

Geochemical Studies in the Coeur d'Alene District Shoshone County, Idaho

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Geochemical Studies in the Coeur d'Alene District Shoshone County, Idaho

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With a section on

GEOLOGY

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CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING
FOR MINERALS

G E O L O G I C A L S U R V E Y B U L L E T I N 1 0 9 8 - A

The use of geochemical prospecting techniques near known lead, zinc, and copper deposits and a discussion of their values



UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

GEOCHEMICAL STUDIES IN THE COEUR D'ALENE DISTRICT, SHOSHONE COUNTY, IDAHO

By VANCE C. KENNEDY

ABSTRACT

The Coeur d'Alene district has long been known for its production of lead, zinc, silver, and copper. These metals, as mined, occur mostly in the minerals galena, sphalerite, and tetrahedrite. The ore is in tabular shoots and pods along generally steeply dipping veins or mineralized faults which cut Precambrian rocks of the Belt series. Some of the veins, including ore shoots and intervening barren gangue filling, can be traced for thousands of feet along the strike and have been developed to depths over a mile below the surface. The soil cover over much of the area ranges from one to several feet in thickness, and has added to the difficulties of prospecting for new deposits.

This study was made to test the feasibility of using geochemical prospecting techniques in the search for ore in the Coeur d'Alene district. Semiquantitative chemical analyses were made principally for copper, lead, and zinc in soils collected near veins and in soils collected at a distance from known veins. In addition, some information was obtained regarding the use of soil analysis in prospecting for antimony and tungsten veins. Samples of leaves, twigs, and fruits were analyzed both from plants growing in normal soils and from plants growing near ore deposits. A few water samples also were collected, and the pH and total heavy-metal concentrations were determined.

Evidence obtained from these studies indicates that analysis of soil for lead, or for lead and zinc, offers promise as a method of prospecting for new lead-zinc ore bodies in this area. Prospecting for copper by soil analysis may be feasible, but present data are not especially encouraging. Plants growing in mineralized areas contain abnormal amounts of the ore metals, but these anomalies are not so pronounced as those in the soil. The use of water analysis in the search for ore within the mining district is limited because of the contamination of surface waters by mine drainage.

INTRODUCTION

A study was made of the distribution of some of the ore metals in the soils (pl. 1), waters, and plants of the Coeur d'Alene district of northern Idaho during the summer and fall of 1950, the summer of 1951, and for a short period in August of 1952. The purpose of this study was to evaluate the usefulness of some known geochemi-

cal prospecting techniques as a means of locating new ore bodies in the district.

In an area such as the Coeur d'Alene district, the technique of applied geochemical prospecting should be a particularly useful tool. The heavy vegetation and prevailing soil cover obscure most vein outcrops. The steep slopes and ramifying drainage lines foster the development of widespread heavy-metal dispersion halos downslope and downstream from weathered outcrops of mineral-bearing parts of the veins. The steep dip and generally linear structure of the mineral belts and of the veins within them are established facts that should help to direct a program of geochemical prospecting to the best advantage.

Experience with geochemical techniques elsewhere indicated that soil analyses should be of help in prospecting an area of this type, and Lyman C. Huff, of the U.S. Geological Survey, obtained encouraging results in a reconnaissance study of the area (Huff, 1951, p. 528). These results led to the more detailed study that is reported in this paper. A preliminary report on the present study has been published (Kennedy, 1952).

To determine the feasibility of prospecting by soil analysis, soil samples were collected near the outcrops of many known ore bodies in the district and were tested for lead, zinc, and, in some samples, copper. (For the purposes of this paper the term "heavy metals" will be used hereafter, instead of listing "copper, lead, and zinc.") In addition, a few soil samples collected near an antimony-bearing vein and near a vein containing both gold and tungsten were analyzed. Both plant and soil samples were collected to see what correlation, if any, existed between the concentrations of copper, lead, or zinc in soil and the concentrations of these metals in plants growing in the soil. Some water samples from springs and streams were analyzed, but not much time was devoted to this phase of the project.

Extensive prospecting and mining have been carried on since the early 1880's. As a result, the entire area of the Coeur d'Alene district and its environs is pockmarked with prospect pits, small and large prospect adits, and the workings of past and present producing mines. The application of the bulldozer to prospecting, whereby many hundreds of miles of roads, trenches, and deep cuts have been made, has resulted in the movement of large volumes of overburden. The effect of this mining and prospecting activity has been to rearrange radically the areal distribution of heavy metals that occurred in the veins, the gossans, and the soil, and any program of geochemical prospecting must recognize and evaluate such artificial disturbances of the natural distribution of these metals.

To give necessary background for the geochemical studies, a geologic description of the ore deposits has been prepared by S. Warren

Hobbs. The discussion of geology is followed by a description of the geochemical studies made by the author. Several analytical methods were tried during the work, and the results obtained varied in accuracy. The method of analysis used is stated for each group of samples, and a detailed description of each method, along with comments on its usefulness, is given in the appendix.

