	45	0.81
01KY-45	23	99	1.1	7.2	0.38	32	2.2
01KY-46	49	100	0.60	12	0.51	3.9	3.8
01KY-52	105	340	0.65	11	0.72	6.9	3.2
01KY-53	225	270	0.19	4.6	38	2.1	1.5
01KY-54	39	2940	0.05	3.4	3.9	51	0.92
01KY-55	47	340	0.47	13	2.0	6.0	3.8
01KY-57	29	73	1.3	16	0.23	5.1	4.8
01KY-58	39	120	1.5	15	0.35	7.0	4.7
01KY-59	33	140	0.89	12	1.1	4.6	3.5
01KY-60	47	35	6.3	12	2.7	7.0	3.6
01KY-61	57	70	0.89	9.7	3.8	19	3.0
01KY-62	44	82	1.0	6.8	8.0	26	1.8
01KY-63	43	70	11	11	0.82	17	2.7
01KY-64	82	660	0.31	9.6	1.8	7.0	3.1
01KY-65	43	130	0.50	6.3	17	4.0	2.4
01KY-66	110	215	0.28	0.91	29	21	0.18

Field No.	MgO %	P2O5 %	SiO2%	TiO2%	B ppm	Ba ppm	Zr ppm	As ppm
01KY-47	0.58	0.16	28	0.32	85	715	88	2570
01KY-48	1.1	0.13	47	0.63	230	420	140	200
01KY-49	0.90	0.40	39	0.50	200	580	140	385
01KY-50	0.96	0.36	44	0.56	220	2940	140	130
01KY-51	0.21	0.23	12	0.17	<20	540	130	87
01KY-45	0.69	0.54	34	0.42	110	555	125	115
01KY-46	1.3	0.27	53	0.73	215	525	210	18
01KY-52	1.0	1.1	51	0.65	195	150	150	62
01KY-53	0.75	<0.02	18	0.27	<20	335	100	11
01KY-54	0.28	0.31	17	0.28	18	405	75	135
01KY-55	1.0	0.10	54	0.87	265	450	235	37
01KY-57	1.4	0.10	55	0.88	325	185	220	25
01KY-58	1.3	0.06	56	0.84	325	240	155	43
01KY-59	1.0	0.05	60	0.69	225	500	120	29
01KY-60	1.2	0.17	56	0.70	265	600	135	48
01KY-61	0.86	<0.02	45	0.62	190	570	160	185
01KY-62	0.75	0.36	37	0.62	69	615	275	255
01KY-63	1.1	0.32	41	0.65	195	465	210	160
01KY-64	2.0	0.71	39	0.54	255	395	125	26
01KY-65	10	<0.02	33	0.48	165	230	155	14
01KY-66	14	3.2	6.2	0.03	<20	505	115	37

Field No.	%As in pyrite	Cd ppm	%Cd in pyrite	Cs ppm	Ga ppm	Ge ppm
01KY-47	5.1	2.1	5.3	4.9	8.2	1.5
01KY-48	9.4	3.1	1.4	10	17	2.5
01KY-49	13	26	0.16	7.2	13	2.7
01KY-50	18	3.3	1.6	8.2	14	2.2
01KY-51		0.53		1.4	2.3	0.66
01KY-45	140	0.81	17	4.9	8.0	1.4
01KY-46	35	0.80	1.7	8.9	16	2.3
01KY-52	36	3.9	1.3	8.2	14	2.4
01KY-53	47	<0.10	12	3.5	5.1	0.92
01KY-54	170	22	0.90	2.0	3.8	1.0
01KY-55	43	2.5	1.4	8.6	15	2.4
01KY-57	36	0.45	4.6	12	20	2.7
01KY-58	42	0.39	10	11	19	2.7
01KY-59	44	1.1	2.6	7.6	14	2.3
01KY-60	45	0.12	39	7.3	17	2.0
01KY-61	48	0.29	27	6.7	13	1.7
01KY-62	47	0.26	40	3.3	8.2	1.2
01KY-63	47	0.53	31	5.3	14	2.3
01KY-64	79	3.0	1.5	6.6	13	2.3
01KY-65	46	0.15	9.9	3.8	7.1	1.2
01KY-66	235	0.49	15	0.35	1.2	0.70

Field No.	Mo ppm	%Mo in pyrite	Nb ppm	Pb ppm	%Pb in pyrite	Rb ppm
01KY-47	215	6.4	3.9	210	0.83	78
01KY-48	500	0.7	9.3	180	3.8	155
01KY-49	370	1.4	7.2	430	0.15	110
01KY-50	435	1.0	8.8	235	3.6	125
01KY-51	80		1.6	105		23
01KY-45	175	9.8	4.9	43	5.0	78
01KY-46	37	3.0	10	12	18	145
01KY-52	59	6.9	9.2	18	43	130
01KY-53	7.6	13	3.9	1.9	96	54
01KY-54	205	12	2.8	21	15	34
01KY-55	175	1.7	11	12	46	140
01KY-57	98	1.7	12	17	19	190
01KY-58	83	4.0	12	17	39	175
01KY-59	59	4.0	9.4	11	39	130
01KY-60	66	6.1	11	15	50	135
01KY-61	70	14	8.0	27	4.4	115
01KY-62	98	13	7.2	14	11	65
01KY-63	360	3.8	10	21	120	96
01KY-64	48	8.0	9.6	45	16	105
01KY-65	6.0	20	7.1	6.3	37	67
01KY-66	3.6	255	0.50	94	1.2	6.4

Field No.	Sb ppm	%Sb in pyrite	Te ppm	Tl ppm	U ppm	Hg ppm	Se ppm
01KY-47	21	37	0.40	6.0	85	0.36	2.6
01KY-48	13	19	0.88	11	110	0.27	12
01KY-49	23	13	0.72	7.0	100	0.43	11
01KY-50	14	21	0.89	7.6	105	0.30	11
01KY-51	12		<0.10	7.4	1.5	0.55	32
01KY-45	16	60	0.33	6.0	9.0	0.41	29
01KY-46	3.7	20	0.33	2.5	17	0.14	13
01KY-52	12	23	0.65	2.9	35	0.17	30
01KY-53	2.5	26	0.11	0.45	12	0.04	4.5
01KY-54	5.4	250	<0.10	7.9	16	0.22	5.9
01KY-55	9.8	20	0.48	9.5	39	0.11	5.9
01KY-57	8.9	13	0.39	7.3	29	0.05	6.1
01KY-58	4.0	56	0.29	7.3	26	0.13	2.0
01KY-59	3.9	40	0.26	6.4	24	0.09	2.4
01KY-60	3.2	85	0.38	4.3	28	0.09	4.0
01KY-61	9.0	61	0.24	6.0	21	0.08	3.2
01KY-62	3.8	190	0.20	3.1	26	0.07	2.9
01KY-63	5.7	160	0.43	6.8	55	0.16	2.4
01KY-64	6.1	42	0.65	1.7	18	0.26	18
01KY-65	1.1	76	0.43	0.39	4.1	0.09	1.4
01KY-66	1.9	280	<0.10	0.28	4.0	0.04	0.32

Field No.	%Se in pyrite	Total S %	S sulfide %	δ••$S_{sulfides}$
01KY-47	28	17	16	-5.5
01KY-48	6.5	4.4	2.3	-26.6
01KY-49	2.5	9.5	5.8	-8.9
01KY-50	9.6	5.5	2.8	-17.2
01KY-51		21		
01KY-45	3.1	20	19	-14.0
01KY-46	1.9	1.5	0.73	-25.4
01KY-52	3.1	3.9	2.6	-29.6
01KY-53	4.9	0.52	0.62	-22.4
01KY-54	22	29	28	-8.9
01KY-55	11	2.7	1.9	-3.8
01KY-57	6.4	1.6	1.1	-19.5
01KY-58	38	3.0	2.2	-22.8
01KY-59	22	1.9	1.5	-17.0
01KY-60	23	3.6	2.6	-20.8
01KY-61	16	12	11	4.6
01KY-62	23	15	14	-18.7
01KY-63	130	9.9	8.8	-19.4
01KY-64	4.8	3.5	2.5	-23.7
01KY-65	20	0.81	0.78	-26.5
01KY-66	150	9.5	10	-33.6

Table II-2. Bulk chemical and sulfide data for shale, efflorescent salts, and soil from the out crop.

Field No.	Sample Description	m along transect
01-KY-12	Reddish soil about 175 m below KY-11	0
01-KY-14	20 cm pit at 01KY-12--reddish soil	0
01-KY-13	Reddish soil halfway between KY11-12R	5
01KY-11	Lt. brown Soil just to right of outcrop	10
01-KY-15-A	White coating on shale	203
01-KY-15-B	Red-brn. shale beneath coating KY-15-A	203
01KY-10-A	Weathered reddish brown shale	258
01-KY-10-B	Shale beneath coating 01KY-10-A	258
01-KY-16-A	Coating on shale	308
01-KY-16-B	Shale beneath coating 01KY-16-A	308
01KY-17-A	Coating on shale	368
01KY-17-B	Shale beneath coating 01KY-17-A	368
01KY-18-A	Coating on shale just before slump block(?)	443
01KY-18-B	Shale beneath 01KY-18-A	443
01KY-19-A	Coating on shale just on slump block(?)	583
01KY-19-B	Fissle shale just on slump block(?)	583
01KY-20-A	Coating on shale near salt encrustations	663
01KY-20-B	Grayish cemented(?) shale beneath KY-20-A	663
01KY-21	Salts encrustation just above & left KY-20	693
01KY-24-A	Reddish saltish surface on shale	813
01KY-24-B	Shale beneath KY-24-A	813
01KY-23	Hard Salts just below KY-24-A&B	815
01KY-27	Salts encrustation near KY-23	845
01KY-22	Lt. yellow salts left of KY21	958
01KY-25-A	Coating on shale at left edge of slump block(?)	1063
01KY-26-A	Coating on shale (back on outcrop proper)	1283
01KY-26-B	More blocky shale beneath KY-26-A	1283
01KY-28-A	Coating on shale	1613
01KY-28-B	Shale beneath KY-28-A	1613
01KY-29	White weathering rind on disaggreg. sh. on bench	
01KY-30	Red weathering rind on disaggred sh. on bench	
01KY-31	Out crop of red weathered shale on bench	

Field No.	Type of Sample	% Ash	% Moisture	Na20 %	Co ppm	Cr ppm
01-KY-12	Soil	91	2.7	0.16	5.1	130
01-KY-14	Soil	93	2.8	0.16	5.6	135
01-KY-13	Soil	93	2.2	0.18	5.9	105
01KY-11	Soil	89	2.4	0.18	5.9	115
01-KY-15-A	Surface sh.	91	1.8	0.22	5.3	96
01-KY-15-B	Unexposed sh.	91	2.0	0.22	4.9	66
01KY-10-A	Surface sh.	91	1.6	0.18	5.2	68
01-KY-10-B	Unexposed sh.	90	1.5	0.22	5.7	65
01-KY-16-A	Surface sh.	90	1.5	0.18	5.6	87
01-KY-16-B	Unexposed sh.	90	1.7	0.20	5.4	68
01KY-17-A	Surface sh.	90	1.6	0.22	6.4	95
01KY-17-B	Unexposed sh.	90	1.5	0.26	5.1	63
01KY-18-A	Surface sh.	90	1.5	0.29	7.2	92
01KY-18-B	Unexposed sh.	88	1.5	0.33	6.1	66
01KY-19-A	Surface sh.	85	1.7	0.34	6.0	86
01KY-19-B	Unexposed sh.	59	1.7	0.35	7.3	65
01KY-20-A	Surface sh.	83	3.3	0.34	19	78
01KY-20-B	Unexposed sh.	83	3.3	0.32	20	59
01KY-21	Salt	72	16	0.17	72	49
01KY-24-A	Surface sh.	82	4.8	0.27	42	64
01KY-24-B	Unexposed sh.	88	1.7	0.33	8.1	68
01KY-23	Salt	61	10	0.01	89	60
01KY-27	Salt	70	5.6	0.06	36	52
01KY-22	Salt	74	4.8	0.23	36	57
01KY-25-A	Surface sh.	83	4.8	0.27	28	63
01KY-26-A	Surface sh.	86	1.6	0.36	12	62
01KY-26-B	Unexposed sh.	86	1.6	0.34	31	68
01KY-28-A	Surface sh.	88	1.9	0.34	6.4	72
01KY-28-B	Unexposed sh.	86	2.1	0.35	17	71
01KY-29	Surface sh.	87	1.3	0.27	5.4	66
01KY-30	Surface sh.	81	1.3	0.45	6.5	64
01KY-31	Unexposed sh.	90	2.4	0.20	6.0	86

