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GEOCHEMICAL STUDIES IN THE COEUR d'ALENE MINING DISTRICT IDAHO

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ABSTRACT

A study of the lead, zinc, and copper content of soils near veins in the Coeur d'Alene mining district of northern Idaho was begun during the summer and fall of 1950. All samples were analyzed by a quick field test which consisted of a nitric acid digestion followed by an estimation of the lead, zinc, and/or copper using the organic reagent dithizone (diphenylthiocarbazone). Relatively large quantities of these metals were found to be dispersed in the soil for several hundred feet downslope from the projected extension of many of the veins. It was possible to trace the Little Pittsburg vein by detailed sampling even where the amount of lead or zinc added to the soil from the vein caused an increase in the concentration of these metals of less than 0.01 percent. From these data the writer concludes that analysis of soils probably would offer an effective method of prospecting in the Coeur d'Alene mining district.

INTRODUCTION

During the summer and fall of 1950, an evaluation of the usefulness of known geochemical prospecting techniques was begun in the Coeur d'Alene mining district of northern Idaho. The area was chosen for study for several reasons: parts of the district are difficult or expensive to prospect by customary means, the ore bodies are large, rich and usually without a prominent outcrop and finally, a reconnaissance soil sampling program in the fall of 1949 by Lyman C. Huff of the U. S. Geological Survey indicated that geochemical prospecting methods are of value in finding lead and zinc mineralization.

A study of the variation of lead, zinc, and copper in the soil near veins was begun and the results obtained are presented here. A few plant samples were analyzed for zinc, but, beyond this, no work has been done on the possibilites of biogeochemical prospecting. Nothing has been done regarding the possibilities of water analysis in prospecting.

It should be emphasized that the present paper is a progress report and that every step in the methods used is open to improvement.

ACKNOWLEDGMENTS

Many members of the Geological Survey, as well as employees of private mining companies, contributed their help during the course of this project.

S. Warren Hobbs of the Geological Survey supplied a great deal of information on the local geology and assisted in selection of suitable sites for sampling.

Claude E. Nugent, secretary-treasurer of the Denver Development Co., permitted the author free access to records concerning the Little Pittsburg mine. This information was valuable in the detailed work done at the mine.

H. E. Crowe, V. J. Kling, A. P. Pierce, and J. P. Schuch helped with field determinations and Harold Bloom performed the laboratory analyses.

SAMPLING PROCEDURE

Soil samples were collected from the desired depth and the material which passed a 5-mesh stainless steel screen was stored in half-pint waxed-paper containers. A sample weighing approximately 150 g was collected at each station in this way.

Most of the samples were of surface soil taken by removing the humus, if present, and collecting a sample representative of the first 4 in. in depth. For places where a deeper sample was wanted, the soil was collected over a range of 4 in. centered at the desired depth.

A pick mattock, which had a handle about 18 in. in length and a metal part 13 in. from point to point, was used as the digging tool. This tool was purchased from a war-surplus store and others of the same type probably may be obtained from many other such stores.

Sample stations were surveyed by tape and compass in all reconnaissance sampling. When detailed sampling was done, as at the Little Pittsburg mine, a plane table was used to map about every fifth sample point on the tape and compass traverses. A red cloth flag was attached to a bush or tree at every third or fourth sample point with the appropriate sample number written on it in black wax pencil. Thus, no difficulty was experienced in returning to the sample points.

A few plant samples were taken at the Little Pittsburg mine after all the soil work was finished. Several twigs were cut from pine or fir trees and the needles stripped from them. The twigs and needles from each tree were stored in separate half-pint waxed-paper containers until analyses were made.

METHODS OF ANALYSIS

Several problems were encountered in deciding upon the method of analysis to be used for samples from this area. These problems fell into essentially two groups; first, those dealing with the accuracy and completeness of extraction needed for the field test, and second, those dealing with the choice of the element or elements for which analyses should be made. These problems have not been completely solved, but some progress has been made.

A general heavy-metals test of the type described by Huff (1951)[1] was used on all samples. This test is designed to indicate the presence of very small amounts of copper, lead, zinc, and any other element which reacts with the organic reagent dithizone (diphenylthiocarbazone) under the conditions of the test. Elements reacting with dithizone, other than copper, lead, and zinc, are present in negligible quantities in most soils, and usually may be disregarded as was done in this report.

Sensitivity of the reagent to changes in concentration is different for each of the three metals, copper, lead, and zinc. This important fact must be taken into account in performing the heavy-metals test. To match the color produced by any given weight of zinc, twice as much copper or four times as much lead by weight is required. Therefore, greater anomalies in copper and lead than in zinc are required in order that the sample be distinguishable by the heavy-metals test as being above background.

Specific tests for lead, zinc, and copper were made using the solutions prepared for the heavy-metal tests. As directions for making specific tests were not included in Huff's paper (1951), the test for zinc described by Lakin, Stevens, and Almond (1949) and the tests for lead and copper devised by Almond and Morris (1951) were used in estimating the quantity of these elements in solution. Huff suggested four possible methods of digestion for putting the soil sample into solution and, of these, two were used in obtaining the results presented in this paper. Method B, consisting of digestion of the soil sample in 1:7 nitric acid for an hour, was used for all samples. Method D, with slight modifications, was used in analyzing 50 samples in order to compare the results with those obtained using method B. These results are shown in table 1 and are summarized in table 2. The modifications used in Method D consist, first, in changing the acid mixture from a 1:1 mixture of concentrated hydrofluoric to concentrated nitric to 2 ml of hydrofluoric and 8 drops of nitric; second, in stirring the sample in the acid before heating; and, third, in digesting 0.2 g samples instead of 1/3 g. The platinum dishes used are of 3 ml capacity, so that the amount of acid used completely covers the sample.