ACKNOWLEDGMENTS

The mining companies in the area were most helpful and cooperative in making information about their properties available. Special attention was given to the area over the workings of the Little Pittsburg mine and to the area near the Vindicator mine because of the very favorable circumstances in these areas for the establishment of basic control data. Acknowledgment is made to the officials of the Denver Development Co., Hecla Mining Co., Vindicator Silver-Lead Mining Co., and Day Mines, Inc., for their full cooperation. Members of the U.S. Geological Survey engaged in studying the geology and mineral deposits of the area contributed invaluable assistance during the work. Particular mention must be made of the contribution of S. Warren Hobbs not only for preparing the section on geology in this report but for the great amount of effort which he devoted to furthering the geochemical studies.

Most of the semiquantitative analyses were performed by H. E. Crowe, F. Frieske, V. J. Kling, A. P. Marranzino, J. H. McCarthy, Jr., A. P. Pierce, and J. P. Schuch, all of the U.S. Geological Survey; the quantitative determinations were made by H. E. Crowe and Harold Bloom, of the U.S. Geological Survey. Field assistants were F. D. Frieske, V. J. Kling, and A. P. Pierce.

GEOLOGY

By S. WARREN HOBBS

The Coeur d'Alene district is in the very rugged mountainous country of the Panhandle of northern Idaho. Narrow V-shaped valleys, sharp ridge crests, and hillsides that in some places have slopes as steep as 45° are evidence of a stage of full physiographic maturity. A complex geomorphic history has resulted in the formation of several terrace levels, but the remains of these are fragmentary and attested today only by the scattered occurrences of relatively small patches of high-level gravels and the moderately extensive lower terrace gravels in the vicinity of Mullan and Kellogg. Valley glaciation modified the uppermost reaches of numerous tributaries to the Coeur d'Alene River, but only in the upper part of Canyon Creek did these glaciers coalesce into a sizeable ice

stream that extended down the main valley and deposited rather extensive morainal debris. Neither the terrace gravels nor the glacial detritus cover appreciable parts of the surface of the Coeur d'Alene district.

Abundant rainfall and snow have fostered the growth of dense vegetation, and, except where logging and forest fires have depleted the large trees, the area is covered by a coniferous forest and fairly heavy underbrush. Soil, ranging from a few inches to many feet in thickness, covers most of the area and is held in place on even the steepest slopes by plant growth. In spite of the extensive soil cover, bedrock exposures are numerous, especially on the high peaks, the sharp ridge crests, the cirque basins and walls, the stream bottoms, and as more resistant rocky ribs on the hill slopes themselves. In certain areas where vegetation has been destroyed by one cause or another, erosion has removed much soil cover leaving a loose rubble of rock nearly in place. This latter condition is especially characteristic of parts of the western end of the valley of the South Fork of the Coeur d'Alene River and its tributaries.

The district lies within a part of a very extensive area that is underlain by slightly metamorphosed, structurally complex sedimentary rocks that are a part of the thick Belt series of Precambrian age. These rocks are predominantly fine-grained quartzite, impure quartzite, and siliceous argillites, which in certain zones contain greater or lesser amounts of calcium, magnesium, and iron carbonate. A group of aligned small monzonite stocks intrude the sedimentary sequence and numerous lamprophyre and diabasic dikes have been localized along faults and fractures in the area. The bedded rocks have been displaced by extensive faulting and folding that has resulted in local overturning. The faults and associated fractures have been the principal loci for the development of the lead, zinc, silver, and copper veins for which the area is famous.

Six units totaling over 20,000 feet in thickness constitute the sedimentary sequence of the Belt series in the district. From base to top these are Prichard formation, Burke formation, Revett quartzite, St. Regis formation, Wallace formation, and Striped Peak formation. The base of the Prichard is nowhere exposed, and the upper part of the Striped Peak and the formations that presumably overlay it have been eroded.

The Prichard formation, for most part, is a very fine grained dark-gray laminated siliceous argillite. Parts of it, particularly near the middle and at the top, contain lighter colored layers interlaminated with argillite layers, which give the rock a sharply laminated or thin-bedded appearance. Some massive pure quartzite beds occur in these more quartzitic parts of the formation. Abundant pyrite

is disseminated through the formation, and, on exposure to weathering processes, it oxidizes to hydrous oxides that color joint and bedding surfaces of outcrops a deep reddish brown. The Prichard formation is at least 12,000 feet thick.

The Burke formation is an impure quartzite usually medium to light gray green, with a few beds that have a delicate pink cast. The rocks are generally well bedded in layers 2 to 6 inches thick and on weathering break into slabs along bedding planes. Lamination is sparse and the individual layers or groups of layers are generally more uniform in composition than in the Prichard. In general, the Burke becomes more quartzitic toward the top, but a few rather thick beds of nearly pure quartzite may be found here and there throughout the section. The Burke formation ranges in thickness from 1,800 to 2,400 feet or more. Its contact with the Prichard formation below is fairly sharp but is completely gradational upward into the Revett quartzite through an interval of several hundred feet.