Field No.	Cu ppm	Li ppm	Mn ppm	Ni ppm	Sc ppm	Sr ppm	V ppm	Y ppm
01-KY-12	63	26	53	12	18	79	515	18
01-KY-14	51	27	52	13	20	84	525	21
01-KY-13	43	24	44	16	15	50	410	12
01KY-11	61	24	54	18	16	82	395	17
01-KY-15-A	29	24	38	23	14	95	255	19
01-KY-15-B	19	23	35	15	13	64	190	18
01KY-10-A	83	24	36	19	13	81	200	16
01-KY-10-B	12	24	39	18	13	72	190	14
01-KY-16-A	43	23	35	20	13	66	215	15
01-KY-16-B	46	24	35	24	13	90	200	16
01KY-17-A	47	23	36	24	14	71	255	15
01KY-17-B	4.3	23	32	22	13	77	190	14
01KY-18-A	10	24	37	33	13	85	260	14
01KY-18-B	1.2	23	35	27	13	94	205	14
01KY-19-A	9.2	21	34	31	12	71	250	12
01KY-19-B	6.4	22	38	29	11	90	325	11
01KY-20-A	67	24	110	84	12	62	180	39
01KY-20-B	45	25	110	90	12	74	175	36
01KY-21	240	31	415	325	17	68	140	170
01KY-24-A	120	26	230	150	13	61	150	60
01KY-24-B	4.3	23	57	26	12	73	185	21
01KY-23	160	16	440	300	10	31	17	62
01KY-27	155	16	225	110	13	50	41	54
01KY-22	79	34	220	130	8.5	110	96	59
01KY-25-A	125	26	120	99	11	46	150	40
01KY-26-A	41	23	59	31	11	69	180	22
01KY-26-B	100	24	165	67	12	83	155	43
01KY-28-A	2.1	23	47	30	11	110	195	20
01KY-28-B	71	23	62	97	11	30	190	23
01KY-29	1.2	22	34	21	13	58	210	15
01KY-30	1.1	35	42	41	10	120	220	13
01KY-31	67	21	36	20	13	115	240	14

Field No.	Zn ppm	Al2O3 %	Fe2O3 %	K2O %	SiO2 %	TiO2 %	B ppm
01-KY-12	39	17	8.2	4.2	60	0.81	170
01-KY-14	38	18	9.0	4.6	58	0.81	190
01-KY-13	27	14	6.0	3.7	65	0.93	130
01KY-11	38	14	8.2	3.7	59	0.82	145
01-KY-15-A	25	14	5.3	3.9	66	0.79	150
01-KY-15-B	19	13	6.3	3.5	65	0.76	140
01KY-10-A	20	13	4.3	3.8	67	0.78	140
01-KY-10-B	18	13	3.8	3.6	67	0.77	135
01-KY-16-A	18	13	5.0	3.7	65	0.77	140
01-KY-16-B	21	13	5.3	3.7	65	0.76	130
01KY-17-A	24	13	6.2	3.6	63	0.76	160
01KY-17-B	17	13	4.3	3.7	65	0.75	140
01KY-18-A	26	13	5.5	3.8	64	0.75	150
01KY-18-B	20	13	4.9	3.7	64	0.74	145
01KY-19-A	19	11	6.5	2.9	52	0.65	130
01KY-19-B	28	12	6.3	3.2	61	0.71	135
01KY-20-A	72	11	6.9	3.1	53	0.66	105
01KY-20-B	63	11	6.7	3.7	55	0.66	125
01KY-21	220	10	7.2	1.6	27	0.31	55
01KY-24-A	105	10	7.2	3.0	46	0.57	210
01KY-24-B	2.5	12	5.5	4.0	60	0.72	280
01KY-23	210	4.5	15	0.22	3.7	0.04	<10
01KY-27	1030	5.2	15	0.70	10	0.13	25
01KY-22	160	7.1	8.2	1.8	32	0.34	54
01KY-25-A	52	11	7.5	3.2	49	0.59	220
01KY-26-A	9.0	12	6.2	3.9	60	0.71	295
01KY-26-B	33	11	8.7	3.5	56	0.68	235
01KY-28-A	10	12	6.4	3.8	57	0.67	200
01KY-28-B	20	11	7.7	3.5	53	0.69	255
01KY-29	2.4	14	2.7	4.7	71	0.96	295
01KY-30	2.3	12	6.5	3.7	54	0.89	180
01KY-31	8.8	17	12	4.2	51	0.78	260

Field No.	Ba ppm	Zr ppm	As ppm	Cd ppm	Cs ppm	Ga ppm	Ge ppm	Mo ppm
01-KY-12	515	130	51	0.16	15	19	2.8	97
01-KY-14	520	135	52	<.10	16	22	3.3	95
01-KY-13	510	150	43	0.27	11	16	2.6	86
01KY-11	520	130	57	0.20	10	17	2.5	110
01-KY-15-A	625	135	42	0.09	9.9	17	2.9	68
01-KY-15-B	555	120	46	<.10	8.5	17	2.4	57
01KY-10-A	585	125	32	0.10	8.9	16	2.2	44
01-KY-10-B	645	115	36	<.10	8.7	17	2.4	49
01-KY-16-A	575	125	39	0.09	8.6	16	2.9	59
01-KY-16-B	570	125	44	0.78	8.7	17	2.3	55
01KY-17-A	690	135	50	0.17	9.3	17	2.8	75
01KY-17-B	570	130	37	0.09	8.8	16	2.2	50
01KY-18-A	520	150	38	0.16	9.7	16	2.7	70
01KY-18-B	410	130	56	0.11	8.5	16	2.3	73
01KY-19-A	440	120	63	<.10	8.2	16	2.3	77
01KY-19-B	1450	135	58	0.12	7.9	15	2.0	68
01KY-20-A	380	100	42	0.41	6.7	13	2.2	75
01KY-20-B	370	110	43	0.31	6.8	13	2.2	62
01KY-21	205	50	72	1.4	4.3	8.7	1.4	26
01KY-24-A	850	120	50	0.75	6.1	13	1.7	40
01KY-24-B	155	150	46	<.10	7.9	16	2.4	43
01KY-23	33	6.3	77	1.3	0.3	3.1	0.24	15
01KY-27	365	110	68	4.6	1.4	6.2	0.63	40
01KY-22	215	63	18	0.73	3.8	7.5	1.0	34
01KY-25-A	310	125	40	0.24	6.5	13	1.8	44
01KY-26-A	425	160	41	0.10	7.8	16	2.3	75
01KY-26-B	525	165	54	0.18	6.8	14	2.0	97
01KY-28-A	550	120	55	<.10	8.0	16	2.2	53
01KY-28-B	495	170	52	0.21	7.0	16	2.2	67
01KY-29	125	200	32	<.10	8.3	19	2.7	51
01KY-30	120	115	52	0.11	6.8	17	2.5	170
01KY-31	545	235	70	0.13	9.4	19	2.4	135

Field No.	Nb ppm	Pb ppm	Rb ppm	Sb ppm	Tl ppm	U ppm
01-KY-12	11	23	215	6.2	8.9	24
01-KY-14	11	23	235	5.6	10	23
01-KY-13	12	21	185	7.1	6.1	20
01KY-11	9.8	28	170	7.4	4.5	24
01-KY-15-A	10	17	165	4.2	4.0	17
01-KY-15-B	11	18	150	3.4	2.7	16
01KY-10-A	8.9	11	155	2.6	2.9	17
01-KY-10-B	13	17	150	3.4	2.8	14
01-KY-16-A	11	12	150	3.4	2.9	17
01-KY-16-B	9.8	17	155	3.2	2.8	16
01KY-17-A	11	21	160	3.9	4.0	17
01KY-17-B	12	17	150	3.2	3.4	13
01KY-18-A	12	20	160	3.8	5.5	13
01KY-18-B	12	20	150	3.7	4.8	13
01KY-19-A	9.6	17	145	3.8	5.6	11
01KY-19-B	11	17	145	3.5	5.1	12
01KY-20-A	9.9	15	125	3.5	3.8	21
01KY-20-B	9.3	14	130	2.9	3.3	19
01KY-21	5.5	8.3	72	1.9	1.1	65
01KY-24-A	8.6	12	110	2.3	2.2	28
01KY-24-B	10	18	145	3.2	2.9	12
01KY-23	0.48	0.40	7.6	0.21	0.27	39
01KY-27	2.3	0.62	27	0.63	0.61	41
01KY-22	4.5	9.8	69	2.0	1.7	19
01KY-25-A	8.5	13	120	2.5	2.6	19
01KY-26-A	11	21	140	3.3	2.9	15
01KY-26-B	9.5	17	125	3.5	3.4	21
01KY-28-A	10	17	150	3.2	3.4	12
01KY-28-B	9.4	17	135	4.3	4.0	19
01KY-29	12	9.6	150	4.5	2.1	20
01KY-30	12	23	130	5.8	8.6	31
01KY-31	12	28	150	5.2	6.5	19

Field No.	Hg ppm	Se ppm	Total S %	$S_{Sulfide}$ %
01-KY-12	0.06	3.9	0.15	0.02
01-KY-14	0.05	4.0	<.10	0.01
01-KY-13	0.05	3.3	0.10	0.003
01KY-11	0.07	4.5	0.33	0.02
01-KY-15-A	0.05	0.25	0.47	0.11
01-KY-15-B	0.06	1.5	0.46	0.12
01KY-10-A	0.05	1.3	0.39	0.05
01-KY-10-B	0.04	1.4	0.62	0.17
01-KY-16-A	0.05	1.7	0.33	0.06
01-KY-16-B	0.05	1.5	0.50	0.08
01KY-17-A	0.05	2.2	0.59	0.06
01KY-17-B	0.05	1.6	0.66	0.20
01KY-18-A	0.05	2.0	1.1	0.28
01KY-18-B	0.06	2.3	1.3	0.45
01KY-19-A	0.07	2.1	1.9	0.29
01KY-19-B	0.07	1.9	1.9	0.30
01KY-20-A	0.07	2.0	3.2	0.52
01KY-20-B	0.06	1.7	2.9	0.57
01KY-21	0.05	0.83	10	
01KY-24-A	0.04	1.3	4.4	0.34
01KY-24-B	0.07	1.7	1.6	0.52
01KY-23	0.05	0.41	15	
01KY-27	0.02	0.29	13	
01KY-22	0.05	0.92	9.0	
01KY-25-A	0.07	1.4	4.1	0.64
01KY-26-A	0.07	1.7	2.7	1.5
01KY-26-B	0.08	2.0	4.5	2.7
01KY-28-A	0.06	1.7	1.7	0.65
01KY-28-B	0.06	1.7	3.3	1.0
01KY-29	0.08	1.9	0.72	1.2
01KY-30	0.13	1.7	1.7	.47
01KY-31	0.06	2.0	1.2	

Table II-3. LA-ICP-MS data of trace-metal concentrations of pyrite in polished sections.

Section	Analysis ID	Description	V ppm
01-KY-56	56-2 Anhedral	Anhedral crystal near massive py	44
01-KY-56	56-3 Anhedral	Anhedral crystal near massive py	160
01-KY-56	56-5 Anhedral		55
01-KY-56	56-6 Anhedral	Roundish pyrite bleb	100
01-KY-56	56-7 Anhedral		20
01-KY-56	56-8 Anhedral		52
01-KY-56	56-9 Anhedral		60
01-KY-56	56-10 Anhedral	Roundish pyrite bleb	11
01-KY-56	56-11 Subhedral	Subhedral pyrite grain	12
01-KY-56	56-12 Anhedral	Roundish pyrite bleb	34
01-KY-56	56-13 Anhedral	Small roundish pyrite bleb	310
01-KY-56	56-14 Anhedral	Roundish pyrite bleb	8.1
01-KY-56	56-15 Anhedral	Roundish pyrite bleb	27
01-KY-56	56-16 Anhedral	Single anhedral grain	19
01-KY-56	56-17 Subhedral	Subhedral pyrite grain	47
01-KY-56	56-18 Anhedral	Elongated pyrite grain	120
01-KY-56	56-19 Anhedral	Elongated pyrite grain	56
01-KY-56	56-20 Anhedral	Roundish pyrite bleb	56
01-KY-56	56-21 Anhedral	Roundish pyrite bleb	96
01-KY-56	56-22 Anhedral	Roundish pyrite bleb	65
01-KY-56	56-23 Anhedral	Roundish pyrite bleb	170
01-KY-56	56-24 Anhedral	Single anhedral grain	46
01-KY-56	56-25 Anhedral	Elongated pyrite grain	23
01-KY-56	56-26 Anhedral	Single anhedral grain	36
01-KY-56	56-27 Anhedral	Small roundish pyrite bleb	59
01-KY-56	56-28 Anhedral	Single anhedral grain	17
01-KY-56	56-29 Anhedral	Roundish pyrite bleb	49
01-KY-56	56-30 Replacement	Roundish pyrite replacement	3.9
01-KY-56	56-31 Anhedral	Roundish pyrite bleb	97
01-KY-56	56-32 Anhedral	Roundish pyrite grain	32
01-KY-56	56-33 Anhedral	Anhedral crystal near massive py	26
01-KY-56	56-34 Massive	Massive pyrite at shale/sulfide interface	18
01-KY-56	56-35 Massive	Massive pyrite	16
01-KY-56	56-36 Massive	Massive pyrite-dark	0.08
01-KY-45	45-1 Framboid		0.59
01-KY-45	45-2 Framboid		1.7
01-KY-45	45-3 Framboid	Framboid near massive	0.52
01-KY-45	45-4 Massive	Massive pyrite at shale/sulfide interface	17
01-KY-45	45-5 Framboid	Framboid	3.7
01-KY-45	45-6 Framboid	Framboid	5.9
01-KY-45	45-7 Framboid	Framboid-elongated	2.1