The specific test for zinc was used for all samples from the vicinity of the Little Pittsburg mine and for selected samples from other areas.

In table 1 asterisks are used to indicate copper values not included in calculating the figure for heavy-metals; however, the figure would not be changed by more 20 ppm by the addition of copper.

Lead tests were performed on all soil samples except some from areas of copper mineralization. Copper tests were made on all samples from areas of copper mineralization and also on selected samples from other areas.

For all soil samples part of the -80 mesh fraction was separated, using a stainless steel sieve, and the soil for analysis was taken from it. The unused -80 mesh fraction was returned to the sample container.

Plant samples were analyzed for zinc by the method described by Reichen and Lakin (1949).

Laboratory determinations were made by the method used by Holmes (1945).

RESULTS

Inasmuch as reconnaissance work in 1949 had indicated promise for prospecting by analysis of the soils in this area, the first job was to establish the limits of applicability of the method. The fact that the Coeur d'Alene mining district is located in a country of high relief and steep slopes was of great importance in deciding upon the method of approach

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[1] See references cited.

Table 1.--Comparison of field tests with laboratory analyses

Sample no.	Heavy metals calculated from laboratory analyses (ppm)	Heavy metals by HF·HNO$_3$ digestion (ppm)	$\frac{\text{HF-HNO}_3\text{ values minus lab values x 100}}{\text{lab values}}$	Heavy metals by 1:7 HNO$_3$ digestion (ppm)	$\frac{\text{1:7 HNO}_3\text{ values minus lab values x 100}}{\text{lab values}}$
Total heavy metals [Numbers marked with asterisk indicate copper values were not included in calculating this figure]					
1	255*	280	+10	250	-2
2	435	420	-3	250	-43
3	715	630	-12	450	-37
4	285	310	+9	280	-2
5	325	180	-45	250	-23
6	630	750	+16	480	-23
7	400*	360	-10	300	-25
8	500	420	-16	300	-40
9	675	420	-38	380	-44
10	350	310	-11	150	-57
11	315*	310	-1	150	-52
12	425*	420	-1	300	-29
13	330*	280	-15	230	-30
14	280*	250	-11	150	-46
15	590*	310	-47	250	-58
16	410*	280	-32	300	-27
17	1000*	630	-37	700	-30
18	440*	420	-4	300	-32
19	345*	420	+22	230	-33
20	265*	230	-13	230	-13
21	220*	210	--5	230	+5
22	265*	310	+17	230	-13
23	290*	210	-28	150	-48
24	3600*	3100	-14	3800	+6
25	1600*	630	-61	1500	-6
26	315*	310	-1	150	-52
27	235*	250	+6	220	-6
28	265*	250	-6	150	-43
29	285*	310	+9	220	-23
30	1800*	1800	0	1500	-17
31	3500*	4100	+17	3800	+9
32	2900*	3100	+6	3000	+3
33	2700*	2500	-7	2300	-15
34	2200*	1800	-18	1900	-14
35	5400*	8300	+54	4500	-17
36	355	310	-13	190	-46
37	575	460	-20	300	-48
38	195	230	+18	100	-49
39	240	310	+29	140	-42
40	180	180	0	80	-55
41	155	160	+3	60	-61
42	255	250	-2	170	-33
43	1200	830	-31	560	-53
44	2400	1800	-25	1000	-58
45	430	310	-28	220	-49
46	1850	1600	-13	1000	-46
47	145	100	-31	80	-45
48	130	100	-23	60	-54
49	310	210	-33	140	-55
50	280	90	-68	60	-79
Zinc					
1	200	200	0	140	-30
2	360	270	-25	180	-50
3	570	470	-18	360	-37
4	260	180	-31	150	-42
5	280	170	-39	130	-54
6	590	630	+7	380	-36
7	360	270	-25	270	-25
8	450	280	-38	270	-40
9	360	250	-31	140	-61
10	220	220	0	120	-45
11	270	270	0	150	-45
12	350	270	-23	270	-23
13	280	310	+11	150	-47
14	230	200	-13	90	-61