The Revett quartzite is a thick- to massive-bedded fine- to medium-grained almost pure quartzite. It is generally very light gray to white on fresh surfaces. Certain parts contain blebs of disseminated iron carbonate which, upon oxidizing on weathered surfaces, form rusty speckles that make the rock appear mottled. Cross lamination is developed in many places. The lamination in the rock is most often marked by a concentration of dark-colored heavy minerals. On some weathered outcrops it is marked by an alinement of small rusty speckles resulting from the oxidation of crystals and clots of iron-bearing carbonate whose localization was controlled by the laminae. Some less pure quartzite layers occur within the Revett, but these are generally not seen except in mine workings. On the surface they are usually covered by soil. Measurements of the Revett quartzite show the thickness to range from 2,400 to 3,400 feet. Toward the top of the formation, the Revett quartzite becomes pinkish or reddish purple and includes increasing amounts of purplish-gray argillite and impure quartzite. Within a relatively short distance a transition is made into the characteristic overlying St. Regis formation.

The St. Regis formation is a somewhat heterogenous formation comprising thin-bedded argillites mixed with thin- to medium-bedded impure quartzites. Some considerable thicknesses of rocks in which argillite is predominant are interspersed in the section. The rocks are generally medium to dark shades of gray, purplish gray, and reddish gray. Although faint purplish coloration pervades the whole formation, only the more argillaceous facies are colored in more vivid shades of reddish gray and purplish gray.

Some parts of the St. Regis formation, particularly toward the top, contain appreciable amounts of ferrodolomite or ankerite that color the oxidized outcrop brown. After prolonged weathering, beds in which the carbonate is abundant become soft and punky, as well as dark brown. Throughout most of the district the purple part of the St. Regis formation is overlain by a sequence of predominantly light-greenish-gray porcelaneous laminated argillites that range up to several hundred feet in thickness. The total thickness of the purple and green rocks included in the St. Regis formation ranges from 1,400 feet to well over 2,000 feet.

The Wallace formation comprises a heterogeneous assemblage of rocks, characterized by more carbonate than any other formation in the area and by certain rather diagnostic lithologic and structural features. Shenon and McConnel (1939) divided the Wallace formation into four parts that total nearly 4,500 feet of rock. Only the lowermost division comprising nearly 3,000 feet of the sections crops out extensively within the area. These rocks are predominantly thin- to medium-bedded alternating light-gray quartzites and dark-gray to black argillites in layers from 2 to 6 inches or more thick. Iron-bearing carbonate minerals are abundant at certain horizons and color weathered exposures brown. Small-scale crumpling and folding characterize much of the formation, and many shallow-water features are well formed. The Wallace formation above the lowest division is divided into three units: in ascending order, a thinly laminated, nearly black noncalcareous argillite; banded, dark-gray to black arenaceous limestone that weathers brick red, and a thinly laminated argillite like unit 1.

The Striped Peak formation overlies the Wallace formation but has, for the most part, been eroded from the area. The largest exposure is on Striped Peak itself where about 1,500 feet of strata of the lower part of the formation occur. The Striped Peak formation is composed principally of alternating purplish- or pinkish-gray and greenish-gray quartzites. Some layers containing carbonate occur in the sequence. The upper several hundred feet of the observable section is more argillaceous, laminated, and more vividly purple than the lower layers.

Stocks and small irregular masses of igneous rock, predominantly monzonite, but ranging from diorite to syenite have been intruded into the sedimentary rocks. These igneous rocks are mostly localized along a line trending north-northeast across the center of the district. An age determination from zircon contained in these rocks places the intrusion during the Laramide orogeny and suggests their relationship to the Idaho batholith. Diabase and lamprophyre dikes are also present in the area and are more randomly distributed than the monzonite stocks.

All sedimentary rocks in the area have been subjected to relatively low-grade regional metamorphism that has converted the original mudstones, limy shales, and sandstones to argillites and quartzites, and in many places sericitic phyllites and schists have been produced in a complex history of deformation. Much of the fine-grained argillaceous material has been converted to sericite which, together with fine-grained quartz, constitutes the bulk of the rocks. Secondary tourmaline is sparsely but widely scattered throughout the sedimentary rocks. Near the intrusives more intense contact metamorphism has been superimposed on the regional effects. Widespread hydrothermal alteration that has bleached the rock has been localized along zones of more intense structural disturbance.

The rocks in the Coeur d'Alene mining area have been folded and faulted into a very complex pattern. The structure is dominated by the great Osburn fault that trends N. 70° W. across the center of the area. Horizontal displacement along this fault is measured in miles, vertical displacement in thousands of feet.

North of the Osburn fault, the rocks have been moderately folded along axes that trend, in general, nearly north and south, but which swing sharply to the east where they adjoin the Osburn fault. South of the fault, the fold axes trend more westerly and tend to parallel the fault. Local contortions and irregularities are abundant, especially near the igneous stocks. There are several extensive areas in which the beds have been subjected to extreme deformation; the beds are in an overturned position and dip 60° to 80°.