Analysis ID	Cr ppm	Co ppm	Nippm	Cu ppm	Zn ppm	As ppm	Se ppm	Mo ppm
56-2 Anhedral	70	255	1690	3125	93	955	39	575
56-3 Anhedral	100	90	965	605	80	595	7.2	130
56-5 Anhedral	90	4.7	145	75	67	335	7.7	1.8
56-6 Anhedral	94	280	1290	1030	88	480	41	315
56-7 Anhedral	83	43	1005	435	27	805	14	65
56-8 Anhedral	83	33	545	250	68	490	4.7	51
56-9 Anhedral	24	41	490	1000	33	750	25	165
56-10 Anhedral	63	0.73	17	46	<.50	115	16	5.0
56-11 Subhedral	50	140	1605	1375	46	1300	41	235
56-12 Anhedral	32	17	355	270	53	555	10	38
56-13 Anhedral	215	49	470	405	170	520	<.50	175
56-14 Anhedral	35	1.9	13	72	28	3080	<.50	6.5
56-15 Anhedral	92	6.7	58	700	56	1710	7.7	165
56-16 Anhedral	53	29	585	480	53	875	15	62
56-17 Subhedral	47	72	810	485	55	670	12	96
56-18 Anhedral	67	30	390	335	52	665	15	80
56-19 Anhedral	79	54	705	405	22	490	17	63
56-20 Anhedral	93	86	1070	980	51	600	39	300
56-21 Anhedral	55	100	980	510	100	755	14	115
56-22 Anhedral	91	7.6	150	50	43	160	24	22
56-23 Anhedral	135	38	385	165	39	350	<.50	57
56-24 Anhedral	67	45	615	430	110	925	5.9	96
56-25 Anhedral	37	36	560	345	9.5	560	<.50	54
56-26 Anhedral	58	42	615	415	14	680	<.50	72
56-27 Anhedral	110	21	370	83	28	305	<.50	27
56-28 Anhedral	69	105	840	1490	245	720	49	240
56-29 Anhedral	59	135	540	520	170	700	30	175
56-30 Replace	31	14	200	1140	17	940	45	225
56-31 Anhedral	115	89	865	1710	125	995	50	515
56-32 Anhedral	63	210	1180	2450	110	1130	48	525
56-33 Anhedral	69	51	775	405	24	875	8.2	52
56-34 Massive	96	4.6	48	38	1.4	1040	1.2	11
56-35 Massive	33	7.3	120	28	23	1410	<.50	6.5
56-36 Massive	65	<0.5	11	2.3	9.6	845	2.6	12
45-1 Framboid	50	21	645	880	495	295	89	70
45-2 Framboid	61	4.9	365	855	28	660	47	39
45-3 Framboid	66	18	740	1020	195	600	160	60
45-4 Massive	52	1.6	38	110	11	190	23	305
45-5 Framboid	67	19	370	1440	47	660	120	180
45-6 Framboid	33	11	455	1270	53	735	165	185
45-7 Framboid	62	8.5	370	1170	30	525	93	97

Analysis ID	Cd ppm	Sb ppm	Hg ppm	Tl ppm	Pb ppm	Fe %
56-2 Anhedral	5.5	290	0.30	93	1170	42.0
56-3 Anhedral	2.0	155	<.10	25	420	40.4
56-5 Anhedral	0.52	30	0.59	1.3	65	40.6
56-6 Anhedral	2.9	160	1.7	55	585	37.9
56-7 Anhedral	1.6	150	2.4	10	345	42.1
56-8 Anhedral	1.4	110	3.0	5.7	210	39.4
56-9 Anhedral	2.1	170	3.1	33	370	40.6
56-10 Anhedral	<.10	11	2.3	1.0	15	35.8
56-11 Subhedral	3.2	235	1.4	24	780	43.2
56-12 Anhedral	0.75	79	1.0	9.9	205	32.7
56-13 Anhedral	0.39	76	<.10	21	195	32.5
56-14 Anhedral	<.10	33	0.74	0.4	64	42.8
56-15 Anhedral	1.8	63	1.1	14	110	42.3
56-16 Anhedral	2.3	135	1.4	7.7	750	43.5
56-17 Subhedral	0.09	140	2.2	10	345	38.6
56-18 Anhedral	2.3	95	0.95	8.4	345	37.6
56-19 Anhedral	1.9	110	0.83	8.8	245	44.4
56-20 Anhedral	<.10	140	0.78	46	485	31.2
56-21 Anhedral	2.8	140	0.56	12	320	43.0
56-22 Anhedral	0.79	10	1.0	4.1	16	33.4
56-23 Anhedral	0.39	46	1.5	4.0	105	36.3
56-24 Anhedral	2.6	130	<.10	13	630	36.5
56-25 Anhedral	5.5	130	1.4	10	500	31.2
56-26 Anhedral	5.8	160	0.29	12	640	33.7
56-27 Anhedral	<.10	31	3.0	1.5	44	38.1
56-28 Anhedral	2.9	180	1.6	75	650	28.8
56-29 Anhedral	1.8	69	1.9	62	225	37.7
56-30 Replace	3.2	125	1.1	72	96	34.5
56-31 Anhedral	3.0	255	5.0	62	820	34.3
56-32 Anhedral	3.0	265	1.8	81	1020	36.8
56-33 Anhedral	1.3	185	1.7	11	650	35.0
56-34 Massive	0.30	86	<.10	1.3	170	31.0
56-35 Massive	<.10	55	<.10	1.9	92	37.7
56-36 Massive	<.10	41	<.10	1.1	2.6	44.0
45-1 Framboid	1.1	29	0.37	32	205	53.3
45-2 Framboid	2.2	20	2.5	20	100	48.4
45-3 Framboid	1.2	31	1.1	25	145	46.2
45-4 Massive	<.10	34	0.47	10	46	38.4
45-5 Framboid	0.91	100	0.82	20	245	41.2
45-6 Framboid	1.2	110	0.78	34	150	39.4
45-7 Framboid	1.6	35	1.2	13	155	40.5

Section	Analysis ID	Description	V ppm
01-KY-45	45-8 Framboid	Framboid-classic	0.08
01-KY-45	45-9 Framboid	Framboid	2.8
01-KY-45	45-10 Framboid	Framboid	1.1
01-KY-45	45-11 Framboid	Framboid	2.0
01-KY-45	45-12 Framboid	Framboid-elongated	3.0
01-KY-45	45-13 Anhedral	Elongated pyrite grain	2.2
01-KY-45	45-14 Framboid	Framboid	2.3
01-KY-45	45-15 Framboid	Framboid	0.92
01-KY-45	45-16 Framboid	Framboid	1.9
01-KY-45	45-17 Framboid	Framboid	4.4
01-KY-45	45-18 Framboid	Framboid	9.5
01-KY-45	45-19 Anhedral	Single anhedral grain	6.2
01-KY-45	45-20 Anhedral	Anhedral grain (flattened fram.?)	2.9
01-KY-45	45-21 Framboid	Framboid	0.93
01-KY-45	45-22 Framboid	Framboid	2.9
01-KY-45	45-23 Anhedral	Roundish pyrite bleb	6.8
01-KY-45	45-24 Massive	Spot on bright massive pyrite	12
01-KY-45	45-25 Massive	Spot on dark massive pyrite	1.4
01-KY-45	45-26 Massive	Spot on bright veinlette in massive	9.9
01-KY-45	45-27 Massive	Dark, round py rimmed with bright py	2.5
01-KY-54	54-01 Anhedral	Roundish pyrite bleb	53
01-KY-54	54-02 Anhedral	Single anhedral grain	40
01-KY-54	54-03 Anhedral	Single anhedral grain	44
01-KY-54	54-04 Anhedral	Roundish pyrite bleb	120
01-KY-54	54-05 Anhedral	Single anhedral grain	30
01-KY-54	54-06 Anhedral	Roundish pyrite grain	58
01-KY-54	54-07 Anhedral	Single anhedral grain	135
01-KY-54	54-08 Framboid	Framboid-classic	17
01-KY-54	54-09 Anhedral	Single anhedral grain	35
01-KY-54	54-11 Framboid	Framboid-classic	41
01-KY-54	54-12 Anhedral	Single anhedral grain	24
01-KY-54	54-13 Anhedral	Single anhedral grain	25
01-KY-56	56-1 Nodule	Edge of T1 (smaller nodule)	0.58
01-KY-56	56-2 Nodule	Across smaller nodule	0.07
01-KY-56	56-3 Nodule	Across smaller nodule	1.9
01-KY-56	56-4 Nodule	Across smaller nodule	0.75
01-KY-56	56-5 Nodule	Across smaller nodule	3.3
01-KY-56	56-6 Nodule	Across smaller nodule	0.07
01-KY-56	56-7 Nodule	Across smaller nodule	59
01-KY-56	56-8 Nodule	Across smaller nodule	1.4
01-KY-56	56-9 Nodule	Across smaller nodule	54

Analysis ID	Cr ppm	Co ppm	Nippm	Cu ppm	Zn ppm	As ppm	Se ppm	
45-8 Framboid	48	3.6	125	520	40	585	19	16
45-9 Framboid	56	17	495	1240	38	515	130	285
45-10 Framboid	69	17	415	915	40	735	74	60
45-11 Framboid	77	22	335	1515	29	790	125	230
45-12 Framboid	59	18	490	1130	45	545	130	210
45-13 Anhedral	65	27	655	1105	29	680	110	170
45-14 Framboid	58	14	395	1020	64	600	63	81
45-15 Framboid	53	5.8	160	760	92	380	85	295
45-16 Framboid	79	9.4	345	1335	38	535	110	120
45-17 Framboid	63	5.5	130	1025	18	875	115	185
45-18 Framboid	47	4.0	165	935	22	765	125	150
45-19 Anhedral	57	3.2	28	695	11	235	11	10
45-20 Anhedral	91	22	495	1420	38	635	135	125
45-21 Framboid	51	8.9	245	1050	42	870	155	185
45-22 Framboid	49	6.2	220	590	63	390	40	31
45-23 Anhedral	36	16	295	1010	57	710	115	160
45-24 Massive	66	1.0	30	76	1.4	70	<.50	58
45-25 Massive	30	<0.50	3.0	5.8	<.50	27	<.50	70
45-26 Massive	55	1.7	29	49	15	61	7.1	110
45-27 Massive	72	18	375	1410	22	1160	135	250
54-01 Anhedral	115	110	860	360	395	145	37	88
54-02 Anhedral	63	51	435	265	125	76	22	64
54-03 Anhedral	62	59	430	265	195	135	31	58
54-04 Anhedral	115	50	60	185	375	240	4.9	205
54-05 Anhedral	48	34	275	230	65	74	23	62
54-06 Anhedral	53	83	735	305	190	180	37	69
54-07 Anhedral	105	48	260	365	440	210	45	105
54-08 Framboid	60	53	525	320	130	145	16	91
54-09 Anhedral	140	210	1600	440	245	310	34	100
54-11 Framboid	78	43	345	220	175	85	30	64
54-12 Anhedral	55	140	1525	345	140	350	42	85
54-13 Anhedral	73	33	665	71	75	140	7.5	55
56-1 Nodule	43	1.7	31	2.5	2.5	770	3.7	13
56-2 Nodule	35	0.30	7.7	2.7	0.07	995	0.07	13
56-3 Nodule	34	0.06	3.6	0.59	6.2	935	1.2	15
56-4 Nodule	37	0.60	38	2.2	0.07	1000	9.1	15
56-5 Nodule	46	0.26	5.6	1.2	5.0	960	0.07	24
56-6 Nodule	35	0.07	1.0	3.2	3.8	910	8.2	59
56-7 Nodule	44	4.1	32	36	36	485	5.1	53
56-8 Nodule	34	<0.50	0.6	5.1	6.3	660	7.2	55
56-9 Nodule	61	1.1	7.3	17	33	570	5.5	64