Table 1.--Comparison of field tests with laboratory analyses--Continued

Sample no.	Heavy metals calculated from laboratory analyses (ppm)	Heavy metals by HF·HNO$_3$ digestion (ppm)	HF-HNO$_3$ values $\frac{\text{minus lab values}}{\text{lab values}}$ x 100	Heavy metals by 1:7 HNO$_3$ digestion (ppm)	1:7 HNO$_3$ values $\frac{\text{minus lab values}}{\text{lab values}}$ x 100
			Zinc--Continued		
15	480	200	-58	270	-44
16	330	310	-6	230	-30
17	670	400	-40	360	-46
18	400	350	-13	270	-32
19	275	350	+27	130	-53
20	240	250	+4	180	-25
21	200	200	0	130	-35
22	240	250	+4	130	-46
23	265	300	+13	130	-51
24	580	320	-45	450	-22
25	530	350	-34	450	-15
26	210	280	+33	90	-57
27	215	250	+16	130	-39
28	230	250	+9	90	-61
29	250	300	+20	180	-28
30	840	1100	+31	450	-46
31	1500	1500	0	1300	-13
32	1600	1500	-6	1300	-19
33	1800	1700	-6	1300	-28
34	1500	1000	-33	1300	-13
35	2150	2900	+35	1800	-16
36	220	180	-14	90	-59
37	260	200	-23	90	-58
38	150	150	0	70	-53
39	115	180	+57	70	-39
40	150	130	-13	70	-53
41	115	100	-15	60	-48
42	130	150	+15	90	-31
43	500	200	-60	180	-64
44	2000	1500	-25	680	-66
45	310	250	-19	180	-42
46	1800	1500	-17	1100	-39
47	125	50	-60	50	-60
48	90	90	0	30	-67
49	210	180	-13	70	-67
50	130	50	-61	30	-83
			Lead		
1	140	240	+72	140	0
2	250	150	-40	180	-28
3	490	250	-49	300	-39
4	55	30	-45	90	+64
5	100	80	-20	140	+40
6	70	50	-29	60	-14
7	80	30	-63	90	+12
8	115	50	-56	140	+22
9	1100	1000	-9	900	-18
10	450	370	-18	380	-16
11	100	80	-20	90	-10
12	230	300	+30	180	-22
13	120	80	-33	90	-25
14	125	50	-60	130	+2
15	350	250	-29	270	-23
16	250	100	-60	270	+8
17	1300	1000	-23	1100	-15
18	70	40	-43	900	+1200
19	275	160	-42	240	-13
20	100	80	-20	130	+30
21	80	40	-50	120	+50
22	90	80	-11	130	+44
23	105	130	+24	90	-17
24	12000	10000	-17	13000	+8
25	4300	5000	+16	4500	+5
26	415	330	-20	450	+8
27	70	40	-43	90	+29
28	130	50	-62	130	0
29	140	60	-56	130	-7
30	3900	5000	+28	4500	+15

Table 1.--Comparison of field tests with laboratory analyses--Continued

Sample no.	Heavy metals calculated from laboratory analyses (ppm)	Heavy metals by HF·HNO_3 digestion (ppm)	HF-HNO_3 values $\frac{\text{minus lab values}}{\text{lab values}}$ x 100	Heavy metals by 1:7 HNO_3 digestion (ppm)	1:7 HNO_3 values $\frac{\text{minus lab values}}{\text{lab values}}$ x 100
			Lead--Continued		
31	8000	7000	+13	9000	+12
32	5200	750	-86	6800	+31
33	3500	5000	+30	2700	-23
34	2800	2500	-11	2500	-11
35	13000	15000	+15	13000	0
36	475	420	-12	460	-3
37	1100	1000	-9	1300	+18
38	35	0	-100	20	-43
39	40	0	-100	10	-75
40	35	0	-100	20	-43
41	45	0	-100	20	-56
42	45	0	-100	50	+11
43	2600	2000	-23	2700	+4
44	1300	2000	+54	2200	+54
45	450	500	+11	450	0
46	110	100	--9	60	-45
47	30	0	-100	10	-67
48	30	0	-100	0	-100
49	225	150	-33	180	-20
50	540	500	-7	680	+26
			Copper		
36	30	100	+230	50	+67
37	80	75	-6	70	-12
38	70	100	+43	60	-14
39	230	330	+43	140	-39
40	45	50	+11	20	-56
41	60	50	-17	50	-17
42	230	250	+9	180	-22
44	120	75	-37	50	-58
46	55	50	-9	20	-64
49	45	100	+122	20	-56

Table 2.--Summary of analytical data in table 1

$\frac{\text{Field values x 100}}{\text{Lab values}}$	Number of samples in indicated group					
	Total heavy metals		Zinc		Lead	
	Method B	Method D	Method B	Method D	Method B	Method D
200+					x	
191-200						
181-190						
171-180						x
161-170					x	
151-160		x		x	x	x
141-150					xx	
131-140				xxx	xxx	
121-130		xx		x	xxxx	xxx
111-120		xxxx		xxxx	xxxxx	xxx
101-110	xxxx	xxxxxx		xxxxx	xxxxxx	
91-100	xxxx	xxxxxxxxxxx	xx	xxxxxxxxxx	xxxxxxx	xxxx
81-90	xxxxxx	xxxxxxxxxxxx	xxx	xxxxxxxxx	xxxxxxxx	xxxxxxxxxx
71-80	xxxxxx	xxxx	xxxxxxxx	xxxx	xxxx	xxxxx
61-70	xxxxxx	xxxxxx	xxxxxxxxx	xxxxxxxx	x	xxx
51-60	xxxxxxxxxxxxx	xx	xxxxxxxxxxx	x	xxx	xxxxxx
41-50	xxxxxxxxx		xxxxxxxxx	xxx	x	xxxx
31-40	x	xx	xxxxxxx	x	x	xx
21-30	x				x	
11-20			x			x
0-10					x	xxxxxxx

to the soil sampling problem. In general, the geology of the vein or veins under study controlled the approximate location of the sample points, and topography controlled the direction and spacing of the sample points. As comparatively rapid downslope migration of soil is characteristic of the mining district, most of the sample traverses were begun at a point upslope from the vein outcrop and were run downslope across the vein into the area where vein material might be expected to be mixed with soil. For veins whose strike was approximately downslope, soil samples where taken in a line perpendicular to the direction of slope.

