

**U.S. DEPARTMENT OF THE INTERIOR**

**U.S. GEOLOGICAL SURVEY**

**PRELIMINARY MINERALOGICAL AND CHEMICAL STUDIES RELATED TO THE  
POTENTIAL MOBILITY OF SELENIUM AND ASSOCIATED ELEMENTS IN  
PHOSPHORIA FORMATION STRATA, SOUTHEASTERN IDAHO**

George Desborough<sup>1</sup>, Ed DeWitt<sup>1</sup>, Jeff Jones<sup>2</sup>, Alan Meier<sup>1</sup> and Gregory Meeker<sup>1</sup>

**Prepared in Cooperation with:**  
U.S. Bureau of Land Management  
U.S. Forest Service  
Agrium U.S., Inc.  
FMC Corporation  
J.R. Simplot, Inc.  
Rhodia, Inc.  
Solutia, Inc.

**Open-File Report 99-129**

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards or with the North American Stratigraphic Code. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

<sup>1</sup>U.S. Geological Survey, Denver, Colorado; <sup>2</sup>U.S. Forest Service, Soda Springs, Idaho

**1999**

## CONTENTS

	Page
Abstract.....	4
Introduction.....	4
Previous work.....	4
This study.....	5
Results.....	5
Stratigraphic variability of selenium.....	5
Electron beam studies.....	7
Oxidizing thermal treatment.....	8
Passive leaching studies.....	11
Summary.....	12
References cited.....	13

## FIGURES

Figure 1. Locations of phosphate mines and the Pritchard Creek locality in southeastern Idaho from which samples were taken for this study.....	14
Figure 2. Selenium concentrations in one-foot intervals from samples of drill cuttings at the abandoned Gay mine on the Fort Hall Indian Reservation, southeastern Idaho.....	15
Figure 3. Selenium concentrations in stratigraphic samples of each bed along Pritchard Creek in the Caribou Range, southeastern Idaho.....	16
Figure 4. Plot of organic carbon versus weight loss for samples of the Phosphoria Formation, southeastern Idaho.....	17
Figure 5. Plot of selenium in leachate versus sulfate in leachate for waste rock sample 220-1 from the Dry Valley mine, southeastern Idaho.....	18
Figure 6. Plot of selenium in leachate versus sulfate in leachate for waste rock sample 220-2 from the Dry Valley mine, southeastern Idaho.....	19
Figure 7. Plot of selenium in leachate versus selenium in rock from samples from the Enoch Valley mine, southeastern Idaho.....	20

## TABLES

	Page
Table 1. Selenium concentrations in samples of Phosphoria Formation at the abandoned Gay mine on the Fort Hall Indian Reservation and along Pritchard Creek in the Caribou Range, southeastern Idaho.....	6
Table 2. Concentrations of selected elements in phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho .....	7
Table 3. Relative abundance of minerals in phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho .....	8
Table 4. Selenium loss during initial thermal treatments of fresh samples of phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho .....	9
Table 5. Selenium loss during second thermal treatments of fresh samples of phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho .....	10
Table 6. Selenium loss during thermal treatment at 300° C for 48-51 hours of fresh phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho .....	10
Table 7. Selenium loss during thermal treatment at 340° C for 24 hours of fresh phosphate-bearing waste rock samples of the Phosphoria Formation from the Enoch Valley mine, southeastern Idaho .....	11
Table 8. Concentrations of selected elements in deionized water leachates of phosphate-bearing waste rock samples of the Phosphoria Formation from the Dry Valley mine, southeastern Idaho .....	12
Table 9. Concentrations of selected elements in deionized water leachates of fresh, phosphate-bearing waste rock samples of the Phosphoria Formation from the Enoch Valley mine, southeastern Idaho .....	12

## ABSTRACT

The Phosphoria Formation in southeastern Idaho is mined for commercial extraction of phosphate to be used either in fertilizer or as elemental phosphorus. Waste beds that are interbedded with the phosphate ore are placed on the surface for disposal. Selenium in these wastes could be leached by normal weathering action and could accumulate in water or vegetation in amounts that might be toxic to both vertebrates and invertebrates. This study (1) determined the residence of selenium in the waste and (2) conducted laboratory experiments applicable to determining the potential for natural weathering processes to leach selenium from the waste in a surficial oxidizing environment.

Concentrations of selenium in fresh waste rocks utilized in this study range from <10 parts per million (ppm) to about 200 ppm. Furnace-grade phosphate samples from the abandoned Gay mine on the Fort Hall Indian Reservation range from about 300 to 400 ppm selenium. Selenium is associated both with organic matter (kerogen) in carbon-rich rocks and with pyrite in rocks that have lower concentrations of organic carbon. The highest selenium concentrations are in carbon-rich rocks from the Gay mine.

Oxidizing thermal treatments above about 350° C for 24-hour exposure periods revealed virtually all selenium was volatilized from all samples. During these exposures, pyrite was oxidized. However, during thermal treatments at 340° C and below for 24-hour periods, pyrite was not oxidized, but most of the organic material was oxidized. Oxidation of the organic material, as determined by weight loss of the sample, resulted in volatilization and removal of significant selenium from many samples, especially those samples that had high original concentrations of selenium. These experiments indicate that both selenium associated with organic material and selenium associated with pyrite are easily mobilized during heating and oxidation. Whether or not these conditions are met in nature should be investigated by field studies.

Passive leaching experiments of fresh waste-rock from two mines indicate that selenium is mobile in the presence of deionized water having a pH of 5.0. Coarse-grained blocks (1.3 to 4.4 cm) of fresh waste that contained about 100 ppm Se were interacted with deionized water in a waste:water ratio of 1:20 for 48 hours. The leachates contained 15 µg/L of selenium. Fine-grained blocks (< 0.5 mm) of the same waste produced a leachate containing about 40 µg/L of selenium. Eleven samples of fresh waste-rock, sized to 0.5 to 2.0 mm, produced a leachate that ranged from 0.2 to 180 µg/L and averaged 78 µg/L. Selenium in the leachate is positively correlated with Mg, Ca, and Fe in the leachate and with Se, Cd, and pyrite in the rock samples that were leached.

## INTRODUCTION

Mammals and other vertebrates may be poisoned by abnormally high concentrations of selenium in surface waters. Southeastern Idaho has the potential for problems related to high levels of selenium due to naturally occurring deposits of phosphate minerals in sedimentary rocks of the Permian Phosphoria Formation. These strata are rich in organic matter and generally have higher selenium (Se) concentrations in fresh rocks than most other Paleozoic strata in the western U.S. (Gulbrandsen, 1960, 1975; Desborough, 1977; Desborough and Poole, 1983; Desborough and others, 1984). In addition, these strata have elevated concentrations of V, Cr, Ni, Zn, Mo, Cd, and Ag (Desborough and Poole, 1983) compared to other Paleozoic sedimentary rocks. Open-pit mining of the phosphate deposits results in the removal of large amounts of interbedded waste rock. This waste may contribute more selenium to the environment than the same beds do in undisturbed or unmined areas. Moving the waste beds results in disaggregation, which probably accelerates oxidation of the rocks and removal of selenium.

### Previous Work

Fresh rocks of the Phosphoria Formation, away from commercially developed phosphate mines, contain less than about 165 parts per million (ppm) selenium (Gulbrandsen, 1960, 1975; Desborough, 1977). The principal residence of selenium in these rocks, as determined by microanalysis, is in pyrite. Four fresh samples from Coal Creek Canyon, which lies about 75 km southeast of the study area, are phosphate-poor, contain about 6.5 to 13 weight percent organic carbon, and have 100 to 150 ppm Se

(Gulbrandsen, 1960). Samples collected at the Maybe Canyon mine, except for the "carbon seam," were too oxidized to supply adequate material for microanalysis by electron microprobe (Desborough, 1977). Samples of the "carbon seam" studied by microanalysis, X-ray diffraction, and bulk chemical analysis, revealed no pyrite, but Se concentrations of 165 ppm and 32 weight percent organic carbon. Selenium in this rock is undoubtedly associated with the organic material.