Analysis ID	Cd ppm	Sb ppm	Hg ppm	Tl ppm	Pb ppm	Fe %
45-8 Framboid	1.4	13	1.2	11	84	41.4
45-9 Framboid	1.3	68	1.8	26	255	42.9
45-10 Framboid	<.10	36	2.3	18	205	41.1
45-11 Framboid	0.90	60	0.46	14	320	39.7
45-12 Framboid	1.7	67	0.59	17	290	39.4
45-13 Anhedral	2.0	62	0.66	19	390	39.8
45-14 Framboid	1.4	39	1.8	17	200	43.3
45-15 Framboid	1.4	50	1.7	17	130	43.5
45-16 Framboid	<.10	45	0.67	14	175	38.4
45-17 Framboid	1.9	70	1.6	26	105	40.2
45-18 Framboid	1.4	58	1.8	16	130	35.5
45-19 Anhedral	<.10	27	<.10	1.2	135	40.7
45-20 Anhedral	1.00	64	2.4	13	295	37.4
45-21 Framboid	<.10	48	0.51	11	135	37.8
45-22 Framboid	0.71	19	1.1	14	110	37.5
45-23 Anhedral	0.50	43	1.2	7.5	240	33.8
45-24 Massive	0.42	7.7	<.10	5.0	41	39.1
45-25 Massive	0.68	2.6	0.18	6.0	0.3	42.2
45-26 Massive	0.20	6.8	0.39	3.7	27.0	36.2
45-27 Massive	0.55	66	1.1	16	390	35.7
54-01 Anhedral	8.7	53	3.9	24	145	41.9
54-02 Anhedral	4.5	29	2.2	10	81	30.6
54-03 Anhedral	3.4	39	1.7	14	105	31.6
54-04 Anhedral	2.2	12	<.10	3.9	190	33.0
54-05 Anhedral	3.5	28	2.1	15	87	28.3
54-06 Anhedral	6.3	58	1.8	17	140	27.3
54-07 Anhedral	3.7	27	3.2	43	87	30.8
54-08 Framboid	1.6	33	0.06	20	130	39.3
54-09 Anhedral	3.7	97	2.2	38	205	37.7
54-11 Framboid	3.5	29	0.66	16	88	29.4
54-12 Anhedral	4.0	100	0.94	20	250	34.2
54-13 Anhedral	1.8	25	1.3	10	81	33.8
56-1 Nodule	0.43	34	1.1	0.81	9.9	47.2
56-2 Nodule	0.86	37	1.1	1.2	2.1	48.5
56-3 Nodule	0.50	50	0.41	1.5	0.76	46.2
56-4 Nodule	0.38	60	0.92	1.7	6.0	46.5
56-5 Nodule	0.39	63	1.1	2.2	1.9	48.8
56-6 Nodule	0.42	97	0.89	4.0	0.06	47.2
56-7 Nodule	0.33	44	1.5	3.7	25	37.6
56-8 Nodule	0.07	38	1.8	1.7	0.54	48.8
56-9 Nodule	0.07	45	1.5	1.9	3.9	44.0

Section	Analysis ID	Description	V ppm
01-KY-56	56-10 Nodule	Across smaller nodule	0.07
01-KY-56	56-11 Nodule	Across smaller nodule	0.36
01-KY-56	56-12 Nodule	Across smaller nodule	1.0
01-KY-56	56-13 Nodule	Across smaller nodule	0.07
01-KY-56	56-14 Nodule	along edge with shale (smaller nodule)	1.0
01-KY-56	56-15 Nodule	along edge with shale (larger nodule)	0.10
01-KY-56	56-16 Nodule	along edge with shale (inter nodule)	1.7
01-KY-56	56-17 Nodule	along edge with shale (inter nodule)	2.6
01-KY-56	56-18 Nodule	along edge with shale (inter nodule)	3.0
01-KY-56	56-19 Nodule	along edge with shale (inter nodule)	12
01-KY-56	56-20 Nodule	Edge of T4 (larger nodule)	2.2
01-KY-56	56-21 Nodule	Across larger nodule	1.3
01-KY-56	56-22 Nodule	Across larger nodule	8.2
01-KY-56	56-23 Nodule	Across larger nodule	4.5
01-KY-56	56-24 Nodule	along edge with shale (larger nodule)	5.5
01-KY-56	56-25 Nodule	edge of larger nodule	18
01-KY-56	56-26 Nodule	edge of larger nodule	8.1
01-KY-56	56-27 Nodule	across larger nodule	16
01-KY-56	56-28 Nodule	Edge of T4 (larger nodule)	5.9
01-KY-56	56-29 Nodule	along edge with shale (larger nodule)	0.09
01-KY-56	56-30 Nodule	Across larger nodule	0.12
01-KY-45	45-01 Lense	lense Across bedding	12
01-KY-45	45-02 Lense	lense Across bedding	16
01-KY-45	45-03 Lense	lense Across bedding	26
01-KY-45	45-04 Lense	lense Across bedding	4.6
01-KY-45	45-05 Lense	lense Across bedding	3.0
01-KY-45	45-06 Lense	lense along bedding	2.2
01-KY-45	45-07 Lense	lense along bedding	8.4
01-KY-45	45-08 Lense	lense along bedding	11
01-KY-45	45-09 Lense	lense along bedding	8.6
01-KY-45	45-12 Lense	lense Across bedding	49
01-KY-45	45-13 Lense	lense Across bedding	30
01-KY-45	45-14 Lense	lense along bedding	2.1
01-KY-61	61-01 Nodule	nodule in from shale	17
01-KY-61	61-02 Nodule	along edge with shale	0.81
01-KY-61	61-03 Nodule	along edge with shale	18
01-KY-61	61-05 Nodule	nodule in from shale	0.60
01-KY-61	61-06 Nodule	along edge with shale	0.64
01-KY-61	61-07 Nodule	sulfide island in shale	8.2
01-KY-61	61-08 Nodule	sulfide island in shale	9.2
01-KY-61	61-09 Nodule	sulfide island in shale	1.7

Analysis ID	Cr ppm	Co ppm	Nippm	Cu ppm	Zn ppm	As ppm	Se ppm	Mo ppm
56-10 Nodule	39	0.13	21	1.5	0.93	590	0.07	53
56-11 Nodule	24	0.19	<.50	1.3	0.10	765	11	44
56-12 Nodule	28	0.74	9.9	1.0	2.4	1130	4.2	16
56-13 Nodule	45	0.07	4.0	0.60	0.10	475	0.10	160
56-14 Nodule	42	0.45	15	1.7	0.10	1230	0.73	35
56-15 Nodule	38	0.20	2.5	2.6	4.7	420	0.10	230
56-16 Nodule	38	0.70	12	1.3	3.0	820	1.6	370
56-17 Nodule	39	0.83	7.7	2.7	0.10	835	6.6	335
56-18 Nodule	38	1.6	27	18	5.2	780	5.7	330
56-19 Nodule	39	1.5	9.9	28	14	560	3.3	310
56-20 Nodule	37	0.66	4.9	3.3	9.8	715	5.1	325
56-21 Nodule	49	0.59	22	2.6	6.2	1020	12	310
56-22 Nodule	42	1.0	14	7.2	0.85	525	3.5	155
56-23 Nodule	39	0.07	4.4	3.5	2.8	450	0.63	160
56-24 Nodule	37	3.8	36	29	2.5	1140	7.3	12
56-25 Nodule	38	6.6	155	102	21	825	10	41
56-26 Nodule	40	0.49	40	19	7.7	1020	0.10	5.0
56-27 Nodule	42	3.4	115	63	11	880	0.26	14
56-28 Nodule	38	0.71	58	16	3.8	905	2.2	31
56-29 Nodule	36	1.4	18	4.4	0.10	135	10	0.07
56-30 Nodule	44	0.57	2.6	4.4	0.10	785	0.38	17
45-01 Lense	47	0.86	26	77	5.3	125	16	280
45-02 Lense	52	1.1	25	63	6.4	105	5.9	205
45-03 Lense	60	1.7	29	92	13	155	18	250
45-04 Lense	39	0.44	8.5	39	10	220	26	410
45-05 Lense	55	0.23	3.5	17	4.0	55	6.4	120
45-06 Lense	56	0.10	0.85	8.3	8.9	34	5.3	86
45-07 Lense	55	0.72	5.8	77	8.2	93	12	180
45-08 Lense	53	0.79	16	78	7.3	125	7.4	240
45-09 Lense	45	0.57	19	86	14	190	36	310
45-12 Lense	70	6.2	123	200	19	335	65	265
45-13 Lense	53	2.9	57	125	28	175	29	255
45-14 Lense	48	0.16	3.9	27	5.0	130	9.4	290
61-01 Nodule	65	3.1	61	50	20	830	2.1	13
61-02 Nodule	54	2.6	51	4.3	3.3	740	1.5	8.1
61-03 Nodule	52	0.9	13	38	13	670	0.21	7.4
61-05 Nodule	58	0.34	5.6	12	0.10	505	3.2	25
61-06 Nodule	44	0.17	0.74	3.9	0.10	675	4.4	3.6
61-07 Nodule	51	0.86	11	48	4.5	615	5.0	4.3
61-08 Nodule	45	7.9	75	125	9.7	1510	1.9	8.3
61-09 Nodule	42	3.9	57	55	0.10	1810	4.4	4.0

Analysis ID	Cd ppm	Sb ppm	Hg ppm	Tl ppm	Pb ppm	Fe %
56-10 Nodule	0.07	43	0.07	1.5	2.8	46.6
56-11 Nodule	0.07	68	1.2	3.1	0.29	48.4
56-12 Nodule	0.64	51	0.43	1.5	4.8	47.0
56-13 Nodule	0.07	56	1.6	3.0	1.6	47.1
56-14 Nodule	0.07	79	1.0	3.2	3.6	45.5
56-15 Nodule	0.82	56	1.3	3.3	1.5	46.4
56-16 Nodule	0.40	70	0.50	4.7	3.0	45.0
56-17 Nodule	0.09	80	0.87	6.7	2.8	43.4
56-18 Nodule	0.95	72	0.69	6.5	13	42.7
56-19 Nodule	0.55	54	1.1	5.6	8.0	42.4
56-20 Nodule	0.47	58	1.0	6.0	1.9	43.8
56-21 Nodule	0.39	91	0.15	6.3	1.2	42.3
56-22 Nodule	0.18	48	1.1	3.2	5.3	34.8
56-23 Nodule	0.65	33	0.58	2.3	0.50	44.0
56-24 Nodule	0.77	55	0.12	2.7	31	39.4
56-25 Nodule	0.87	105	0.82	6.8	66	36.5
56-26 Nodule	0.76	63	0.83	2.4	25	38.3
56-27 Nodule	1.5	82	0.42	1.9	73	37.5
56-28 Nodule	0.33	84	1.2	4.2	7.9	39.2
56-29 Nodule	0.07	12	1.2	0.22	4.5	36.4
56-30 Nodule	0.07	38	0.51	1.4	0.64	42.9
45-01 Lense	0.31	16	1.1	7.6	22	42.3
45-02 Lense	0.20	13	1.2	7.6	33	42.2
45-03 Lense	0.07	23	0.72	7.8	57	39.6
45-04 Lense	0.6	31	0.67	9.2	4.9	41.2
45-05 Lense	0.07	6.9	1.0	5.3	5.7	40.9
45-06 Lense	1.4	2.7	1.0	3.1	1.1	42.3
45-07 Lense	0.39	9.7	1.4	18	15	38.8
45-08 Lense	0.22	15	1.6	8.3	24	37.7
45-09 Lense	0.87	33	1.7	15	23	39.3
45-12 Lense	1.2	35	2.0	7.6	81	32.2
45-13 Lense	0.49	21	1.0	6.7	59	30.0
45-14 Lense	0.31	14	1.1	6.0	1.1	35.9
61-01 Nodule	0.58	24	0.9	1.2	62	37.1
61-02 Nodule	0.57	26	0.21	2.5	27	42.6
61-03 Nodule	0.61	19	0.81	0.79	54	38.5
61-05 Nodule	0.80	14	1.3	2.5	1.0	38.9
61-06 Nodule	0.16	12	0.07	0.58	26	37.3
61-07 Nodule	0.60	33	0.58	0.72	140	35.0
61-08 Nodule	0.20	32	0.49	0.64	125	34.8
61-09 Nodule	0.49	44	0.96	0.64	205	37.3

Section	Analysis ID	Description	V ppm
01-KY-61	61-10 Nodule	sulfide island in shale	34
01-KY-61	61-11 Nodule	sulfide island in shale	11
01-KY-61	61-12 Nodule	along edge with shale	1.6
01-KY-61	61-13 Nodule	nodule in from shale	6.2
01-KY-61	61-14 Nodule	nodule in from shale	0.18
01-KY-61	61-15 Nodule	nodule in from shale	0.62
01-KY-61	61-16 Nodule	nodule in from shale	0.07
01-KY-61	61-17 Nodule	nodule in from shale	0.33
01-KY-61	61-18 Nodule	nodule in from shale	1.0
01-KY-61	61-19 Nodule	nodule in from shale	0.76
01-KY-61	61-20 Nodule	nodule in from shale	0.55
01-KY-54	54-01 Lense	lense along bedding	3.5
01-KY-54	54-02 Lense	lense along bedding	34
01-KY-54	54-03 Lense	lense along bedding	33
01-KY-54	54-05 Lense	lense along bedding	37
01-KY-54	54-06 Lense	lense along bedding	37
01-KY-54	54-07 Lense	lense along bedding	5.0

Analysis ID	Cr ppm	Co ppm	Nippm	Cu ppm	Zn ppm	As ppm	Se ppm	Mo ppm
61-10 Nodule	52	7.9	40	135	33	805	8.2	27
61-11 Nodule	59	0.64	6.4	31	23	1100	2.9	7.1
61-12 Nodule	73	1.7	4.4	13	6.5	320	0.52	29
61-13 Nodule	62	1.3	16	22	7.2	555	0.10	39
61-14 Nodule	72	0.81	3.1	3.3	2.2	165	7.9	115
61-15 Nodule	63	0.49	4.1	4.4	7.1	165	0.10	125
61-16 Nodule	68	0.45	2.5	3.4	2.5	240	0.10	43
61-17 Nodule	66	0.12	3.6	1.5	0.10	295	1.0	205
61-18 Nodule	69	0.17	1.1	1.9	0.14	215	8.3	150
61-19 Nodule	64	0.91	4.6	2.0	0.10	355	1.3	7.9
61-20 Nodule	51	0.22	3.9	3.4	1.2	360	0.08	3.3
54-01 Lense	69	2.1	92	9.4	6.8	190	3.5	165
54-02 Lense	69	2.8	96	60	52	445	11	50
54-03 Lense	90	1.4	90	66	42	420	2.4	47
54-05 Lense	99	2.7	85	74	71	395	11	57
54-06 Lense	115	7.2	100	104	39	685	15	54
54-07 Lense	80	0.78	25	27	13	145	2.3	150

Analysis ID	Cd ppm	Sb ppm	Hg ppm	Tl ppm	Pb ppm	Fe %
61-10 Nodule	0.56	35	0.82	11	120	32.8
61-11 Nodule	0.33	28	0.55	0.66	110	36.1
61-12 Nodule	1.0	8.7	1.0	1.8	0.66	38.6
61-13 Nodule	0.94	15	1.0	2.3	3.9	39.1
61-14 Nodule	0.33	4.0	1.3	3.3	0.28	41.6
61-15 Nodule	0.07	4.1	0.92	2.8	1.1	39.2
61-16 Nodule	0.48	6.0	0.58	1.3	0.12	38.8
61-17 Nodule	0.92	7.9	0.42	3.8	0.17	39.7
61-18 Nodule	0.07	5.3	0.91	4.1	0.13	39.6
61-19 Nodule	0.63	11	1.6	1.7	1.5	35.1
61-20 Nodule	0.94	9.7	1.7	1.1	2.0	36.0
54-01 Lense	2.2	11	0.78	6.5	5.4	32.4
54-02 Lense	2.2	29	1.5	9.1	24	31.2
54-03 Lense	0.41	24	1.5	5.5	34	33.1
54-05 Lense	1.9	24	1.7	7.5	33	32.1
54-06 Lense	2.2	33	1.3	14	48	31.4
54-07 Lense	1.6	7.2	0.76	7.4	4.9	35.6

Table II-4. SEM/EDX analyses of efflorescent salts. Mineral identification based on morphology and chemistry. *, mineral was detected by XRD.