In order that the results obtained might be valid for the mining district as a whole, the sampling was done in different parts of the district. In many instances, the sample traverses were not extended into completely nonmineralized areas, because the size of the dispersion pattern was not known at the time of sampling. In most places where analyses of the samples indicated that the outer limit of the dispersion pattern was not reached in preliminary sampling, no attempt was made to complete the job of mapping the dispersion pattern for each vein in detail. Instead, the results of the preliminary sampling across eighteen mineralized zones and the detailed study of one mineralized zone are recorded here. The results of the preliminary sampling are summarized in table 3. Every effort was made to obtain soil samples that were uncontaminated by material derived from prospect pits of tailings piles. The writer believes that the results are the equivalent of those which would have been obtained had the mineralized zones been undiscovered prior to sampling.

In order to obtain a better understanding of the possible uses of soil analyses in prospecting, the vicinity of the Little Pittsburg mine in the Yreka (Pine Creek) mining area was selected for detailed sampling. The data resulting from a general heavy-metals test, a zinc test, and a lead test on each sample are shown on plates 1-3.

An effort was made to record the results of the field tests as simply as possible. The method of recording numerical data as obtained by the field analyses was discarded because of the tendency to attach too much accuracy to these values once they were recorded and to save space. As the accuracy of the tests was about the same regardless of the total amount of the element present in any sample, it seemed logical that any grouping of values should take this fact into account. Also, as the absolute amount of the element being sought is not as important in geochemical prospecting as the ratio of the amount present to the amount in background (normal) samples, it seems necessary to relate the recorded data to the average background.

The method used, therefore, divided the values into groups with the midpoint of each group being 50 percent higher than the midpoint of the preceding group. The average background for the area was made the midpoint of the lowest group and all values less than this average were recorded as being equal to background. To obtain the midpoint of each group, the formula [Background x $(3/2)^n$] was used and the exponents (n-.5) and (n+.5) were substituted for n to obtain the limits of a group. The value for n is the integral number recorded on plates 1-3 instead of a number for parts per million. For this area the background for the zinc and heavy-metals test is about 100 ppm and the background for lead about 40 ppm when the dilute nitric acid digestion is used. The value, 3/2, was used in the formula because it is believed that, for any two samples, a 50 percent difference in copper, lead, or zinc by the field test indicates that there is, in most instances, a real difference in the copper, lead or zinc content of the two samples.

Plate 1, showing the results of the general heavy-metals test at the Little Pittsburg mine, is essentially a summary of plates 2 and 3 which show lead and zinc values. This is because copper values, when measured, were very low, and other metals, which would react with dithizone, are believed to be present in negligible amounts. It should be remembered that the value for total heavy metals approximately represents the sum of all the zinc, one half the copper, and one fourth the lead, owing to the different sensitivity of dithizone for these elements.

The outcrop of the Little Pittsburg vein, as projected from the underground workings, is shown on plates 1-3. Moderately good correlation with anomalous values of lead and zinc in the soil, as well as with two prospect pits containing iron-stained rock, was obtained. Apparently the strength of mineralization varies along the vein, inasmuch as the amount of heavy metals entering the soil from the vein shows pronounced changes. This is to be expected, for the vein at depth is barren at some points and carries ore several feet in width at other points. The vein contains only slight amounts of lead and zinc above level 5 in the area between the two portions of level 4. This fact probably accounts for the small amounts of lead and zinc in the soil at the outcrop of this portion of the vein. To the northwest of this barren area the major ore shoot extends toward the surface, but its top is at least 300 ft from the surface down dip on the vein. Nevertheless, geochemical evidence of this shoot is present at the surface for some of its length.

Several unexplained anomalies were found during the course of the sampling. The anomaly in lead, zinc, and heavy metals at point H cannot be explained at this time by upward extension of the Little Pittsburg vein nor can those at points B, C, or I be explained on the basis of underground information. There is a series of anomalies indicated by sampling about 150 ft to the east of the projected outcrop of the Little Pittsburg vein. The anomalies are slight to the north of point I, but at points B and C they are quite pronounced. The anomalous values in lead at point Q may be part of this same parallel zone. Some sampling at depths of 12-18 in. was done on the east-west traverses lying just south of points B and C. The results are compared with analyses of surface samples in table 4. Apparently little indication of a second zone of mineralization paralleling the Little Pittsburg vein was found by the mining company near the southeastern end of level 5; however, level 5 follows the slightly mineralized Crystalite fault for about 300 ft in this area and the wall rock is probably broken enough so that the intersection with another fracture zone containing only slight mineralization could easily go unnoticed.