Although minor or trace concentrations of pyrite are present in almost all of the unoxidized organic-rich strata of the Phosphoria Formation in the study area, the presence of carbonate minerals (dolomite and, or, calcite) tends to neutralize production of sulfuric acid from the oxidation of pyrite. Unfortunately, selenium is most mobile, or soluble, in high-pH aqueous environments. Natural oxidation due to weathering will eventually mobilize selenium that may be bound in either pyrite or organic-rich material (kerogen). The fresh, organic-rich waste rock is almost black, and therefore absorbs sunlight which generates high surface temperatures and promotes oxidation. Also, freezing and thawing accelerate oxidation due to an increase of surface area of the rock.

### **This Study**

This study focuses on determining the residences of selenium in waste rock associated with phosphate mines. If the mineralogical siting of selenium can be determined, efforts to ameliorate potential pollution that may be associated with oxidation and weathering of waste rock may be enhanced. Knowledge of the citing of selenium may aid in understanding selenium mobility and thereby permit storage of mine waste by techniques that would decelerate the rate of release of selenium to surface water. We also want to understand which climatic and weathering factors are important in the release of potentially harmful levels of selenium to the environment.

Although the average concentration of selenium in the waste rocks was relatively well known, the range and variation of selenium from bed to bed was not well known. We conducted a stratigraphic sampling of waste rock at three localities to better understand the variability of selenium within the waste rock.

Because most individual non-phosphate grains of the waste are less than about 0.030 mm across, and because they contain opaque, intergranular organic material (kerogen), petrographic study is of limited use in determining individual minerals and their spatial relations. We therefore studied the waste rocks with a combination of scanning electron microscopy (SEM) with an energy dispersive system (EDS) and an electron microprobe using wavelength X-ray emission analyzers.

Although bulk chemical analysis reveals the concentration of elements present, it does not show the residence of elements in mineral or organic material. Mineralogical, or organic, residence of elements is critical to understanding the potential mobility (solubility) of any metal species that may relate to their bioavailability. Therefore, we employed oxidizing thermal treatment and leaching techniques in order to better understand the citing of selenium in the waste rocks.

This study also attempted to design simple, inexpensive, and time-efficient methods to evaluate the residence(s) of selected elements, especially selenium, and how that residence may control potential short-term and long-term mobility under natural weathering conditions. For background information, a sample of the waste rock containing five weight percent of pyrite, which contains 0.2 weight percent of selenium and no selenium in the organic fraction, would contain 100 ppm of Se. A waste rock containing 20 weight percent of organic carbon, which contains 0.1 weight percent of Se and no selenium in pyrite, would contain 200 ppm of Se.

## **RESULTS**

Results of the four methods of investigation are reported below. Discussion of the results follows in this section.

### **Stratigraphic Variability of Selenium**

Samples were collected at one-foot intervals from one drill hole at the abandoned Gay mine on the Fort Hall Indian Reservation, and samples were collected from each bed along Pritchard Creek in the Caribou Range (fig. 1). A 34-foot stratigraphic section of rock at the Gay mine was sampled and a 31-foot stratigraphic section was sampled at Pritchard Creek (Table 1). The numbered beds do not correlate

from one location to the other. Selenium concentrations range from less than 10 to 139 ppm at the Gay mine and vary by as much as a factor of 7 from bed to bed (fig. 2). Selenium concentrations range from less than 10 to 280 ppm along Pritchard Creek and vary by as much as a factor of 6 from bed to bed (fig. 3). Due to the extreme variation from bed to bed, no average concentration of selenium is calculated for either section.

Fresh waste rock samples of phosphate-bearing strata of the Phosphoria Formation were selected from the Dry Valley, Enoch Valley, and Gay mines (Table 2). The three fresh samples

**Table 1.** Selenium concentrations in samples of Phosphoria Formation at the abandoned Gay mine on the Fort Hall Indian Reservation and along Pritchard Creek in the Caribou Range, southeastern Idaho [Samples collected by Simplot Inc. in 1985; Selenium analyses by energy-dispersive X-ray fluorescence (EDXRF) by G.A. Desborough]

<u>Gay mine, Fort Hall Indian Reservation</u>		<u>Pritchard Creek, Caribou Range</u>	
<u>Footage</u>	<u>Se (ppm)</u>	<u>Bed number</u>	<u>Se (ppm)</u>
1	25	1	14
2	48	2	5
3	48	3	12
4	41	4	78
5	34	5	160
6	39	6	230
7	32	7	110
8	5	8	25
9	73	9	180
10	68	10	66
11	38	11	96
12	18	12	69
13	48	13	40
14	28	14	280
14	18	14	150
15	24	15	240
16	5	16	100
17	17	17	100
18	35	18	70
19	54	19	57
20	112	20	110
21	126	21	60
22	135	22	67
23	83	23	67
24	80	24	60
25	100	25	85
26	120	26	67
27	50	27	0
28	30	28	0
29	35	29	0
30	55	30	50
31	35		
32	10		
33	25		

from the Gay mine were previously used in petroleum source-rock studies and have total organic carbon concentrations of 10.6 to 22.5 weight percent (Desborough and others, 1988). The fresh waste rocks range in Se concentration from < 20 to 360 ppm, have about a four-fold range in total organic carbon, and about a three-fold range in pyrite concentration, as determined by analyses of commercial laboratories and by analysis of panned concentrates (G.A. Desborough, unpub. data, 1998).

**Table 2.** Concentrations of selected elements in phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho [Analyses by energy-dispersive X-ray fluorescence (EDXRF) by G.A. Desborough; Four non-phosphatic samples (2, 20, 60, and 85 ppm Se) were provided by Steve Wilson of the U.S. Geological Survey for standards by which the EDXRF was calibrated for determination of Se; Pb and As in all samples are less than 50 ppm; all rocks are fresh unless otherwise indicated; samples from Dry Valley mine in the Soda Springs area collected in January, 1998; samples from Enoch Valley mine in the Soda Springs area collected in February, 1998; samples from Gay mine on the Fort Hall Indian Reservation collected in 1983]

Sample	Fe Wt %	Cu ppm	Zn ppm	Se ppm	Rb ppm	Sr ppm	Y ppm	Zr Ppm	Mo ppm	Cd ppm	Ba ppm
<u>Dry Valley mine</u>											
220-1	1.8	< 30	1400	110	90	100	30	300	55	1	250
220-2	2.0	< 30	1100	90	85	160	55	300	30	< 1	330
20-3 (oxidized)	2.3	370	450	< 20	120	600	240	130	< 10	4	520
<u>Gay mine</u>											
83FP211	0.9	120	1500	360	60	540	230	160	60	16	130
83FP215	0.8	230	3500	290	50	560	110	100	420	50	140
83FP216	1.0	180	2000	300	55	440	140	140	270	29	170
<u>Enoch Valley mine</u>											
MW 11	1.6	50	2900	190	65	410	150	250	200	7	190
MW 10	2.0	< 30	4200	30	65	150	60	280	10	2	200
MW 9	1.1	70	2400	85	45	470	110	150	15	5	130
MW 8	1.7	160	1400	100	70	480	170	240	40	4	210
MW 7	1.8	75	1200	70	60	250	120	250	125	2	200
MW 6	1.9	130	1300	130	75	420	170	250	85	2	240
MW 5	1.9	< 30	200	< 20	55	100	25	400	70	< 1	180
MW 4	1.3	< 30	1800	40	50	300	150	300	35	1	250
MW 3	1.4	90	2000	< 20	55	330	130	250	70	1	160
MW 2	1.2	35	1100	75	55	290	110	310	60	< 1	240
MW 1	1.3	100	910	140	70	270	130	320	110	1	250

The relative abundance of minerals in samples of waste rock of the Phosphoria Formation was determined by X-ray diffraction studies of back-packed sample mounts (Table 3). Relative peak intensities of the diffraction maxima (strongest X-ray peak) are given, excluding the quartz, orthoclase, and muscovite maxima because their strongest peaks are essentially coincident. For orthoclase, the 040, 002 maxima was used; for quartz the 112 maxima was used. For mica, the 002 peak was used. Trace amounts of marcasite may be present in Enoch Valley mine samples MW 10 and MW 5, and siderite may be present in MW 5.