Sample	Salt morphology	Al2O3 %	FeO %	K2O %	MgO %	SO3 %
01KY-05	Plates	7.3	31	0.08	0.42	61
01KY-05	Needles-1	16	21	0.06	0.6	62
01KY-05	Needles-2	18	21	0.27	0.66	60
01KY-05	Needles-3	19	20	0.18	0	61
01KY-05	Fuzzy	0.90	51	0.37	0.89	47
01KY-05	Tablets	0.74	41	0	0.59	58
01KY-05	Euhedral	3.0	33	5.6	1.5	57
01KY-05	Rosettes	1.5	59	0.24	0.34	39
01KY-15	Euhedral	1.8	64	8.3	0.31	26
01KY-21	Needles-1	20	14	0.61	3.9	61
01KY-21	Needles-2	24	12	0.57	4.5	59
01KY-21	Needles-3	20	16	0.35	2.3	62
01KY-21	Plates	0.82	45	0.20	0.43	50
01KY-21	Massive	15	23	0.23	3.2	59
01KY-23	Rhombs	0.29	55	0.13	2.1	43
01KY-23	Plates	27	8.7	0.23	0	64
01KY-23	Rosette	4.0	39	0	3.6	54
01KY-23	Thin Sheet 1	18	20	0	0.32	61
01KY-23	Thin Sheet 2	28	6.6	0.14	0	65

Sample	Salt morphology	Possibilities (*found by XRD)	Formula
01KY-05	Plates	coquimbite*	$Fe_2^{3+}(SO_4)_3 \cdot 9H_2O$
01KY-05	Needles-1	halotrichite*	$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$
01KY-05	Needles-2	halotrichite*	$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$
01KY-05	Needles-3	halotrichite*	$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$
01KY-05	Fuzzy	malanterite*, szomolnokie*	$Fe^{2+}SO_4 \cdot 7H_2O$, $Fe^{2+}SO_4 \cdot H_2O$
01KY-05	Tablets	malanterite*, szomolnokie*	$Fe^{2+}SO_4 \cdot 7H_2O$, $Fe^{2+}SO_4 \cdot H_2O$
01KY-05	Euhedral	voltaite?	$K_2Fe_5^{2+}Fe_4^{3+}(SO_4)_{12} \cdot 18H_2O$
01KY-05	Rosettes	malanterite*, szomolnokie*	$Fe^{2+}SO_4 \cdot 7H_2O$, $Fe^{2+}SO_4 \cdot H_2O$
01KY-15	Euhedral	jarosite* + FeOOH	$KFe_3^{3+}(SO_4)_2(OH)_6$
01KY-21	Needles-1	halotrichite	$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$
01KY-21	Needles-2	halotrichite	$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$
01KY-21	Needles-3	halotrichite	$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$
01KY-21	Plates	malanterite-szomolnokie	$Fe^{2+}SO_4 \cdot 7H_2O$, $Fe^{2+}SO_4 \cdot H_2O$
01KY-21	Massive	Al-,Mg-rich copiapite?	$(Fe,Mg,Al)_x(SO_4)_6(OH)_2 \cdot 20H_2O$; x=combination to = 14^+
01KY-23	Rhombs	copiapite*	$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$
01KY-23	Plates	alunogen* (+FeOOH?)	$Al_2(SO_4)_3 \cdot 17H_2O$
01KY-23	Rosette	Al-rich copiapite*	$Al_{2/3}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$
01KY-23	Thin Sheet	alunogen*	$Al_2(SO_4)_3 \cdot 17H_2O$
01KY-23	Thin Sheet	alunogen*	$Al_2(SO_4)_3 \cdot 17H_2O$

Table II-5. Chemical composition of efflorescent salts and FeOOH precipitate on a dry weight basis calculated from dissolution experiment data, and the percentage of metal removed from solution when titrated to pH = 7 (no titration data for 01KY51).

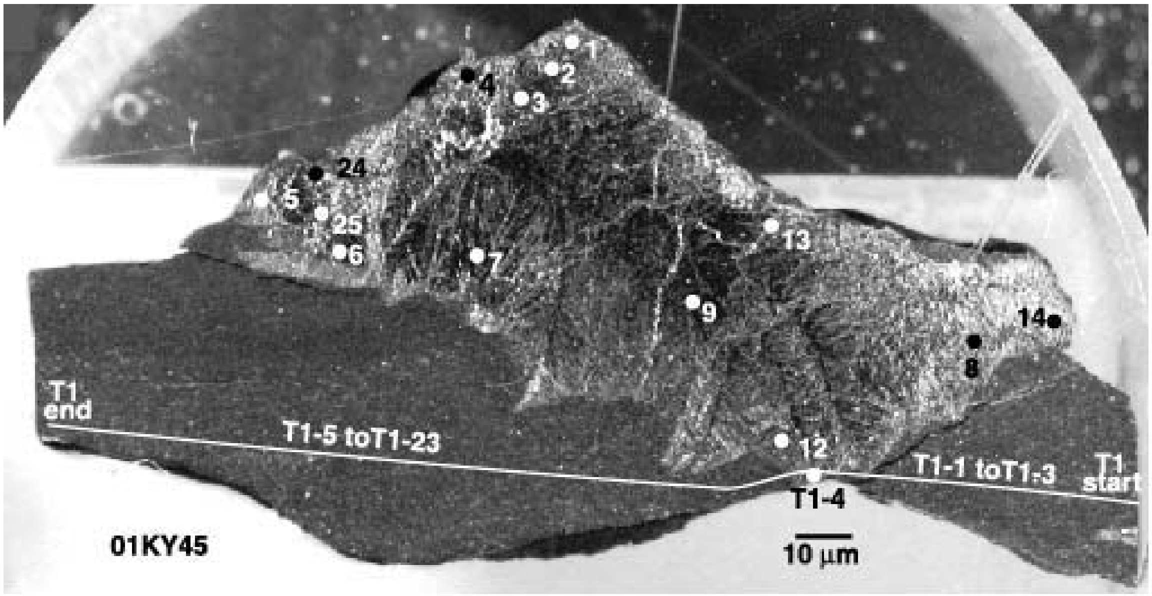
Field No.	01KY05			01KY21			01KY23			01KY51
Location	outcrop			outcrop			outcrop			core
	salt	FeOOH	%ppt'd	salt	FeOOH	%ppt'd	salt	FeOOH	%ppt'd	salt
As ppm	160	470	100	165	585	100	98	290	100	92
Cd ppm	2.1	5.8	97	3.0	9.7	93	1.5	4.2	95	0.50
Co ppm	97	270	96	235	820	99	135	385	96	9.2
Cr ppm	22	61	94	36	99	78	27	75	95	82
Cu ppm	100	290	97	240	840	99	90	255	96	315
Fe %	11	32	99	6.4	23	100	10	30	100	33
Mn ppm	115	19	56	725	240	93	405	83	69	29
Mo ppm	66	185	97	21	63	88	17	49	95	84
Ni ppm	240	680	97	580	2040	99	265	750	94	125
P ppm	165	475	100	650	2300	99	355	1060	100	1080
Pb ppm	6.0	16	98	0.41	<	0	2.4	4.7	87	108
Se ppm	0.87	2.5	100	3.7	13	100	1.0	3.0	100	34
SO4%	33	<	0	36	1.7	2	34	<	0	66
Th ppm	8.8	26	99	35	125	100	12	34	99	<
U ppm	32	94	100	175	620	100	39	115	100	1.6
V ppm	38	110	100	70	245	100	15	44	100	19
Zn ppm	245	690	98	465	1580	97	210	585	93	53

Appendix III

Photographs of polished sections used for SEM/EDX and LA-ICP-MS analyses are presented in Figure AIII-1. The locations of laser spots (LA-ICP-MS) are superimposed on the photographs. The pyrite lense in 01KY-45 is evident. Microscopic sulfides were analyzed along a transect (T1). In 01KY-54, laser spots number 1-7 are located in an intensively sulfidized portion of the section. Microscopic sulfides were analyzed along the transect T1. Section 10KY-56 has two large pyrite nodules that coalesce. Microscopic sulfides in the shale were analyzed along two transects, T1 and T2. Section 01KY-61 almost is entirely a pyrite lense. No microscopic sulfides were analyzed in this section.

Representative SEM photomicrographs of microscopic sulfides in the shale are shown in Figure AIII-2.

Representative SEM photomicrographs of crystals in efflorescent salts are in Figure AIII-3. These crystals were analyzed by SEM/EDX (Table AII-1)



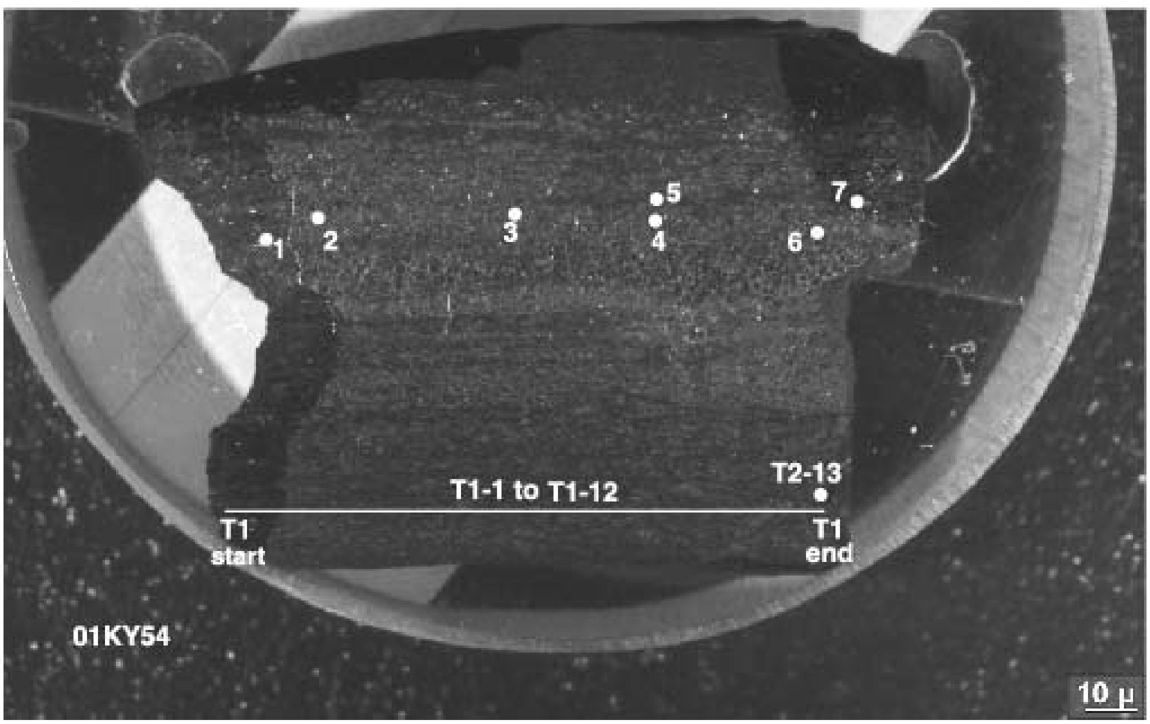
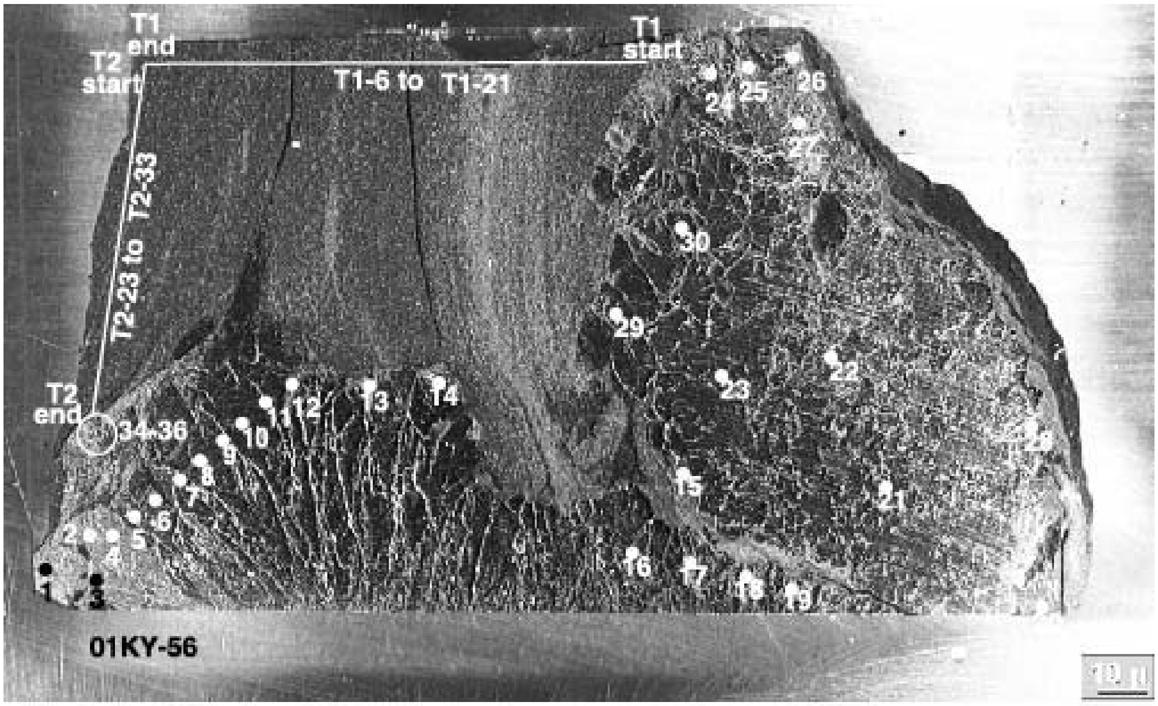