Table 3.--Results of preliminary sampling

Name of mineralized zone	Heavy metals found in greatest quantity	Known ore at depth	Maximum ratio to background				Spacing of samples on traverse (in feet)	Remarks
			Total heavy metals	Lead	Zinc	Copper		
(1) Little Pittsburg vein.	lead, zinc.	yes	180	1000	36	(*)	50	The sample traverse was made downslope, almost perpendicular to the strike of the vein. The lead content of the soil exceeded three times background for more than 400 ft downslope and 75 ft upslope from the vein outcrop. The angle of slope was about 30°.
(2) Frisco vein--------	lead, zinc.	yes	16**	50**	9**	3**	50	The sample traverse was downslope and almost perpendicular to the strike of the vein. The lead content of the soil exceeded three times background for more than 400 ft downslope and for 150 ft upslope from the vein outcrop. A ridge crest was located 150 ft upslope from vein outcrop. The angle of slope was about 35°.
(3) Page mine-----------	lead, zinc.	yes	10**	18**	9**	(*)	50	The angle between the direction of slope and the sample traverse was about 60°-75°. The traverse crossed an area believed to contain vein outcrops striking almost perpendicular to the sample traverse. The samples containing anomalous amounts of lead and zinc were distributed erratically along the traverse, but contamination due to smelter smoke may account for this. The angle of slope is about 25°.
(4) Blue Jay stringer zone.	lead, zinc.	no	4	6	3	1	100	The sample traverse was along the slope and perpendicular to a zone of veinlets. A slight anomaly in lead and zinc was found only in the first sample taken. The angle of slope was about 30°. Exact location of veinlets was unknown.
(5) Sunset minerals-----	lead, zinc.	yes	2	1	2	(*)	50	The sample traverse was downslope almost perpendicular to the vein outcrop. No anomaly in lead or zinc was detected at the vein outcrop, but a slight anomaly in zinc was found about 100 ft downslope from the outcrop. The ore is about 1000-1500 ft downdip on the vein at the point where the sample traverse crossed the vein outcrop. The angle of slope at the vein was about 15°.

*No determinations were made for copper in the field.

**Background values were estimated as 10 ppm copper, 40 ppm lead, 100 ppm zinc, and 100 ppm total heavy metals as the sample traverse obviously did not extend into an area containing no mineralization.

Table 3.--Results of preliminary sampling--Continued

Name of mineralized zone	Heavy metals found in greatest quantity	Known ore at depth	Maximum ratio to background				Spacing of samples on traverse (in feet)	Remarks
			Total heavy metals	Lead	Zinc	Copper		
(6) Gold Hunter--------	lead	yes	5	60	2	1	50	The sample traverse was downslope and perpendicular to the vein outcrop. The lead content of soil exceeded three times background for more than 400 ft downslope and for 200 ft upslope from the vein outcrop. The angle of slope varied from 0 degrees above the outcrop to 5° at the outcrop and then to 20° below the outcrop.
(7) Star vein---------	lead	yes	3**	50**	2**	1	100	The sample traverse was downslope and perpendicular to the vein outcrop. The lead content of soil exceeded three times background for more than 350 ft downslope and more than 500 ft upslope. Contamination due to prospect pits prevented further sampling downslope. A second source of lead may be present upslope to account for the lead found there. The angle of slope was about 25°.
(8) Sidney vein--------	lead	yes	3**	20**	2**	5**	20	The sample traverse was along the slope and perpendicular to the vein outcrop. The exact location of the vein was unknown, but the lead content of the soil exceeded three times background for the full length of the 100-ft traverse. The angle of slope was 25°.
(9) Vindicator vein----	lead	no	3	25	1	7	20	The sample traverse was downslope and perpendicular to the vein outcrop. Lead content of soil exceeded three times background for more than 200 ft downslope and for 60 ft upslope from the vein outcrop. The angle of slope was 30°.
(10) Hercules----------	lead	yes	3**	20**	3	1	50	The strike of the vein forms an angle of about 15° with the direction of slope. A sample traverse was made along the slope and crossing the vein outcrop. All samples contained more than three times the background amount of lead, however, the maximum distance of sampling from the vein was 100 ft. The angle of slope was 30°.

(11) Jack Waite vein----	lead	yes	3	7	1	(*)	50	Several traverses were made across the projected outcrop of the vein and anomalies in lead in excess of three times background were found at a distance of 25 ft downslope and along the slope from the estimated location of the outcrop. Two anomalies in lead were found which are not known to be associated with the Jack Waite vein.
(12) "Barren" vein between Sherman and Tamarack mines.	lead	no	2**	45**	1	1	100	The sample traverse was downslope and about perpendicular to the strike of the vein outcrop. Soil contained lead in excess of three times background for more than 1000 ft downslope and for more than 100 ft upslope from the projected vein outcrop. The ridge crest was about 150 ft upslope from the projected vein outcrop. The angle of slope was 30°-35°.
(13) Standard-Mammoth---	lead	yes	3	20	3	(*)	50	The sample traverse was downslope and perpendicular to the strike of the projected vein outcrop. Lead content of soil exceeded three times background values for more than 100 ft downslope and for 150 ft upslope. The angle of slope was about 25°.
(14) Carbonate vein south of Star vein.	zinc	no	15**	6**	15**	1	10	The sample traverse was along the slope and perpendicular to the strike of the vein outcrop. The soil contained zinc in excess of three times background for the full 100-ft traverse. The vein outcrop was believed to lie at about the mid-point of the sample traverse. The angle of slope was about 30°.
(15) About 700 ft north of Missoula tunnel.	copper	no	3	3	1	20	5	The sample traverse was downslope and almost perpendicular to the strike of the vein. The copper content of soil exceeded three times background for only 20 ft downslope from the vein outcrop. No samples were taken upslope from the vein outcrop.

*No determinations were made for copper in the field.

**Background values were estimated as 10 ppm copper, 40 ppm lead, 100 ppm zinc, and 100 ppm total heavy metals as the sample traverse obviously did not extend into an area containing no mineralization.