### Electron Beam Studies

Two polished thin sections (sample numbers 220-1 and 220-2) of fresh waste rock from the Dry Valley mine were studied with the SEM. The average diameter of most mineral grains ranges from about 0.005 to 0.040 mm. Major minerals, as determined by both X-ray diffraction and the energy-dispersive

**Table 3.** Relative abundance of minerals in phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho. [Numerical values listed are intensities for selected peaks determined by X-ray diffraction; reflections (hkl) used for each mineral are noted. – not detected; all rocks are fresh unless otherwise indicated.

hkl = Sample	apatite 112	orthoclase 040, 002	albite 002	dolomite 104	Calcite 104	pyrite 311	quartz 112	mica 002
<u>X-ray diffraction peak intensities</u>								
<u>Dry Valley mine</u>								
220-1	6	20	35	20	--	14	11	6
220-2	9	23	46	7	--	17	34	7
20-3 (oxidized)	24	11	4	0	5	--	20	4
<u>Gay mine</u>								
83FP211	56	6	--	--	--	5	17	5
83FP215	36	9	6	--	5	6	14	4
83FP216	31	11	8	4	5	6	19	3
<u>Enoch Valley mine</u>								
MW 11	30	15	15	4	--	15	29	6
MW 10	7	15	16	11	--	--	26	-
MW 9	19	8	18	100	--	8	21	4
MW 8	23	15	13	3	--	6	32	6
MW 7	19	17	18	4	--	4	35	6
MW 6	28	11	11	3	5	5	29	7
MW 5	6	25	37	25	--	--	38	-
MW 4	23	15	17	4	--	3	45	6
MW 3	37	14	15	4	--	2	41	7
MW 2	14	17	21	--	--	--	49	7
MW 1	15	18	19	--	--	7	35	6

system on the SEM, are quartz, albite, and orthoclase. Minor minerals include apatite, pyrite, and a clay mineral which is similar to smectite. Traces of detrital zircon and monazite are present. An intergrowth of pyrite and TiO<sub>2</sub> is present and probably represents pyrite replacement of a detrital Fe-oxide containing ilmenite or rutile. The organic material (kerogen) interstitial to the minerals contains a few tenths to a few percent of sulfur. Authigenic minerals include albite, orthoclase, apatite, two kinds of pyrite, and the clay mineral. The two kinds of pyrite include framboids and angular pyrite. The feldspars, albite and orthoclase are high-purity end member., as expected for authigenic feldspars.

SEM analysis of numerous pyrite grains of both types using the EDS did not detect selenium because the limit of detection for selenium may be as much as 0.5 weight percent, or higher, we cannot determine which phases in the sample contain selenium.

Electron microprobe wavelength dispersive analysis, with a Se detection limit of about 0.01 weight percent (100 ppm), of sample 220-1 revealed that pyrite has Se concentrations in both framboidal and angular pyrite of from < 100 ppm to about 2000 ppm. The concentration varied widely among several grains. Ten kerogen masses analyzed under similar conditions showed no detectable Se; sulfur concentrations in kerogen ranged from about 1 to 3 weight percent.

### **Oxidizing Thermal Treatment**

Prior work showed that the weight percent of organic carbon of the waste rock was proportional to the weight loss after ashing at 500°C (Desborough, 1977, fig. 2). This technique is applicable because of the low concentration of carbonate or hydrous minerals in the rock. In addition, the technique is an inexpensive way to determine organic carbon concentration. If two data points from the present study are combined with the results from Desborough (1977), the correlation of the regression analysis for calculated organic carbon concentration versus weight loss for ashed samples has an R<sup>2</sup> value of 0.985.

Clearly the correlation is quite good (fig. 4), and suggests that ashing at 500° C for 24 hours can be used to estimate the organic carbon concentration of these samples with an uncertainty of about  $\pm 1$  weight percent for concentrations less than 15 weight percent.

A second reason for examining the effects of oxidizing thermal treatments was to determine if selenium associated with non-sulfide phases such as kerogen could be volatilized without affecting the selenium in pyrite. Experiments were conducted to quantify the percentage of pyrite using X-ray diffraction (XRD) and to measure the concentration of selenium before and after heating under controlled environments. For these experiments, numerous XRD and X-ray fluorescence (XRF) analyses were completed on both fresh and thermally treated samples in order to determine loss of mineral phases and elements. Pyrite was detected by XRD in most of the samples studied (table 3) used in these thermal experiments.

Virtually all of the selenium is lost in oxidizing thermal treatments of samples heated at 350° to 500°C for 24 hours (Tables 4 and 5). Most of the organic matter and its associated selenium is removed by oxidizing treatments at 340° C for 19.5 to 72 hours, but such heating does not oxidize pyrite and its associated selenium. Significant differences in the amount of selenium removed from sample 83FP211 (table 5) may be due to the presence of oxides of selenium or selenate minerals along fractures. Such compounds decompose at less than 350° C and selenium is volatilized.

**Table 4.** Selenium loss during initial thermal treatments of fresh samples of phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho [Samples heated in beakers 45 mm in diameter and 70 mm tall]

Sample	Grain size mm	Organic C wt. %	Sample wt. grams	Temp. ° C	Heating time hours	Weight loss percent	Se loss percent	pyrite lost
<u>Dry Valley mine</u>								
220-2	< 0.044	5.0	3.0	500	17.0	9.4	100	yes
220-2	< 0.044	5.0	2.0	450	1.5	12.4	0	yes
220-2	< 0.044	5.0	2.0	400	4.3	7.8	100	yes
220-2	< 0.044	5.0	2.0	300	17.0	1.8	0	no
220-2	< 0.044	5.0	2.0	340	23.0	7.9	0	no
<u>Gay mine</u>								
83FP211	< 0.044	10.6	3.0	340	24.0	15.9	54	no
83FP215	0.063-0.090	22.5	3.0	500	3.0	30.7	100	yes
83FP215	< 0.044	22.5	3.0	340	19.5	32.1	46	no

**Table 5.** Selenium loss during second thermal treatments of fresh samples of phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho [Samples heated in petri dish 96 mm in diameter and 12 mm tall]

Sample	Grain size mm	Se ppm	Sample wt. grams	Temp. ° C	Heating time hours	Weight loss percent	Se lost percent	pyrite lost
<u>Dry Valley mine</u>								
220-2	0.063-0.150	60	3.0	340	26.0	8.3	28	no
220-2	< 0.50	80	3.0	340	25.5	7.7	10	no
220-2	0.044-0.150	75	3.0	340	27.0	9.5	100	yes
<u>Gay mine</u>								
83FP211	0.063-0.150	315	3.0	340	26.0	16.1	95	no
83FP211	0.090-0.150	295	3.0	340	27.0	15.1	45	no
83FP211	0.090-0.150	220	3.0	340	72.0	15.7	90	no
83FP211	0.090-0.150	220	3.0	340	72.0	15.0	60	no
83FP215	0.063-0.150	290	3.0	340	26.0	31.2	63	no
83FP215	0.150-0.250	335	3.0	340	46.5	32.3	95	no
83FP216	0.063-0.150	215	3.0	340	26.0	29.6	100	no
83FP216	0.063-0.150	255	3.0	340	44.0	30.1	86	no
83FP216	< 0.044	340	3.0	340	26.0	35.0	80	no

Heating of fresh waste rock from the Dry Valley mine (sample 220-1) to 300° C for 48 to 51 hours did not result in any loss of selenium (table 6). As determined by electron microprobe study, the pyrite from this rock contains < 100 to about 2000 ppm selenium. Kerogen from the rock contained no selenium. Because pyrite is not affected by heating at 300° C, selenium associated with the pyrite was not lost.