Figure AIII-1. Photos of polished sections from selected core samples used in SEM and LA-ICP-MS analyses, showing location of laser spots along transects in the shale and laser spots in massive lenses and nodules. Spot numbers correspond to numbers in Table AII-2.



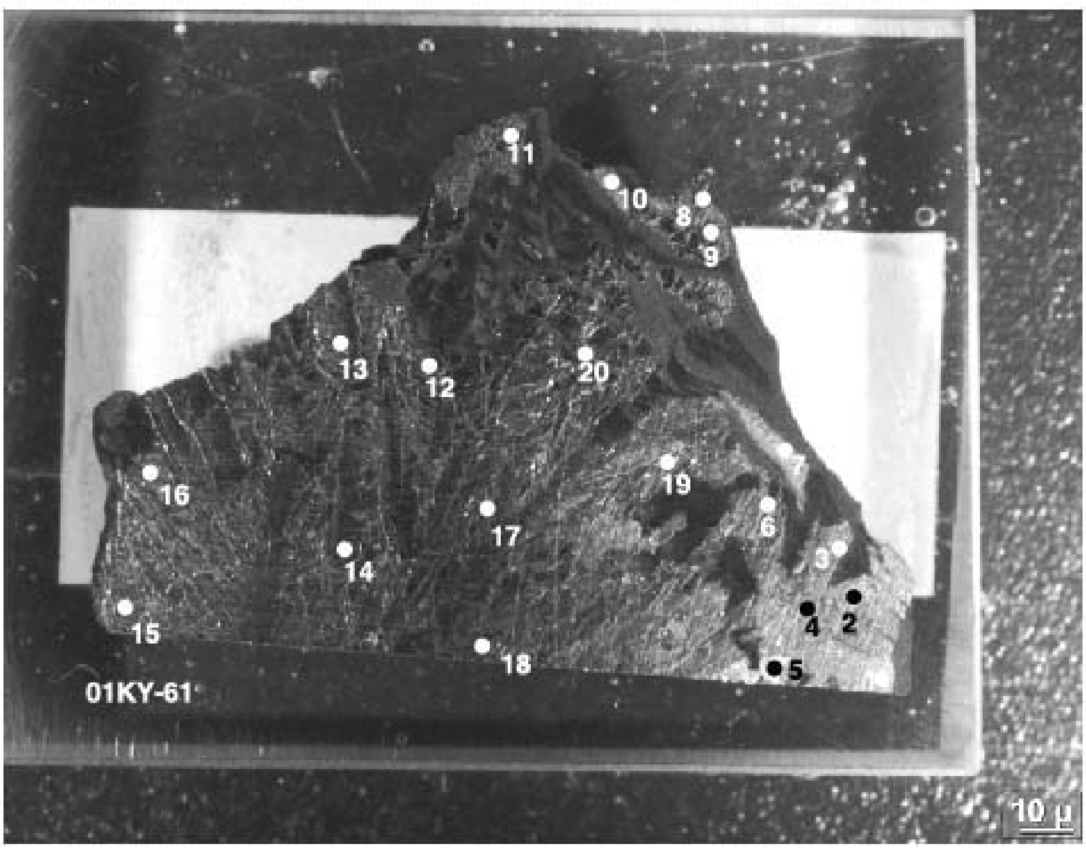


Figure AIII-1 (cont).

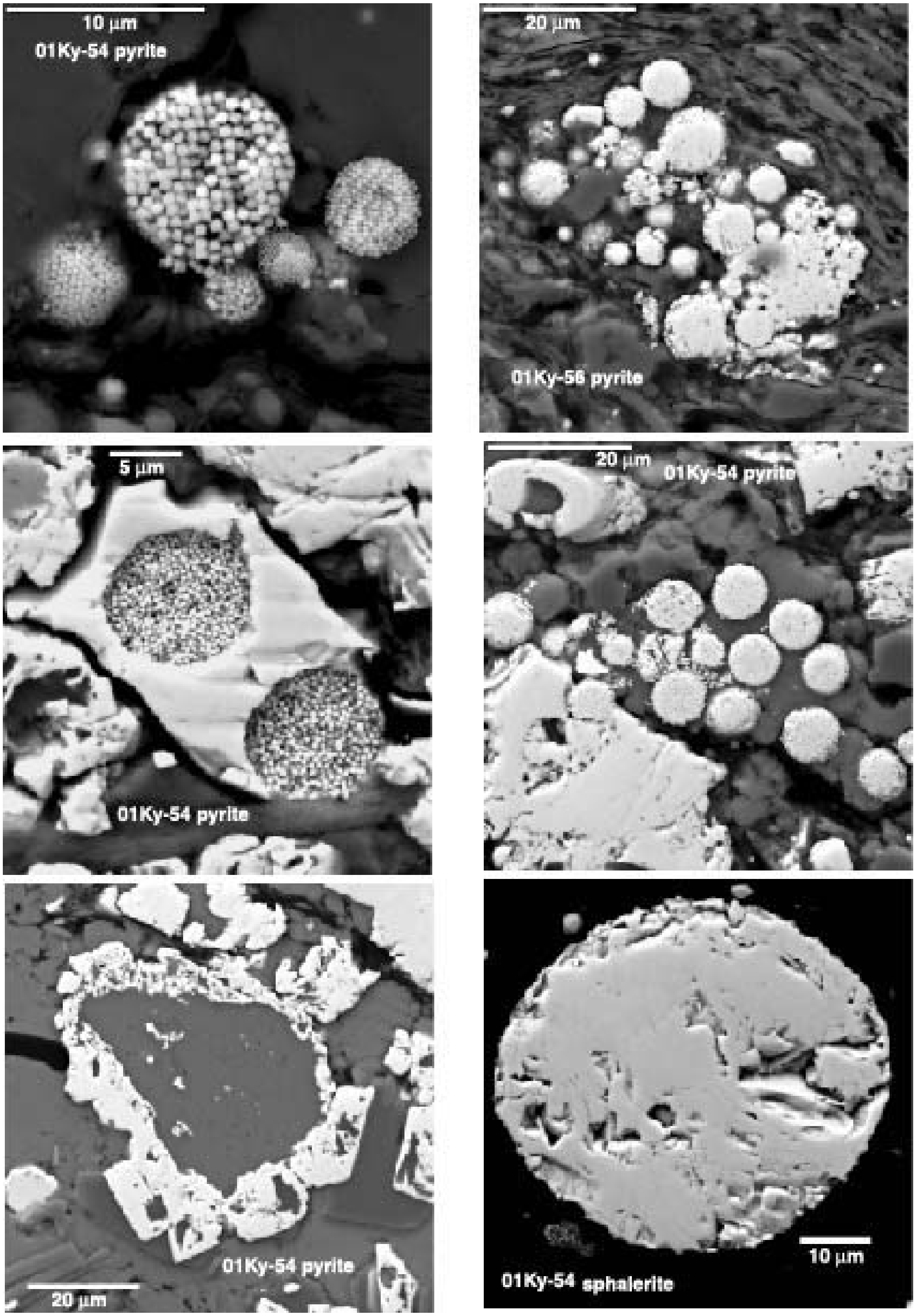
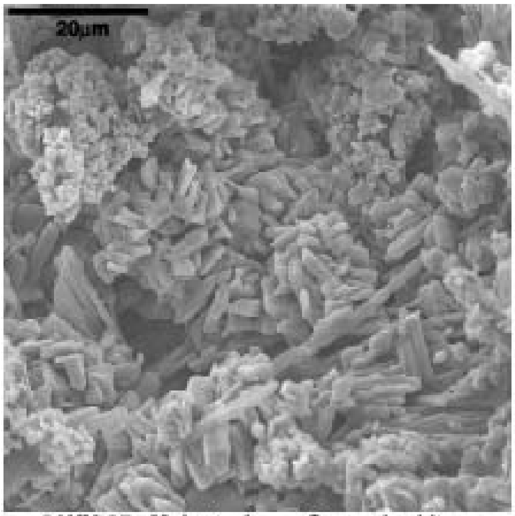
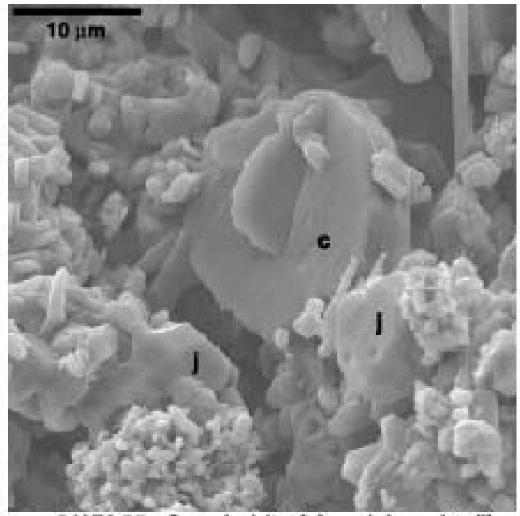


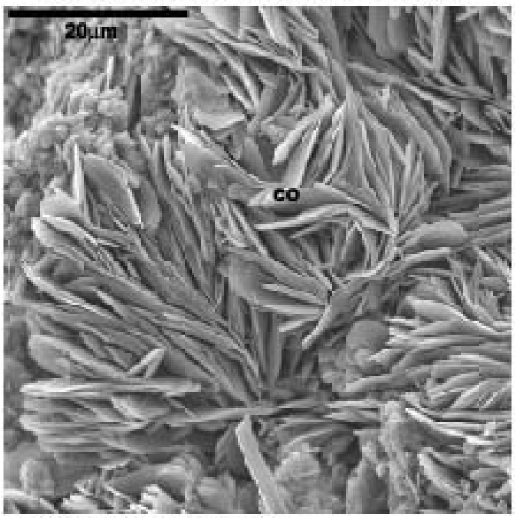
Figure AIII-2. SEM photomicrographs of sulfides in polished sections of selected core samples.