Numerous faults, subparallel to the main Osburn zone, occur in a zone on either side of it. At a distance from the Osburn fault—most notably to the north—the faults tend to trend more north-south. Apparent displacement on the faults is normal on some and reverse on others. At least one low-angle thrust fault and one low-angle normal fault are exceptions to the generally steep dip of most of the faults.

The economically important metals for which the district is famous are lead, zinc, silver, and copper. Antimony, cadmium, tungsten, and small amounts of several minor metals are produced as byproducts. By far the greatest proportion of these metallic elements occurs in the minerals galena, sphalerite, and tetrahedrite. Gangue minerals of the productive veins include siderite, ankerite, quartz, pyrrhotite, pyrite, barite, and locally, some silicate minerals.

The economically important concentrations of these minerals form tabular ore shoots in generally steep-dipping veins or mineralized faults that are usually much more extensive than the ore shoots themselves. More than one ore shoot may be developed within a vein or fault; in some places the fault connecting the shoots may be barren or filled with gangue minerals. Some of the veins, including

ore shoots and barren gangue filling, can be traced for thousands of feet along the strike and have been developed to depths of more than a mile. Some of the ore shoots crop out at the surface; others have their tops at depths of as much as several thousand feet even though, in some places, the barren vein can itself be traced to the surface. Ore shoots in the district range in size from the smallest pod of ore than can be mined to such fabulous examples as the Morning-Star ore shoot that was more than 2,000 feet in strike length and over 6,000 feet from the surface to the lowest levels mined. In the larger shoots the ore may be 20 or more feet wide, but the average width of minable ore in all shoots is probably 5 to 6 feet. The shoots tend to be longer down the dip than along the strike of the veins, and many of them are many times as deep as they are long. Most are essentially vertical in the plane of the vein, or they rake steeply in either direction. A few shoots, which are exceptions to the rule, have a flat rake or are essentially equidimensional in length and depth.

Most of the productive veins can be grouped in eight mineralized belts or zones, each of which is several thousand or more feet wide and from 6 to 12 miles long. These belts in general trend west-northwest. Within each belt the individual veins may strike in several directions, but most approximate the trend of the mineral belt itself. Barren veins or veins of slight productivity occur outside the mineral belts, but usually they comprise gangue minerals of what is known as the early barren stage of mineralization. Such barren veins may contain scattered pockets of ore minerals, but very few have yielded more than a very small tonnage of commercial ore.

GEOCHEMISTRY

SOIL AND ROCK STUDIES

The soil study constituted by far the largest part of the geochemical work done in the Coeur d'Alene area. This was for two reasons: first, from the start of the project, work on the soils showed promise; and second, plant and water analyses have disadvantages for prospecting in this district that limit their usefulness. The advantages of residual soil samples for prospecting include the following: The sample can be collected easily almost anywhere that information is needed; the sample is easily prepared for analysis; and the concentration of the ore element in the sample usually is related in a relatively simple way to the amount of the ore element present in the parent rock.

Rock analyses were made so that some understanding could be gained of the changes in heavy-metal concentration as rocks were weathered to form soil.

METHODS OF SAMPLING SOILS AND ROCKS

Soil samples were collected from the depth desired and then passed through a 5-mesh stainless steel screen at the sample spot. About 150 grams of the minus 5-mesh fraction was stored in half-pint waxed paper containers for later analysis.

Most samples were of surface soil taken by removing most of the humus and collecting a sample representative of the first 4 inches below the surface. In places where a sample was wanted from a greater depth, the soil was collected over a range of 4 inches centered at the desired depth.

Rock samples were usually obtained by breaking rock from exposures in roadcuts. A few boulders were broken open, and relatively fresh rock was obtained from their centers.

NORMAL SOILS AND ROCKS

As part of the work on soils, a total of 109 samples were collected beyond the periphery of the known mineralized district to serve as a basis for comparison with soil near mineralized areas. These samples were analyzed for copper, lead, and zinc by semiquantitative tests. Care was taken to be sure that the samples collected were typical of the soils on all sides of the mining district. The area surrounding the mining district was divided into quadrants by arbitrary lines, one north-south and one east-west, passing through a point about 4 miles northeast of the town of Osburn, Idaho. Approximately one-quarter of the samples were collected in each quadrant.

To assure that no soil sample collected for background study contained anomalous quantities of heavy metals, the data from the field analyses were carefully examined, and three samples containing obviously abnormal quantities of copper, lead, or zinc were removed from the group of samples. The remaining 106 samples were divided into 4 groups representing each of the 4 quadrants, and 4 composite samples were prepared by taking 3 grams of the minus 80-mesh fraction from all samples in each quadrant and mixing thoroughly. In this way an average background sample for each quadrant was obtained. These average samples were analyzed by quantitative methods for copper, lead, and zinc. Similarly, 87 rock samples were grouped by quadrant and analyzed by field method. The anomalous samples were discarded, and composited samples were analyzed by quantitative methods which included a digestion in hydrofluoric acid. A total of 22 stream-sediment samples were collected at the same time as the soil and rock samples, and portions of the minus 2-millimeter fraction were mixed together to produce 1 sample of stream sediment

representing the whole area immediately surrounding the limits of the known mining district.