Table 3.--Results of preliminary sampling--Continued

Name of mineralized zone	Heavy metals found in greatest quantity	Known ore at depth	maximum ratio to background				Spacing of samples on traverse (in feet)	Remarks
			Total heavy metals	Lead	Zinc	Copper		
(16) Snowstorm--------	copper	yes	1	1	1	18	50	The sample traverse was downslope and perpendicular to the strike of the vein. The copper content of the soil exceeded three times background for more than 150 ft downslope and for 50 ft upslope from the vein outcrop. The angle of slope was 25°.
(17) Gentle Annie Gulch area.	copper	no	2	1	2	45**	10	The sample traverse was along the slope and almost perpendicular to the strike of a mineralized zone containing slight amounts of copper. The soil contained more than three times the background amount of copper for a distance of 50 ft on one side of the copper zone. Samples were not taken on both sides of the outcrop of copper mineralization. The angle of slope was about 20°.
(18) Big Iron Carbonate vein.	none	no	1	1	1	1	50	Samples were taken along the slope perpendicular to the vein outcrop at two points, but no soil samples were found to contain anomalous amounts of copper, lead, or zinc. The angle of slope at both traverses was about 30°.

*No determinations were made for copper in the field.

**Background values were estimated as 10 ppm copper, 40 ppm lead, 100 ppm zinc, and 100 ppm total heavy metals as the sample traverse obviously did not extend into an area containing no mineralization.

As there appears to be a mineralized zone lying to the east of, and approximately parallel to, the Little Pittsburg vein, an effort was made to determine whether the anomaly at point H lies on a similar zone to the west of the Little Pittsburg vein. The series of east-west sample traverses extending east from the ridge crest between points E and H was made to intersect this zone, if present, and additional samples were taken to the north and west of point H for the same reason. At point E there is a slight hint of mineralization, but the connection between this and the anomaly at point H is, at best, tenuous. The anomalies immediately to the south and east of point H can be explained by soil movement downslope, but the anomaly in the vicinity of a point 75 ft northwest of point H cannot be explained in this manner and so a northwest strike is indicated for the mineralization at point H. It is interesting that the slight anomaly at point J is in line with the anomalies near point H, but the mineralization is apparently so slight, if present, between points J and H, that it would be difficult to draw any conclusions about the relationship. A hanging-wall vein rises almost vertically from the number 4 level of the Little Pittsburg vein in the area to the southeast of point H. The approximate length and position of this shoot of ore is indicated by the short section of level 4. Point F is just east of a stope on this vein which has broken through to the surface. If the hanging-wall vein undergoes an abrupt change in strike, it may account for the anomaly at point H, but quite detailed work would be necessary to establish this. Two faults, paralleling the Crystalite fault and exposed on level 5, lie about 70 and 120 ft, respectively, northeast of the Crystalite fault. The anomaly at point H may be the outcrop of one of these mineralized faults, but again there is no way of checking this other than by detailed surface or underground work. The slight anomaly at point L is not known to be related to any mineralized zone and the relationship of the anomalies at points O, S, and Q to known ore or to each other is not clearly understood.

The most pronounced anomalies are in lead. Zinc shows the smallest percentage increase over background. The heavy-metals test, as might be expected, occupies an intermediate position in percentage increases.

The ratio of lead to zinc in the soil near the outcrop of the Little Pittsburg vein is 1:1 or more despite the fact that the lead to zinc ratio in the ore, as mined, is in the range of 1:3 to 1:2. Nugent has informed the writer that there is a tendency for the lead-zinc ratio to increase as the top of the ore is reached and this may account for the change in ratio. Another possibility is that the zinc is more easily leached from the soil and the ratio of lead to zinc is thereby increased.

The series of samples taken just to the west of the road, and paralleling it, show what the results would be if one were doing reconnaissance prospecting by sampling on the upslope side of roads. It is evident that the Little Pittsburg vein would have been located by this means.

Two sets of samples were taken to show the extent of the contaminating effect of prospect pits and mine dumps. Four samples were collected at the surface and a similar number from a depth of 1 ft on the downslope side of the prospect pit at point A. The results are shown for lead and zinc in table 4. Three sample traverses were made across the drainage from the dump at the entrance to level 3. In each traverse one surface sample was taken of the material entering the drainage from each side and one sample was taken of the material in the center of the drainage. In each case the sample from the middle of the drainage carried much more lead than the material entering from the sides. Apparently the dump is contaminating the drainage for a distance of at least 200 ft.

A study of the movement of heavy metals from point H was attempted by sampling between points G and H and by sampling the drainage below point G. This anomaly can be detected by lead tests at a distance of 200-300 ft from the source, but the zinc and heavy-metals test do not permit tracing the anomaly quite so far. This is undoubtedly because of the much higher quantity of lead present at the source.

A beginning was made on the problem of the size fraction which should be analyzed to give the greatest anomaly near lead, zinc, or copper mineralization. One sample representing background and two, representing high lead and zinc content, were chosen and broken into seven size fractions. These fractions were analyzed for lead and zinc using laboratory methods and the results are shown in table 5.

A similar study was made of three samples containing different amounts of copper and the results are also in table 5.

Nineteen trees were sampled in the area near the Little Pittsburg vein and their locations and sample numbers are plotted on plate 2. The zinc values for needles and twigs may be found in table 6.

CONCLUSIONS

From the results of the work done thus far on the use of geochemical prospecting techniques in the Coeur d'Alene district, it appears that soil analysis may be a powerful tool in locating new mineralized zones and in tracing known ones. These studies indicate that the heavy-metals test may be used for prospecting in the Coeur d'Alene district where large anomalies in lead, zinc, or copper are expected, or where zinc is the major heavy metal entering the soil profile from the mineralized zone. The zinc test can be used where zinc is the major heavy metal and the lead test might well be used where the lead entering the soil is equal to or greater than one-fourth the zinc in zinc-lead areas or half the copper in copper-lead areas. The copper test should be used only where copper is the major heavy metal present. In general, a combination of the lead test with either the zinc or the heavy-metals test will detect vein outcrops containing appreciable amounts of lead or zinc provided that the distance between samples does not exceed 100 ft. As little lead or zinc accompanied the copper in the copper areas tested, a specific test for copper seems the best way of discovering copper mineralization although large anomalies were not obtained in using the copper test in areas of strong copper mineralization.