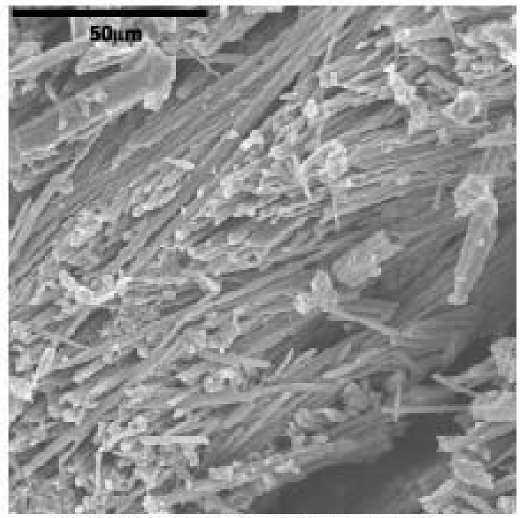
01KY-05. Malanterite or Szomolnokite



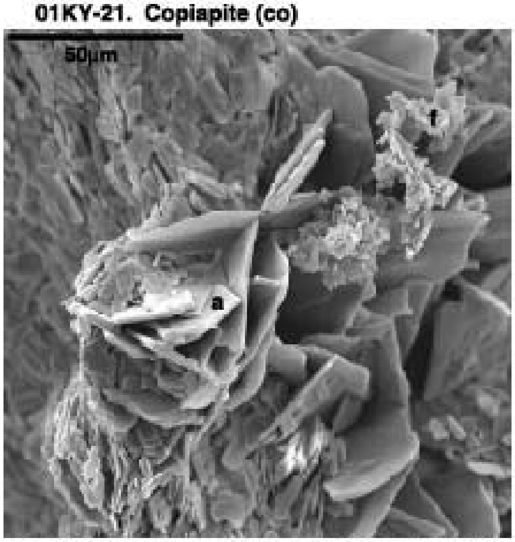
01KY-05. Coquimbite (c) and Jarasite (j)



01KY-21. Copiapite (co)



01KY-21. Wupatkite or Halotrichite



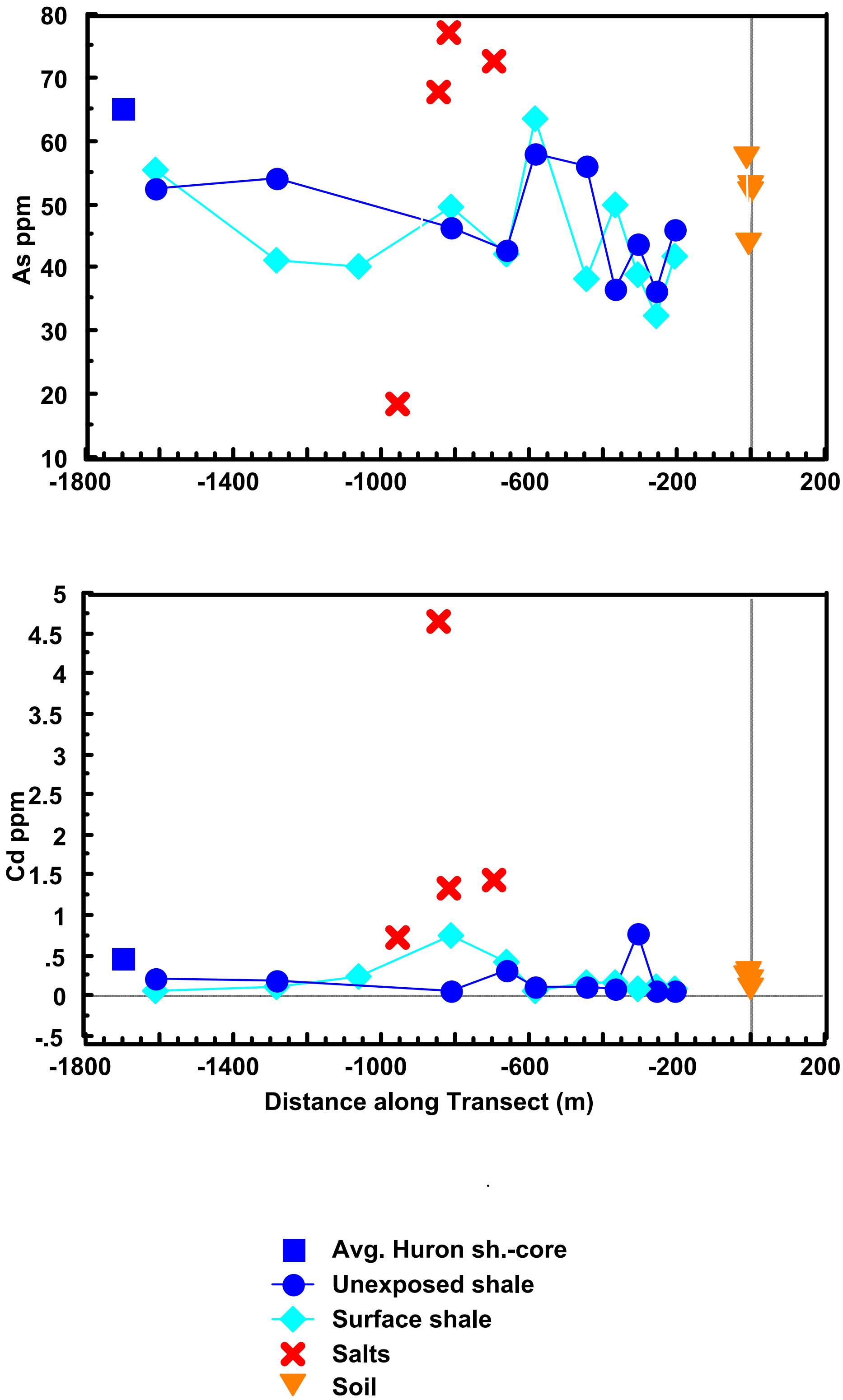
01KY-23. Alunogen (a) + FeSO4•nH2O? (f)

01KY-23. Copiapite

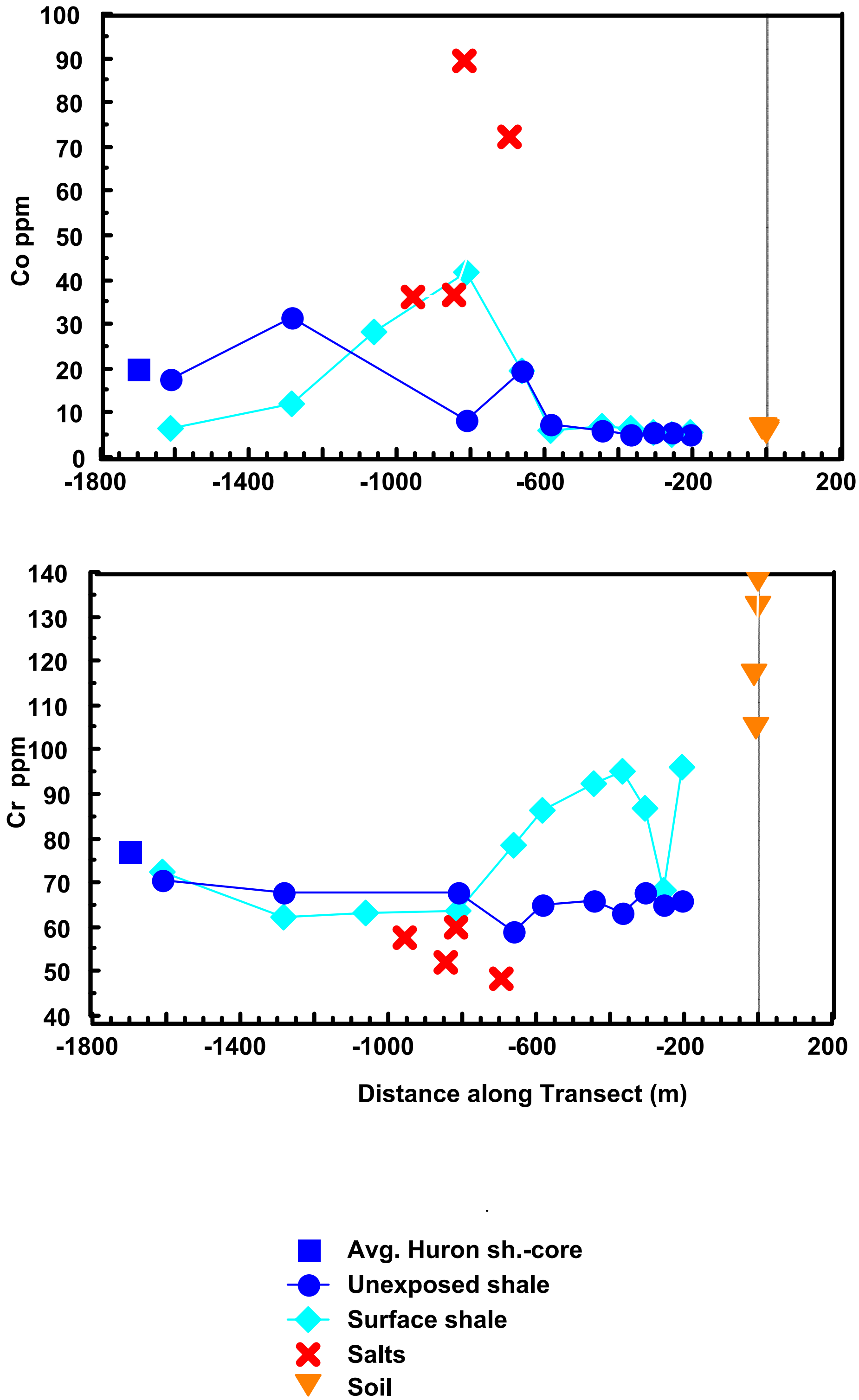
Figure AIII3. SEM photomicrographs of efflorescent salts from the out crop. [Note: wupatkite was identified in 01KY-21 as a possible salt by XRD, however, it is extremely rare and it's presence in this sample is doubtful.]

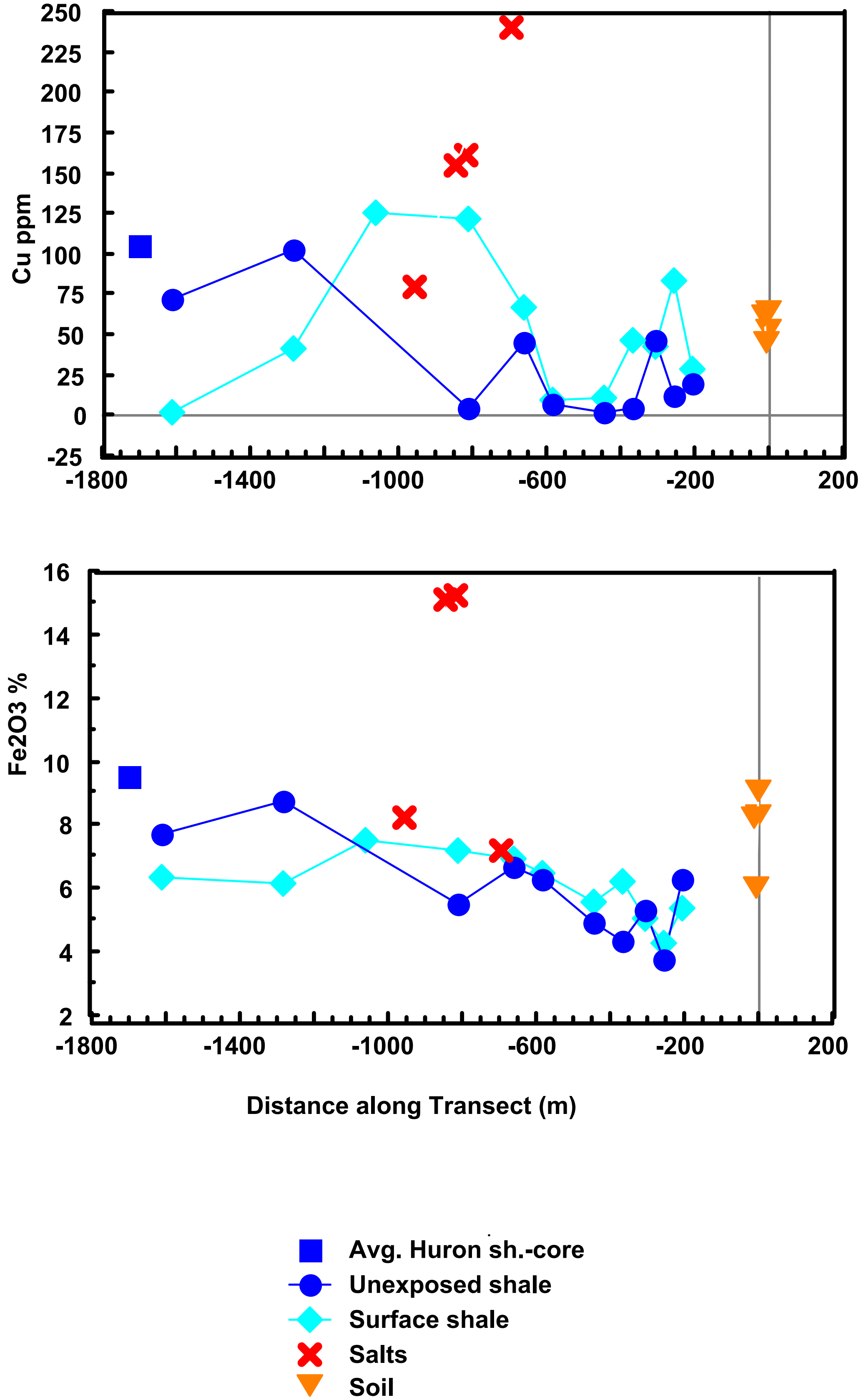
Appendix IV

The plots present in Appendix IV show the changes in metal concentration in surface and unexposed shale along the outcrop transect. Concentrations of metals in Huron shale (average calculated from Huron shale data in the core), efflorescent salts, and soil are also plotted for comparison. Note that the vertical axis for the metal zinc is plot on a logarithmic scale.