The data from the analysis of the composite soil, rock, and sediment samples are presented in table 1. The average composition of background soil was found to be about 21 ppm (parts per million) lead, 100 ppm zinc, and 24 ppm copper. It is evident that the lead, zinc, and copper concentrations in rock are less than that in the soil. The principal cause of this apparent enrichment in soil is not known, but there are several probable reasons. First, the soil samples were all minus 80 mesh and hence contain a higher percentage of fine grains than the soil as a whole, therefore, the heavy-metal content would be higher because the fine-grained material usually contains more copper, lead, and zinc than do the coarser grained parts of the samples. The rocks sampled were those found in roadcuts and outcrops (an attempt was made to get rock as fresh as possible); and these, being in general the more resistant rocks, usually contained less fine-grained material than the average rock in the area. The net result would be to cause the average soil to appear to have more heavy metals than the average rock collected. Second, selective leaching from the rocks of elements other than the heavy metals could cause enrichment. Third, concentration of metal-organic compounds in the soil could help account for the increase in heavy metals.

TABLE 1.—*Normal, or background, content of lead, zinc, and copper in soils, rocks, and stream sediments near the Coeur d'Alene mining area*

Quantitative methods of analysis were used; analysts, H. E. Crowe and Harold Bloom, U.S. Geological Survey]

| Quadrant in which composite sample was collected | Lead (ppm) | | | Zinc (ppm) | | | Copper (ppm) | | |
|--|------------|------|-----------------|------------|------|-----------------|--------------|------|-----------------|
| | Soil | Rock | Stream sediment | Soil | Rock | Stream sediment | Soil | Rock | Stream sediment |
| Northeast..... | 24 | 15 | ----- | 120 | 56 | ----- | 22 | 9 | ----- |
| Northwest..... | 20 | 15 | ----- | 90 | 50 | ----- | 23 | 17 | ----- |
| Southwest..... | 22 | 10 | ----- | 95 | 28 | ----- | 27 | 13 | ----- |
| Southeast..... | 20 | 10 | ----- | 100 | 42 | ----- | 24 | 14 | ----- |
| Average..... | 21 | 12 | 40 | 100 | 44 | 76 | 24 | 13 | 45 |

The table shows that lead and copper are present in stream sediments in amounts greater than in rocks and soil and also that zinc is held in the stream sediments in amounts that are less than that in soil, but more than in the rock. The reasons for this are not known, but it seems probable that difference in particle size is not the entire explanation, for the sediments in general were coarser grained than were the soils.

When soil samples are digested in chemical reagents that are less

vigorous than the nitric-perchloric mixture used to obtain the results in table 1, only an incomplete extraction of the heavy metals can be expected, and the concentrations obtained for normal soils may be less than those listed. Should such an incomplete extraction of a sample indicate a concentration of ore metals that is several times background, a source other than normal bedrock can be safely assumed for the sample. In general, when using the standard field tests, ore-metal concentrations from 2 to 4 times the normal or background concentrations of lead, zinc, and copper given in table 1 probably represent an anomalous condition; and concentrations greater than 4 times background, with a few exceptions, represent definite anomalies.

SOIL SAMPLING NEAR MINERALIZED AREAS

When the present geochemical work was begun in the Coeur d'Alene district, soil samples were collected in 20 mineralized areas to measure the heavy-metal concentrations in soil near veins known to contain at least a small quantity of an ore metal, either at depth or near the surface. At most places the lack of time made it impractical to study the extent of any anomaly beyond the mere proof of its existence or absence. However, from the 20 areas, 2 more or less representative ones were selected for detailed study and analysis. These areas were: (1) near the Little Pittsburg vein in the Pine Creek area close to the west edge of the district; and (2) near the Vindicator vein, in the vicinity of Mullan at the east end of the district (pl. 1). The Little Pittsburg vein, for at least part of its length, crops out as a conspicuous quartz vein containing limonite and secondary lead and zinc minerals. The Vindicator vein is also mainly quartz, but its outcrop is much narrower and not as highly mineralized as the outcrop of the Little Pittsburg vein.

In addition to the studies of lead, zinc, and copper veins in the district, some soil samples were collected over the Golden Chest gold vein near Murray and over the Star Antimony vein in the Pine Creek area. The Golden Chest contains at least one shoot of tungsten ore, and soil samples were collected to determine whether anomalous amounts of tungsten could be detected in soil near this vein.