Thermal treatment of fresh waste rock from the Enoch Valley mine to 340° C for 24 hours showed variable loss of selenium, from none to more than 80 percent (table 7). Percent of selenium lost is not proportional to weight loss, estimated organic carbon concentration, or pyrite concentration. At this temperature, pyrite should not have been affected by the thermal treatment but kerogen was. The lack of correlation of any single factor with selenium loss suggests that selenium in the samples may be contained in multiple presently unknown phases.

**Table 6.** Selenium loss during thermal treatment at 300° C for 48-51 hours of fresh phosphate-bearing waste rock samples of the Phosphoria Formation, southeastern Idaho [\*], minimum selenium lost; all samples < 0.150 mm diameter; pyrite remained in all samples, based on X-ray diffraction; organic carbon estimated from percent of weight lost; samples heated in petri dish 96 mm in diameter and 12 mm tall]

Sample	Weight loss percent	Initial Se ppm	Se lost ppm	Pyrite XRD peak intensity	Estimated organic C wt. %
<u>Dry Valley mine</u>					
220-1	6.6	95	0	14	3.0
220-2	7.8	75	0	12	3.5
220-2	7.1	95	0	10	3.0
<u>Gay mine</u>					
83FP211	16.3	410	390*	5	10
83FP215	37.4	375	350*	5	23
83FP216	32.8	295	270*	5	20

**Table 7.** Selenium loss during thermal treatment at 340° C for 24 hours of fresh phosphate-bearing waste rock samples of the Phosphoria Formation from the Enoch Valley mine, southeastern Idaho [pyrite remained in all samples based on X-ray diffraction; organic carbon estimated from the percent of weight lost; all samples < 0.150 mm in diameter]

Sample	Weight loss percent	Initial Se ppm	Se lost ppm	Pyrite XRD peak intensity	Estimated organic C wt. %
MW 11	7.4	180	55	8	3.5
MW 10	5.7	30	0	0	2.5
MW 9	8.7	95	40	3	5.0
MW 8	14.6	115	35	4	8.0
MW 7	14.4	90	25	5	8.0
MW 6	11.9	100	25	5	7.0
MW 5	0.2	< 10	0	0	0.0
MW 4	9.0	50	0	3	5.0
MW 3	7.6	30	> 20	4	3.5
MW 2	8.9	85	40	3	5.0
MW 1	11.4	100	40	6	7.0

## Passive Leaching Experiments

Passive leaching experiments were conducted of waste-rock samples of the Phosphoria Formation in order to evaluate the solubility of selected elements. Deionized water having a pH of 5.0 in a waste:leachate ratio of 1:20 was interacted with the samples for 48 hours. The final pH of the leachate was measured for each sample. Acidified and filtered (0.45 micrometer) leachates were analyzed by inductive-coupled plasma/ mass spectrometry (ICP/MS). Leaching of waste samples utilized a passive (at rest with no stirring) method. Samples exposed to the leachates ranged in weight from 5 to 20 grams.

For the unoxidized samples, more selenium and sulfate are leached from the rock as grain size decreases (table 8). The concentration of selenium and sulfate in the leachate are positively correlated (figs. 5 and 6). The oxidized waste behaved in the same fashion as the fresh waste, but less selenium was concentrated in the leachate. The final pH of leachates increased with decreasing grain size, as did the concentrations of Mg, Ca, and Zn in the leachates. Leachates were decanted and the samples were allowed to dry. Fine white precipitates of gypsum (identified by XRD) developed on the dried samples

**Table 8.** Concentrations of selected elements in deionized water leachates of phosphate-bearing waste rock samples of the Phosphoria Formation from the Dry Valley mine, southeastern Idaho [size fraction exposed to deionized water for 48 hours in a waste:leachate ratio of 1:20; analysis by inductive-coupled plasma mass spectrometry (ICP-MS); all metal concentrations in  $\mu\text{g/L}$ ; all leachates had  $\text{Cr} < 15 \mu\text{g/L}$  and  $\text{As} < 2 \mu\text{g/L}$ ]

Size mm	final pH	Mg	Ca	SO <sub>4</sub>	Se	Fe	Zn	Cu	Mo	Cd	Pb
Sample 20-3, oxidized											
12.7-44.4	6.22	200	820	< 300	0.4	90	3	7	1.6	0.3	0.3
4.2-12.7	6.41	210	850	900	0.7	90	8	14	1.1	0.3	0.4
1.65-4.2	6.43	250	970	1000	0.8	110	2	9	1.1	0.3	0.4
0.5-1.65	6.43	350	1500	1000	1.0	120	3	11	< 0.5	0.4	0.4
< 0.5	6.51	1800	1800	1300	1.0	120	3	11	< 0.5		
Sample 220-1, unoxidized											
12.7-44.4	6.01	4200	3900	21000	13	15	460	< 0.5	5.1	0.8	0.1
4.2-12.7	6.44	5500	4700	28000	17	17	250	< 0.5	9.0	0.2	0.1
1.65-4.2	6.79	5400	13000	57000	31	33	510	< 0.5	16.8	0.4	< 0.1
0.5-1.65	6.96	5600	16000	73000	39	38	510	< 0.5	34.0	0.3	0.2
< 0.5	7.18	6500	20000	85000	44	45	220	< 0.5	320	0.2	0.1
Sample 220-2, unoxidized											
12.7-44.4	4.24	1700	4500	23000	6.30	3100	1400	6	0.7	1.4	1.5
4.2-12.7	4.37	3200	7000	32000	15	2300	2100	20	0.7	2.1	55.0
1.65-4.2	4.08	5300	19000	74000	25	6500	5400	42	1.4	7.7	79.0
0.5-1.65	4.43	6200	23000	88000	34	1600	5600	7	< 0.5	6.9	2.4
< 0.5	5.50	5500	24000	100000	36	46	7200	5	< 0.5	6.0	2.4

Fresh waste samples from the Enoch Valley mine were likewise used for leaching experiments. Ten grams of sample was used for each experiment. Sulfate concentrations were not determined for the leachates (table 9). For the eleven samples, selenium in the leach is positively correlated ( $R > 0.7$ ) with Mg, Ca, and Fe in the leach and is strongly correlated ( $R > 0.8$ ) with Se, Cd, and pyrite in the rock. Final pH does not correlate strongly with any other factor. In general, waste rock having the highest Se concentration (table 2) yielded the highest concentration of Se in the leachate (fig. 7).

**Table 9.** Concentrations of selected elements in deionized water leachates of fresh, phosphate-bearing waste rock samples of the Phosphoria Formation from the Enoch Valley mine, southeastern Idaho [all samples were 0.5-2.0 mm in diameter; samples exposed to deionized water for 48 hours in a waste:leachate ratio of 1:20; analysis by inductive-coupled plasma mass spectrometry (ICP-MS); all metal concentrations in  $\mu\text{g/L}$ ; all leachates had  $\text{Cr}$  and  $\text{As} < 10 \mu\text{g/L}$  and  $\text{Pb} < 0.2 \mu\text{g/L}$ ]

Sample	final pH	Mg	Ca	Se	Fe	Zn	Cu	Mo	Cd
MW 11	6.32	1860	9030	182	47	1570	12	290	37
MW 10	7.15	940	4500	27	< 0.2	40	1	23	0.3
MW 9	6.98	1730	5000	184	21.0	110	2	37	3.5
MW 8	6.38	680	3200	123	< 0.2	60	1	26	1.1
MW 7	6.41	730	2800	95	< 0.2	46	1	46	0.9
MW 6	6.63	620	2400	82	< 0.2	34	2	54	0.5
MW 5	7.06	1300	2730	0.2	< 0.2	20	3	320	0.6
MW 4	6.25	280	1100	19	< 0.2	50	3	50	0.2
MW 3	6.04	260	1540	3	< 0.2	87	2	68	0.3
MW 2	5.65	135	1400	17	< 0.2	84	0.6	75	0.5
MW 1	5.55	2040	8540	130	41	500	0.7	85	11

## SUMMARY

Samples of fresh waste rock from the Phosphoria Formation in southeastern Idaho contain from < 20 to 360 ppm selenium. Concentrations of selenium vary by a factor of 6 or more for adjacent beds. Due to the extreme variation between beds, an average concentration for the investigated beds is not

calculated. The waste-rock beds consist of variable concentrations of extremely fine-grained (0.005 to 0.040 mm diameter) quartz, albite, orthoclase, apatite, dolomite, a clay mineral similar to smectite, pyrite, and calcite in a matrix of organic-rich (kerogen) material. Selenium is associated both with pyrite in carbon-poor rocks and rocks of average composition, and with kerogen in carbon-rich rocks.