Subject to further study, the method of sieving the sample through an 80-mesh screen and using

Table 4.--Analyses of soil

[See plates 2 and 3 for explanation of numbers in parentheses]

Distance in feet down slope	Analyses of surface soil		Analyses of soil at depth 12-18 in. (near bedrock)		Remarks
	Lead (ppm)	Zinc (ppm)	Lead (ppm)	Zinc (ppm)	
Traverse down slope from Point A (distance measured from edge of mine dump)					
0	1400 (9)	270 (2)	1600 (9)	360 (3)	
25	900 (8)	270 (2)	900 (8)	270 (2)	
50	900 (8)	360 (3)	900 (8)	450 (4)	
75	1400 (9)	450 (4)	1800 (9)	900 (5)	
Traverse just south of Point B (distance measured from east end of traverse)					
0	30 (0)	90 (0)	--	--	
50	230 (4)	230 (2)	--	--	
100	1500 (9)	550 (4)	--	--	
115	--	--	--	--	Approximate location of Little Pittsburg vein outcrop.
125	1800 (9)	450 (4)	--	--	
150	900 (8)	550 (4)	--	--	
200	3600 (11)	800 (5)	--	--	Beginning of trenching operations.
230	3600 (11)	800 (5)	3600 (11)	500 (5)	
232	--	--	--	--	1st vein outcrop; 3 in. wide; strike N.30°W.; 2.33 percent lead; 0.56 percent zinc.
239	--	--	--	--	2d vein outcrop: 0.5-1.0 in. wide; strike N.50°W.; 0.43 percent lead; 0.34 percent zinc.
244	--	--	--	--	3d vein outcrop: 4-6 in. wide; strike N.50°W.; 1.62 percent lead; .47 percent zinc.
250	11000 (14)	1000 (6)	22000 (16)	1400 (7)	
270	11000 (14)	1400 (7)	22000 (16)	2700 (8)	4th vein outcrop: 0.5-2 in. wide; strike N.20°W.; 0.78 percent lead; 0.39 percent zinc.
280	--	--	--	--	5th vein outcrop: 0.5-2 in. wide; strike N.57°W.; 1.52 percent lead; 0.11 percent zinc.
285	11000 (14)	1600 (7)	15000 (15)	3200 (9)	
294	--	--	--	--	6th vein outcrop: 3 in. wide; strike N.30°W.; 1.51 percent lead; 0.65 percent zinc.
300	9000 (13)	1800 (7)	38000	3600 (9)	End of trenching operations.
325	27000 (16)	1800 (7)	27000 (16)	2000 (7)	
350	18000 (15)	2300 (8)	27000 (16)	2500 (8)	
375	9000 (13)	1500 (7)	23000 (16)	3200 (8)	
400	20000 (15)	2700 (8)	14000 (14)	1500 (7)	
Traverse just south of Point C (distance measured from east end of traverse)					
0	90 (2)	270 (2)	90 (2)	180 (1)	
10-47	--	--	--	--	Sunken area at intersection of Crystalite fault and hanging-wall vein.

Table 4.--Analyses of soil--Continued

Distance in feet down slope	Analyses of surface soil		Analyses of soil at depth 12-18 in. (near bedrock)		Remarks
Traverse just south of Point C (distance measured from east end of traverse)					
	Lead (ppm)	Zinc (ppm)	Lead (ppm	Zinc (ppm)	
50	140 (3)	360 (3)	90 (2)	180 (1)	
70	90 (2)	270 (2)	90 (2)	180 (1)	
95	--	--	--	--	Approximate. location of the Little Pittsburg vein outcrop.
100	4500 (12)	450 (4)	700 (7)	200 (2)	
120	900 (8)	600 (4)	900 (8)	360 (3)	
145	7000 (13)	900 (5)	4500 (12)	1100 (6)	
170	4500 (12)	1100 (6)	4500 (12)	1100 (6)	
195	9000 (13)	1100 (6)	45000	1800 (8)	
220	14000 (14)	1400 (7)	16000 (15)	1400 (7)	
245	14000 (14)	1800 (7)	36000	2300 (8)	
270	14000 (14)	1800 (7)	14000 (14)	2200 (8)	
295	11000 (14)	1800 (7)	18000 (15)	2200 (8)	
320	9000 (13)	1600 (7)	11000 (14)	1600 (7)	
345	4500 (12)	1400 (7)	3600 (11)	1800 (7)	