Details of the soil analyses from the vein localities that were studied are presented on the following pages together with geologic information which might be of value in the interpretation of the analytical results. The descriptions of the studies are grouped according to the major ore metal present in the vein near the surface. Plate 1 is an index map showing the locations of the soil-sampling areas.

VEINS CONTAINING MAINLY LEAD MINERALS NEAR THE SURFACE

Jack Waite vein.—The Jack Waite mine is near the head of Tributary Creek, a branch of the East Fork of Eagle Creek, about 6 miles east-northeast of Murray (pl. 1). Umpleby and Jones (1923, p. 85) state that—

"It is enclosed in Prichard beds at horizons probably between 3,000 and 4,500 feet below the base of the Burke quartzite. The vein strikes N. 55° W. and dips 52° SW., crossing the bedding of the enclosing slates and quartzites, which dip 20°–40° NE. The deposit is a quartz-filled fissure that ranges from a fraction of an inch to 10 feet in width and averages perhaps 4 feet."

The soil samples were collected near the crest of the high ridge marking the Idaho–Montana State line and lying southeast of the main mine entrance. Two short prospecting crosscuts have been driven on the vein in the sampling area, but these have not contaminated the soil beyond the immediate vicinity of the dumps. Vein quartz was found on the dumps in small quantities, but apparently the vein did not contain much ore where these tunnels intersected it.

The location of the soil-sampling sites in relation to the projected outcrop of the Jack Waite vein, is shown on figure 1. The soil samples were analyzed for lead, zinc, and, when the samples were

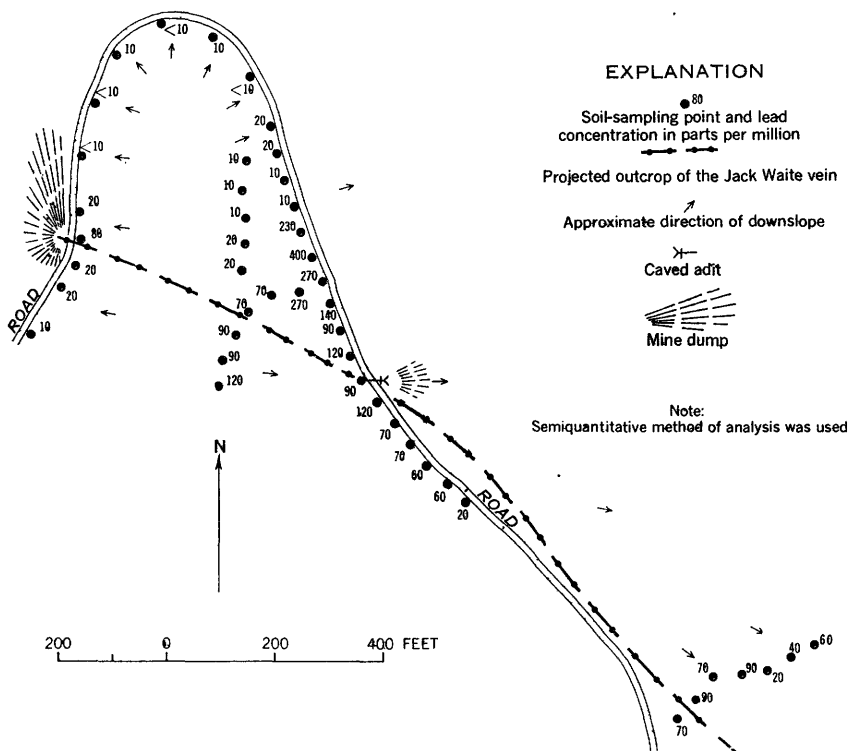


FIGURE 1.—Plan view of soil-sampling traverses near the Jack Waite vein.

high in lead, for copper using the 1:7 HNO_3 method of extraction. (See appendix for detailed description of method.) No samples were found which contained anomalous quantities of zinc or copper; hence, only the lead concentrations are shown on the map.

There are no large clear-cut anomalies associated with the Jack Waite vein in the area sampled. In the vicinity of the vein, the lead content of the soil certainly exceeds the normal background value of 10 to 20 ppm; but, compared to the lead content of soil near other veins in the district, the anomaly is very small. About 150 feet north of the Jack Waite vein on the east side of the ridge crest, a group of soil samples was taken which contains more lead than samples taken near the main vein. These samples may indicate the outcrop of a branch structure in the footwall of the Jack Waite vein.

Hercules vein.—The Hercules vein, according to Ransome and Calkins (1908, p. 115), strikes west-northwest and dips south at a high angle.

The Hercules mine, about $1\frac{3}{4}$ miles north of Burke (pl. 1), has produced large amounts of ore from one main ore shoot that extended to the surface where its strike length was between 400 and 500 feet. The principal metals mined were lead and silver. The position of the ore shoot, now essentially mined out in the upper parts, is marked by a large elongate caved area over the old stopes. The soil sampling was done near the large caved area above the uppermost tunnel of the Hercules mine.