Oxidizing thermal treatment of the waste rock indicates that selenium associated with kerogen is readily volatilized at temperatures below 300° C. Selenium associated with pyrite is volatilized at temperature above 340° C. Total organic carbon concentration can be determined by ashing the sample at 500° C and using a regression equation for samples of this and a prior study.

Passive leaching experiments indicate that much of the selenium in the rock is mobile in the presence of deionized water having a pH of 5.0. The highest concentrations of selenium and sulfate in the leachate are derived from samples crushed to the finest grain size. Selenium and sulfate in leachates from these samples are positively correlated. The final pH of these leachates increase with decreasing grain size.

Selenium in leachates interacted with eleven waste-rock samples is positively correlated ( $R > 0.7$ ) with Mg, Ca, and Fe in the leachate and is strongly correlated ( $R > 0.8$ ) with Se, Cd, and pyrite in the rock.

## REFERENCES CITED

- Desborough, G. A., 1977, Preliminary report on certain metals of potential economic interest in thin vanadium-rich zones in the Meade Peak Member of the Phosphoria Formation in western Wyoming and eastern Idaho: U.S. Geological Survey Open-File Report, 77-341, 27 p.
- Desborough, G. A., and Poole, F. G., 1983, Metals in marine black shales of western United States: Society of Economic Geologists/American Institute of Mining and Engineering, Cameron Volume on Unconventional Mineral Resources, p. 99-110.
- Desborough, G. A., Poole, F. G., Hose, R. K., and Green, G. N., 1984, Metalliferous oil shale in the Upper Devonian Gibellini facies of the Woodruff Formation in the southern Fish Creek Range, Nevada: U.S. Geological Survey Bulletin 1694, p. 93-104.
- Desborough, G. A., Poole, F. G., Harris, A. G., and Dav 3, Ted, 1988, Thermal history and organic maturation of Paleozoic rocks, Pocatello area, southeastern Idaho: U.S. Geological Survey Open-File Report 88-0289, 8 p.
- Gulbrandsen, R. A., 1960, Petrology of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation at Coal Canyon, Wyoming, *and* a method of X-ray analysis for determining the ratio of calcite to dolomite in mineral mixtures: U.S. Geological Survey Bulletin 1111-C, D, 152 p.
- Gulbrandsen, R. A., 1975, Analytical data on the Phosphoria Formation western United States: *Geochimica et Cosmochimica Acta*, v. 30, p. 769-778.

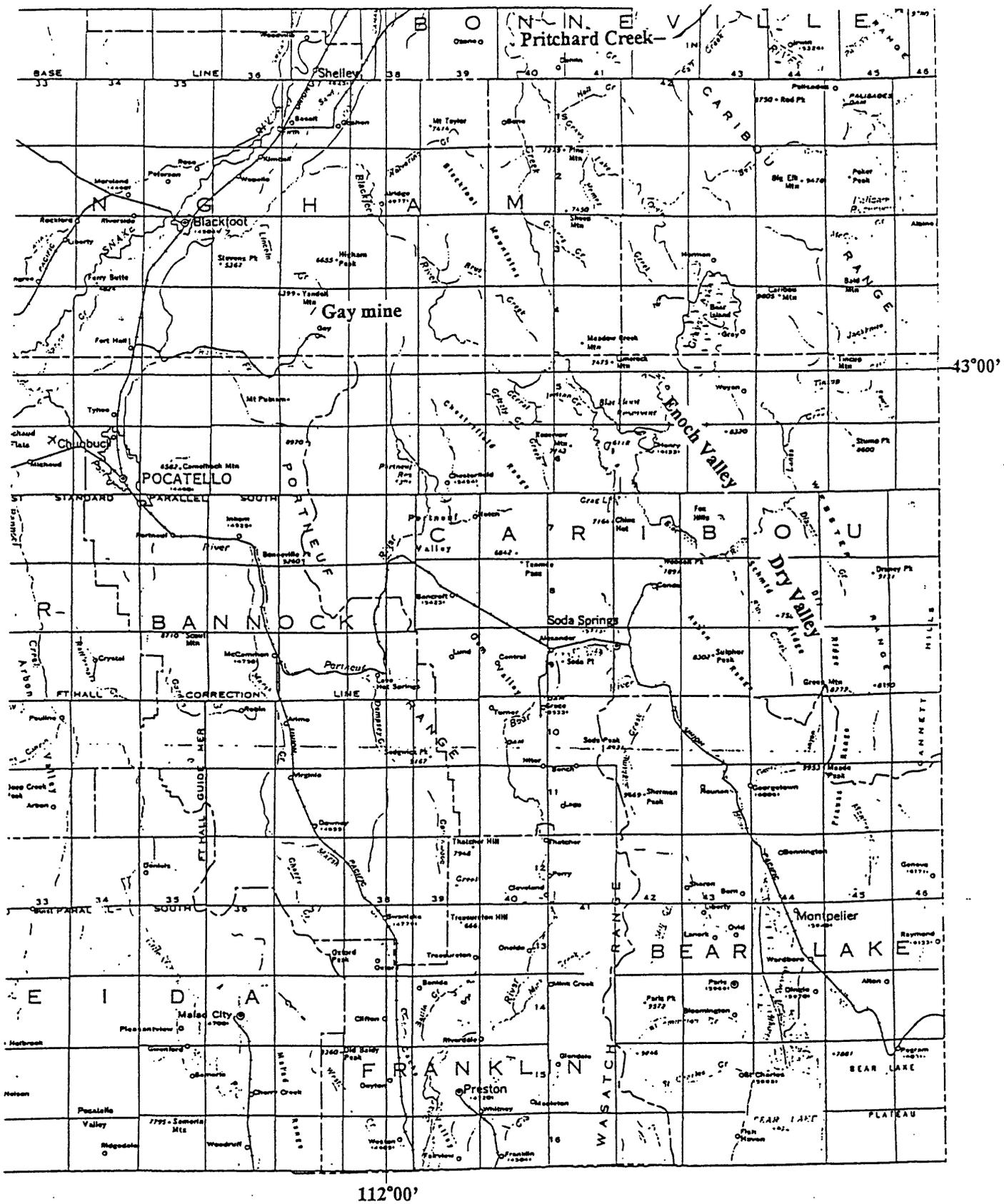


Figure 1. Locations of phosphate mines and the Pritchard Creek Locality in southeastern Idaho from which samples were taken for the present study.