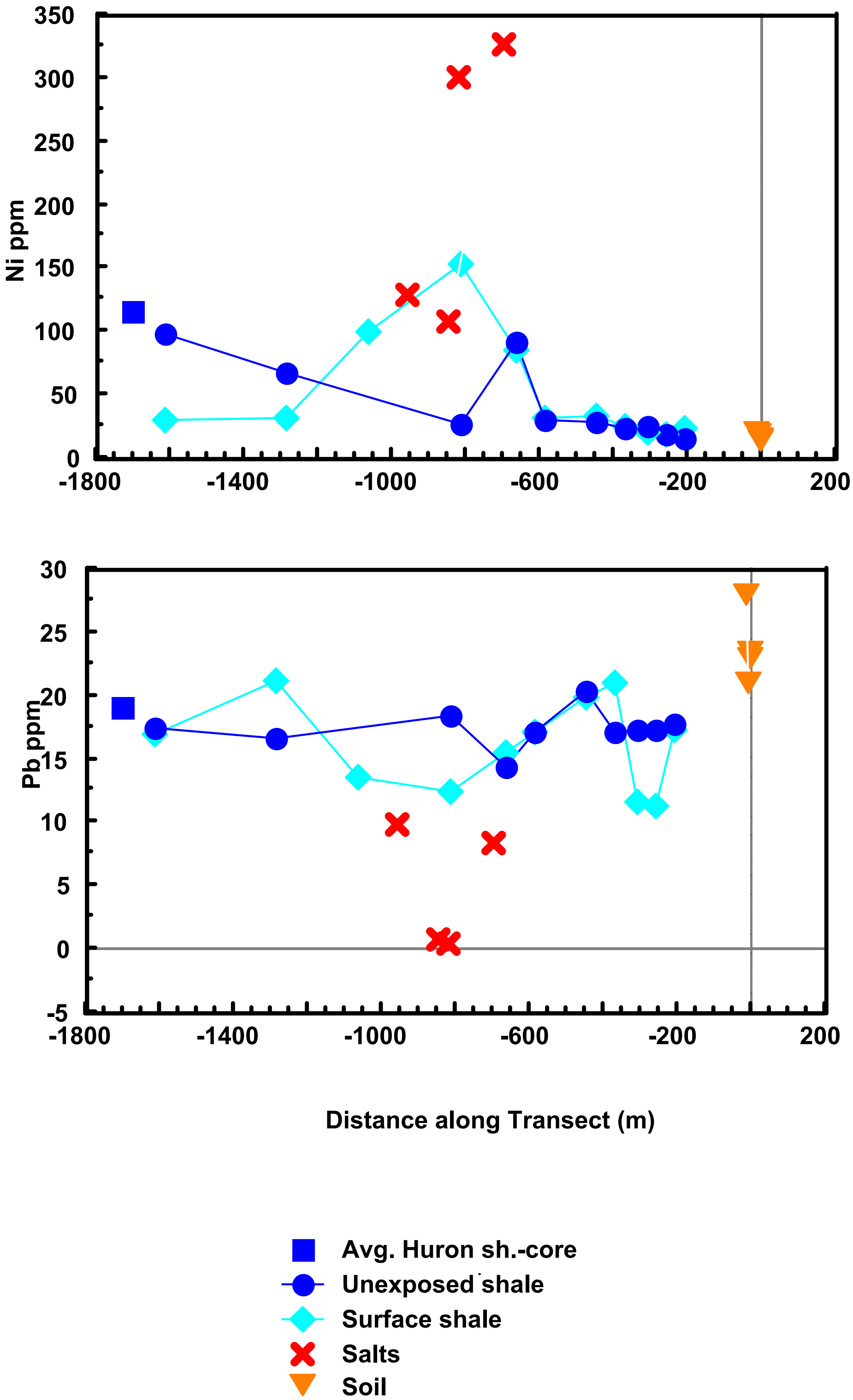


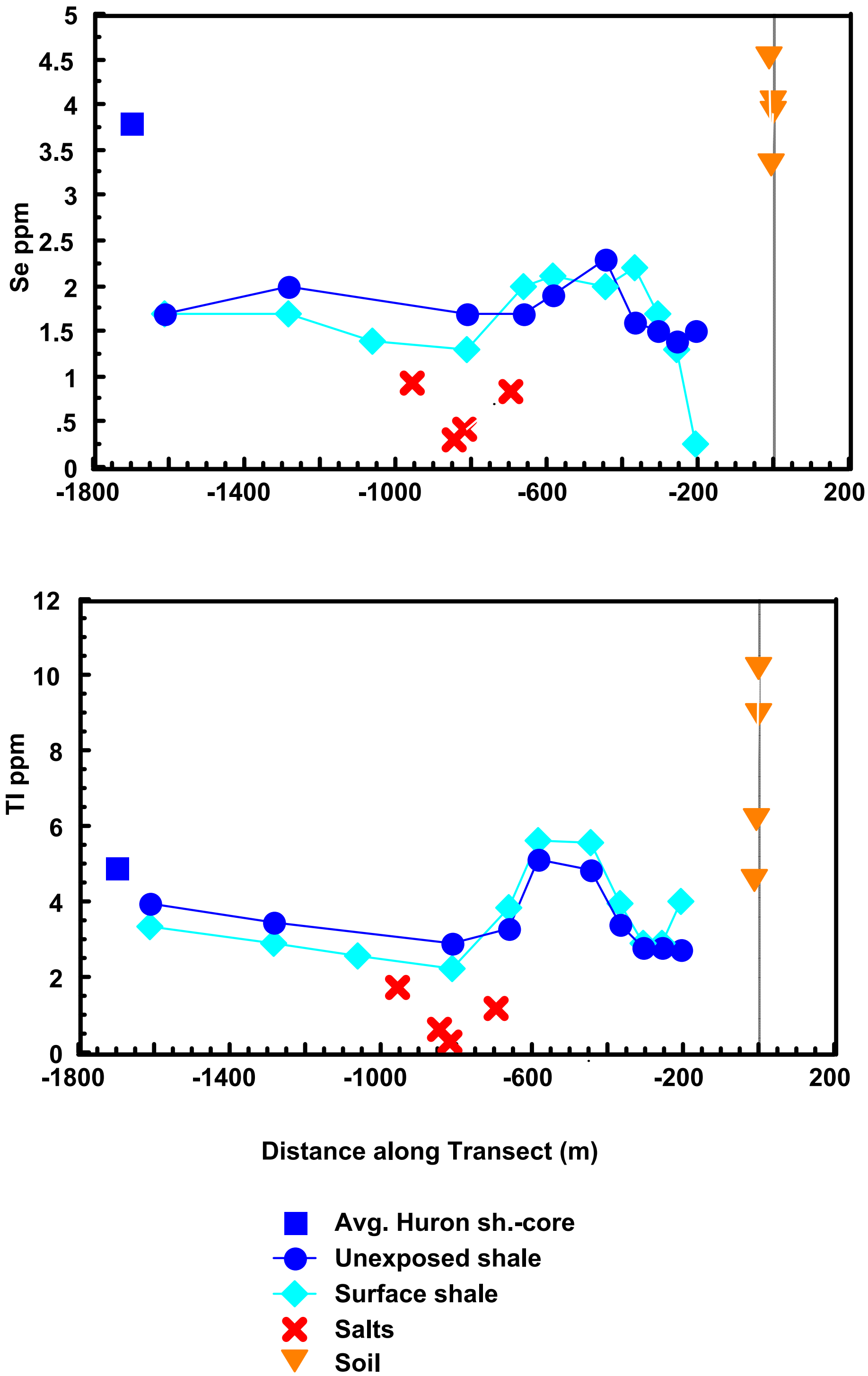
As ppm
80
70
60
50
40
30
20
10
-1800
-1400
-1000
-600
-200
200
Cd ppm
5
4.5
4
3.5
3
2.5
2
1.5
1
.5
0
-.5
Distance along Transect (m)
Avg. Huron sh.-core
Unexposed shale
Surface shale
Salts
Soil


Co ppm
100
90
80
70
60
50
40
30
20
10
0
-1800
-1400
-1000
-600
-200
200
Cr ppm
140
130
120
110
100
90
80
70
60
50
40
-1800
-1400
-1000
-600
-200
200
Distance along Transect (m)
Avg. Huron sh.-core
Unexposed shale
Surface shale
Salts
Soil

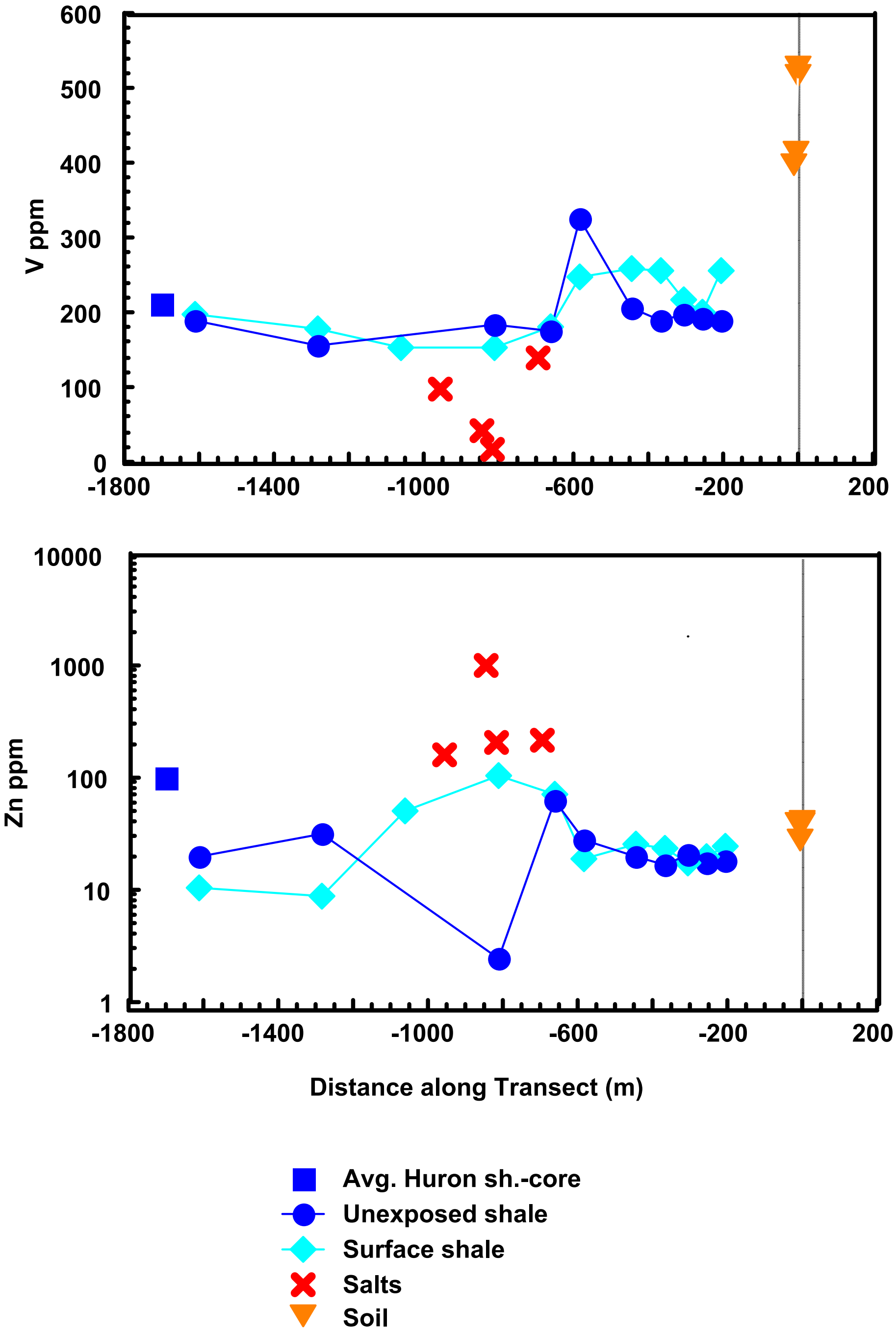


250
225
200
175
150
125
100
75
50
25
0
-25
Cu ppm
-1800
-1400
-1000
-600
-200
200
16
14
12
10
8
6
4
2
Fe2O3 %
-1800
-1400
-1000
-600
-200
200
Distance along Transect (m)
Avg. Huron sh.-core
Unexposed shale
Surface shale
Salts
Soil


Ni ppm
350
300
250
200
150
100
50
0
-1800
-1400
-1000
-600
-200
200
Pb ppm
30
25
20
15
10
5
0
-5
-1800
-1400
-1000
-600
-200
200
Distance along Transect (m)
Avg. Huron sh.-core
Unexposed shale
Surface shale
Salts
Soil



Se ppm
5
4.5
4
3.5
3
2.5
2
1.5
1
.5
0
-1800
-1400
-1000
-600
-200
200
Tl ppm
12
10
8
6
4
2
0
-1800
-1400
-1000
-600
-200
200
Distance along Transect (m)
Avg. Huron sh.-core
Unexposed shale
Surface shale
Salts
Soil


600
500
400
300
200
100
0
V ppm
-1800
-1400
-1000
-600
-200
200
10000
1000
100
10
1
Zn ppm
-1800
-1400
-1000
-600
-200
200
Distance along Transect (m)
Avg. Huron sh.-core
Unexposed shale
Surface shale
Salts
Soil