Table 5.--Relationship of zinc, lead, and copper content to particle size

Diameter of soil particles (mm)	Background sample	Composition (ppm)		Ratio	
		High sample no. 1	High sample no. 2	High sample no. 1 background	High sample no. 2 background
Zinc					
Less than 0.06	210	800	1230	3.8	5.9
0.061-0.117	200	770	1230	3.8	6.2
0.117-0.234	200	780	1230	3.9	6.2
0.234-0.447	200	750	1160	3.7	5.8
0.447-0.98	190	720	1060	3.8	5.6
0.98-1.90	160	600	880	3.7	5.5
1.90-4.04	190	520	750	2.7	3.9
Lead					
Less than 0.06	40	1200	670	30	17
0.061-0.117	40	1850	750	46	19
0.117-0.234	60	2150	750	36	13
0.234-0.447	70	1830	690	26	9.9
0.447-0.98	40	1260	550	31	14
0.98-1.90	30	970	470	32	16
1.90-4.04	30	680	420	23	14
Copper					
Less than 0.06	50	350	450	7.0	9.0
0.061-0.117	50	360	460	7.2	9.2
0.117-0.234	55	330	430	6.0	7.8
0.234-0.447	60	360	430	6.0	7.2
0.447-0.98	45	390	320	8.7	7.1
0.98-1.90	45	330	300	7.3	6.7
1.90-4.04	40	250	200	6.2	5.0

Table 6.--Zinc in plants

[Measurements of height are approximate]

Plant field no.	Description of plant		Zinc (ppm)		
	Name	Height (feet)	Needles	Twigs	By field test on any soil samples taken within 25 ft of plant
P- 1	Western yellow pine-----	30	120	130	1,800-3,000
P- 2	Western white pine------	60	170	400	1,400-3,000
P- 3	Douglas fir-------------	10	70	150	1,400-3,000
P- 4	Douglas fir-------------	10	40	60	350
P- 5	Western yellow pine-----	50	40	50	250
P- 6	Western yellow pine-----	12	50	30	150
P- 7	Western yellow pine-----	25	40	40	100-250
P- 8	Douglas fir-------------	20	40	60	150
P- 9	Western yellow pine-----	25	100	40	200-750
P-10	Douglas fir-------------	20	20	60	400
P-11	Western yellow pine-----	75	90	50	300
P-12	Western yellow pine-----	30	60	40	150-300
P-13	Douglas fir-------------	20	20	40	200
P-14	Western yellow pine-----	20	50	50	100
P-15	Douglas fir-------------	20	30	80	100
P-16	Douglas fir-------------	15	40	40	150
P-17	Western yellow pine-----	15	40	40	150
P-18	Western yellow pine-----	25	70	90	(1)
P-19	Douglas fir-------------	15	90	140	(1)

[1] Growing in outcrop of Little Pittsburgh vein.

the -80 mesh fraction for lead, zinc, and copper analysis is satisfactory.

The results obtained by the analysis of the needles and twigs of coniferous trees suggest that plants may show anomalous amounts of zinc if the soil contains 500 ppm zinc or more. Unfortunately, western white pine, the plant containing more zinc than any of the others sampled, is found only occasionally in the area near the Little Pittsburg vein and only one specimen was sampled. For the Douglas fir and western yellow pine, twigs and needles seem to be equally good for detecting anomalous amounts of zinc in the soil. These conclusions are based on samples taken from nineteen trees, hence it seems wise to postpone more definite conclusions until such time as more work can be done. Certainly the present results are encouraging enough to indicate the need for more work on this phase of geochemical prospecting.

As the soil samples near bedrock exceeded 3 percent lead in two instances in the vicinity of point C, the writer feels that there is good evidence for believing that a rather strong zone of mineralization underlies this area. Further evidence for this belief is the presence of six veinlets found in trenching along the traverse just south of point B. This anomaly, paralleling the Little Pittsburg vein, cannot very well be the result of the breakdown of float from the Little Pittsburg since the zone is still present at point N after the Little Pittsburg outcrop has crossed the ridge and is shedding lead and zinc downslope to the west.

The mineralization at point H has not been shown to be a part of any particular zone of mineralization; however, closely spaced samples taken at bedrock would probably solve the problem.

At the present time no general conclusions can be drawn regarding the best method or methods of digesting the sample. Either of the two methods mentioned in this paper could profitably be used if the expected anomaly is at least five times background. Digestion method B appears to be more satisfactory than method D if only lead tests are being made. If heavy-metal tests, zinc tests, copper tests, or all tests are being made, method D appears preferable.

COMMENTS CONCERNING THE USE OF THE CHEMICAL TESTS

1. The pointed test tubes used for digestion should have nearly the same design in order that efficiency of heat transfer and violence of boiling be about the same in all tubes.

2. Care should be taken to insure violent boiling, as the completeness of extraction seems to depend, at least in part, upon this. A poor extraction followed by a good extraction on a second sample containing the same amount of heavy metals may, in extreme cases, make the second sample appear anomalously high and result in useless time-consuming check tests.

3. In digesting highly organic soil samples there is a tendency for the sample to creep up the side of the tube and be removed from the acid. This will result in erratically low results. The material on the side of the tube should be washed down frequently, but care should be taken to keep the volume of solution close to the original amount present.

4. The value of frequent introduction of standard soil samples as checks in the routine field analyses is very great. A comparison of field analyses with accurate laboratory analyses of these standards will provide a convenient means of measuring the reliability of the field tests.

5. If too much iron or organic material is present in the sample being analyzed by the

heavy-metals test, there may be oxidation of the dithizone with the result that a yellow-brown color appears in the reagent. Even though a distinct yellow-brown color may not appear, the colors obtained in the analysis may appear to be off-shade from the standards and the presence of oxidation may then be suspected. The addition of 0.1-0.2 g of hydroxylamine hydrochloride at the same time as the soil aliquot will, in most cases, reduce the oxidation sufficiently. If this is done, a neutralization step should be included to account for the extra acid present.

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