Selenium concentrations in 1-foot samples of drill cuttings, South 40, Fort Hall Indian Reservation

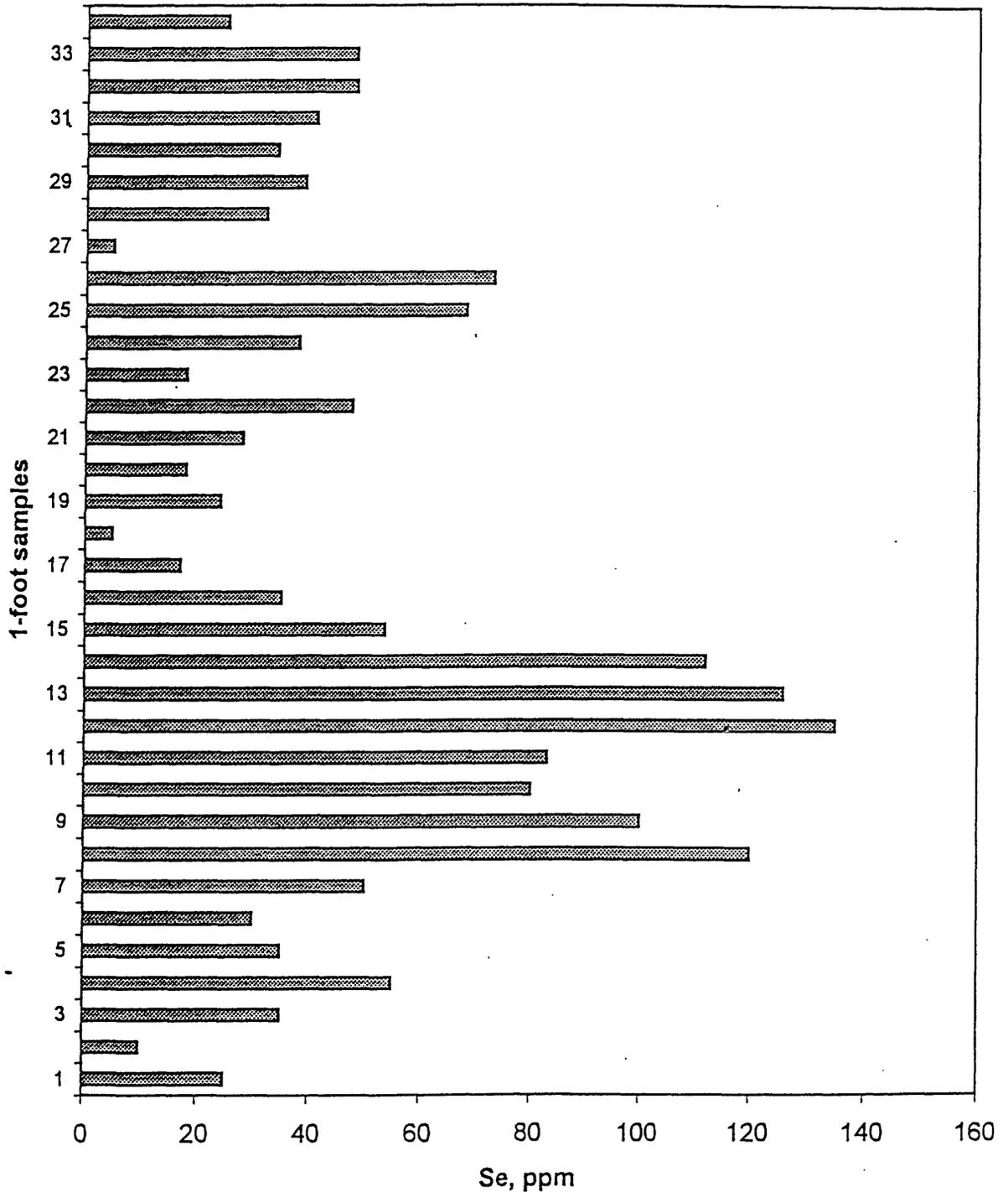


Figure 2. Selenium concentrations in one-foot intervals from samples of drill cuttings at the abandoned Gay mine on the Fort Hall Indian Reservation, southeastern Idaho.

### Selenium concentrations in unoxidized Pritchard Creek section

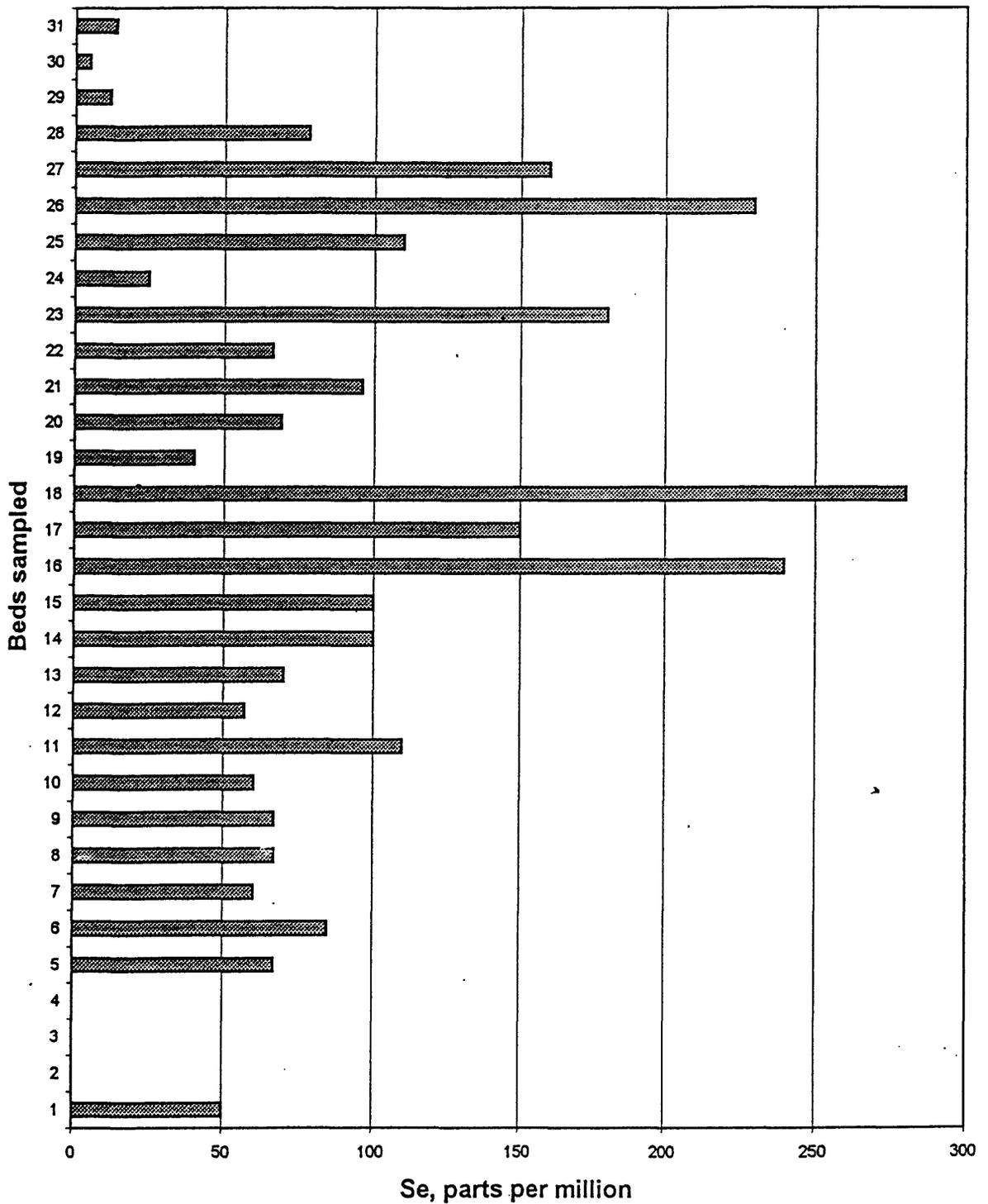


Figure 3. Selenium concentrations in stratigraphic samples of each bed along Pritchard Creek in the Caribou Range, southeastern Idaho.