Figure 2 is a sketch map of the sampling area. Lead concentrations in every sample were at least 10 times the normal lead concen-

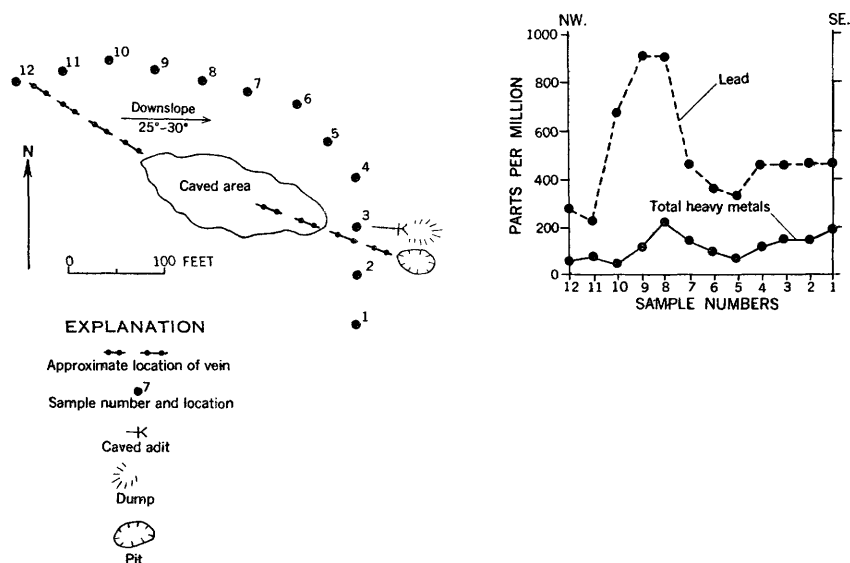


FIGURE 2.—Plan view of soil-sampling traverse, and graph showing concentration of lead and heavy metals in soil near the Hercules vein.

tration in soil; so the sampling traverse was entirely within, or downslope from, the mineralized area. Because the samples were collected so near the mine workings, contamination may have been a factor in the high-lead concentrations found. However, evidence against the likelihood of much contamination is the fact that very little rock was thrown out near the large caved area. Considering the direction of landslope and the vein location, the soil anomalies indicate that there is a mineralized zone in the area rather than one distinct vein. Analyses for zinc and copper showed no definite anomalous concentrations of these elements in the samples collected. Sample extraction was by 1:7 HNO_3 .

On figure 2 it should be noted that the lead concentrations are greater than those of the total heavy metals. This is because of the different sensitivity of dithizone in analyzing for copper, lead, and zinc. To produce a given color change in dithizone, about four times as much lead or twice as much copper is required compared to zinc.

Because the relative proportions of the metals being estimated in the heavy metals test are not known, the total heavy-metals content is arbitrarily expressed as zinc even though the dithizone color obtained during analysis could also be produced by considerably more lead. Thus a sample containing 400 ppm of lead and no zinc or copper would yield a dithizone color equal to that produced by a sample containing only 100 ppm of zinc. A total heavy-metals determination would result in an estimate of 100 ppm of total heavy metals for either sample.

Custer Peak area.—Custer Peak is about 1 mile northwest of Burke (pl. 1). A mineralized zone connecting the Sherman and Tamarack mines is believed to cross high on the south slope of the mountain. Only a little surface prospecting has been done in this area; so the slope is essentially uncontaminated by dump material. However, this mineralized zone has been explored at depth by a drift that connects the Sherman and Tamarack mines and is considered barren insofar as commercial ore is concerned. Figure 3 is a sketch showing the sample points in relation to topography and estimated location of the vein. Also shown are graphs of the lead content of soil samples taken from 2 to 4 inches and 10 to 12 inches below the surface. Soil analyses were made using a 1:1 HNO_3 digestion. Apparently there is a concentration of lead in the soil as high as 100 times background, but neither copper nor zinc anomalies were found in the area. The lead anomalies here are several times as large as those over the Jack Waite vein, and yet there are no known ore bodies within 1,000 feet of the point where the sampling traverse crosses the vein.