Organic C versus weight loss by ashing at 500 C

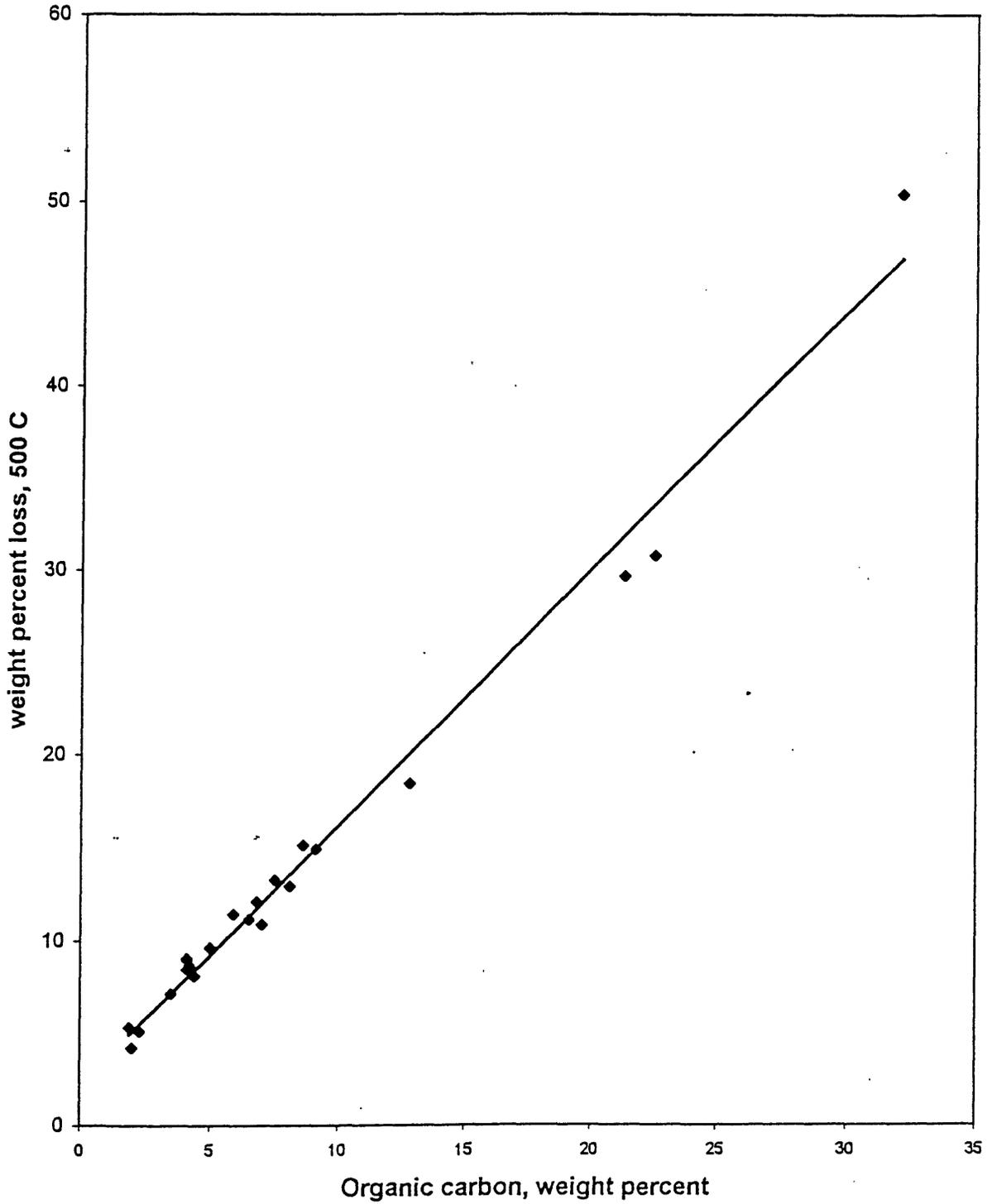


Figure 4. Plot of organic carbon versus weight loss for samples of the Phosphoria Formation, southeastern Idaho. Samples were ashed at 500°C for 24 hours.

Se versus Sulfate in leachate of sized fractions-Sample 220-1

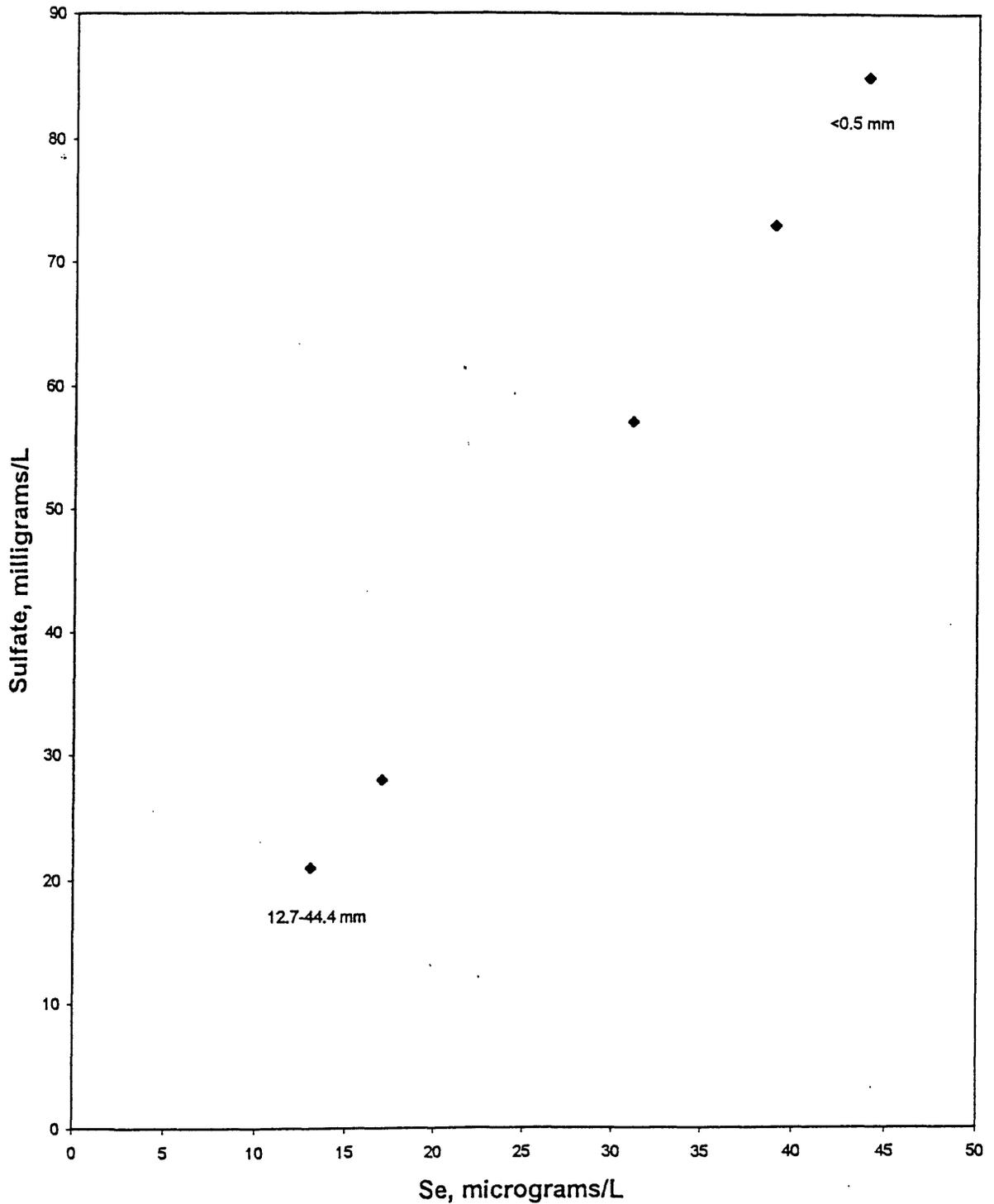


Figure 5. Plot of selenium in leachate versus sulfate in leachate for waste-rock sample 220-1 from the Dry Valley mine, southeastern Idaho. Five sized fractions of the sample were interacted with deionized water (pH = 5.0) for a 48-hour period using a waste:leachate ratio of 1:20.

Se versus Sulfate in leachate of sized fractions-Sample 220-2

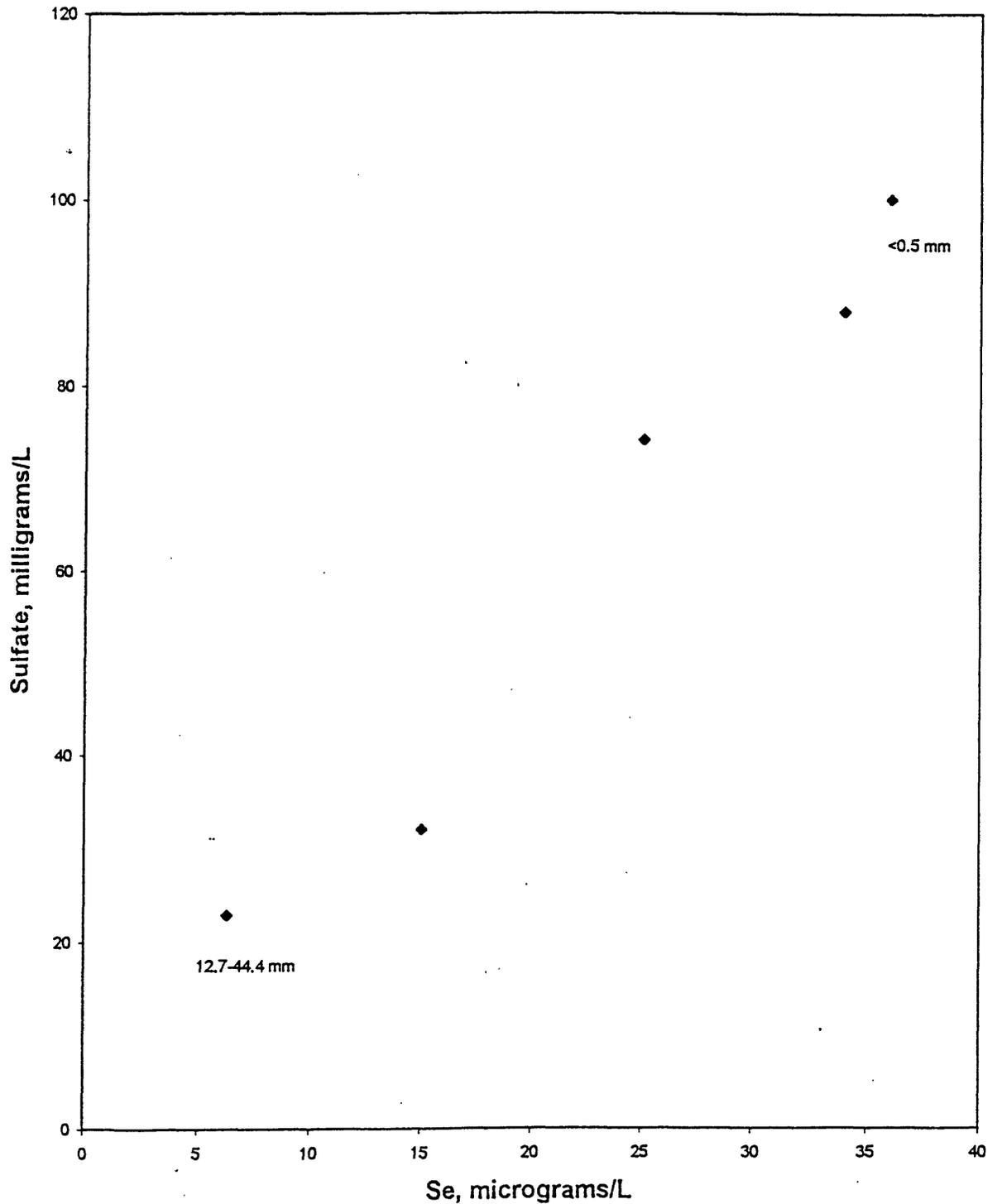


Figure 6. Plot of selenium in leachate versus sulfate in leachate for waste-rock sample 220-2 from the Dry Valley mine, southeastern Idaho. Five sized fractions of the sample were interacted with deionized water (pH = 5.0) for a 48-hour period using a waste:leachate ratio of 1:20.

## Se in Enoch Valley waste rock vs. Se in leachate

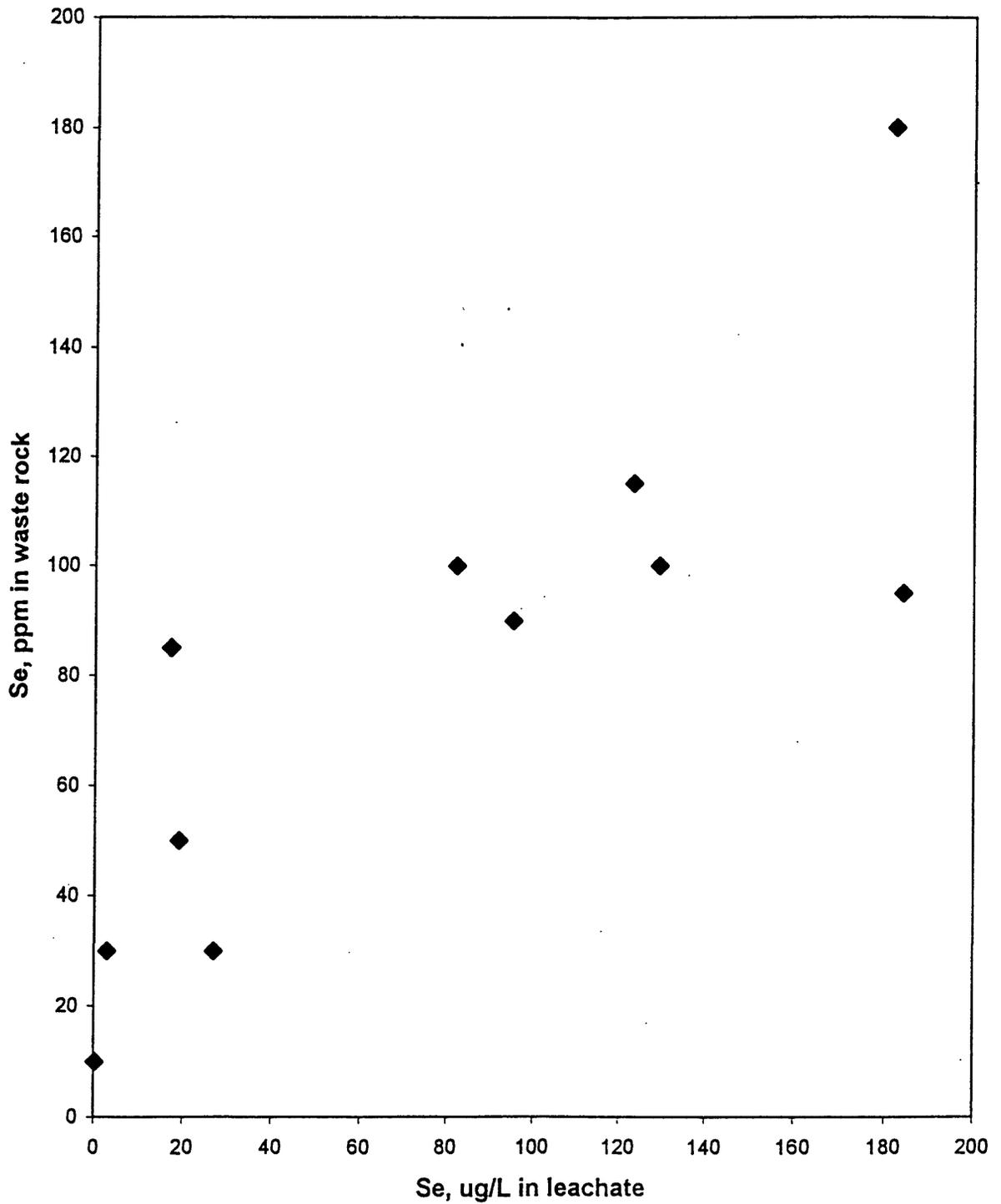


Figure 7. Plot of selenium in leachate versus selenium in rock from samples from the Enoch Valley mine, southeastern Idaho. Rocks were interacted with deionized water (pH = 5.0) for 48 hours.