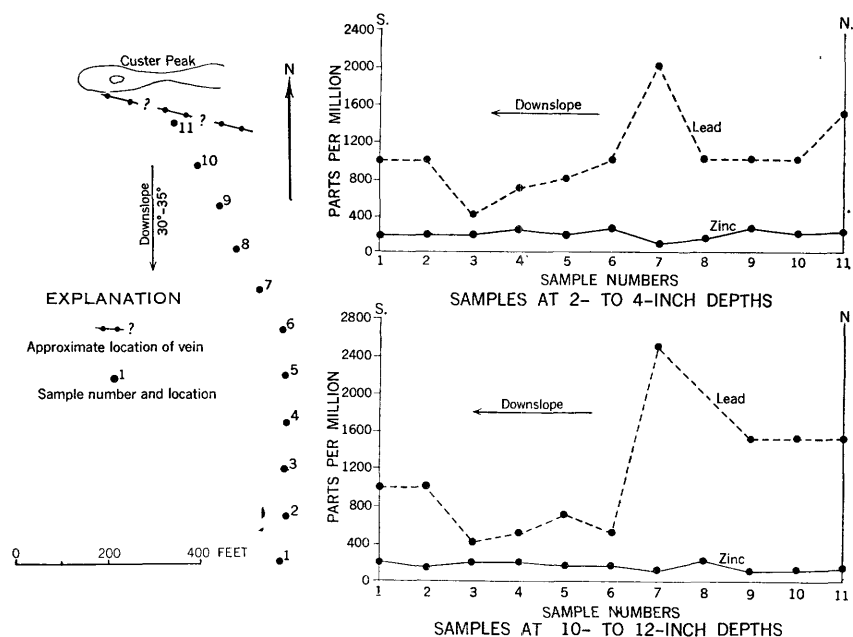


FIGURE 3.—Plan view of soil-sampling traverse, and graphs showing concentration of lead and zinc in soil in the Custer Peak area.

The persistence of the anomalous concentration of lead in the soil downslope from the vein may be caused by several factors. There is very little vegetation on the steep slope below the vein and, as a result, rains cause very rapid downslope movement of soil. The presence of additional veins downslope could add more lead to the soil to produce the effect noted, and evidence for this can be seen in the way in which the lead concentration increases near samples 2 and 7. It is possible that the vein being studied intersects the traverse upslope from sample 7 instead of upslope from sample 11, for the exact vein location is not known. If this is so, however, a source of lead upslope from sample 11 must be assumed.

It may be of interest to calculate the total quantity of lead lying on the slope in the soil. If the lead concentration is assumed to remain constant for 50 feet on both sides of the line of traverse and the soil is about 1 foot thick, the lead in this area would amount to at least 6 tons if the soil contains an average of 0.06 percent lead.

Standard-Mammoth vein.—Two sample traverses were run just east of an area where stoping on the vein had reached the surface about a mile northwest of Mace (pl. 1). Figure 4 shows both the locations where the soil samples were taken and the results of this soil sampling. The Standard-Mammoth vein strikes N. 83° W., dips about 80° N., and is entirely within the Burke formation. The

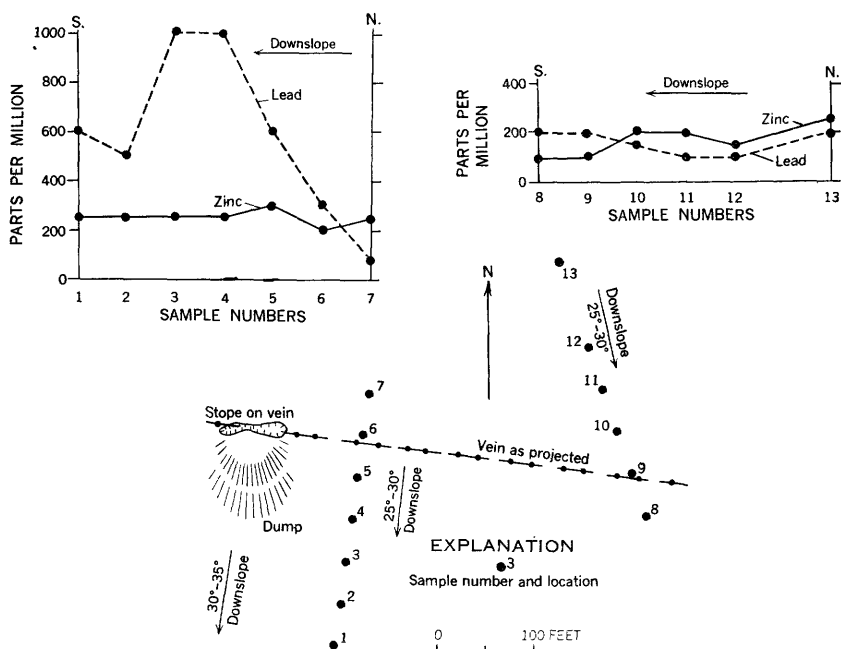


FIGURE 4.—Plan view of soil-sampling traverse, and graphs showing concentration of lead and zinc in soil near the Standard-Mammoth vein.

ore body where mined ranged in width from 5 to 15 feet; the principal ore mineral was galena. Some sphalerite and chalcopyrite were associated with the galena (Ransome and Calkins, 1908, p. 177).

Anomalous quantities of lead were found, but zinc was present in concentrations only slightly in excess of background. All samples were taken within the area of anomalous lead concentration; so the maximum distance downslope at which the presence of the vein was indicated by anomalous quantities of lead in the soil is unknown.

The samples which are highest in lead content are not immediately downslope from the projected vein outcrop. The reasons for this are not known; however, it is possible that the strike of the vein between the stope and the first sample traverse (samples 1 to 7) is not the same as the general strike of the vein—the strike used in projecting the outcrop location. The second traverse was apparently not extended downslope far enough to cross the vein extension. Nevertheless, the presence of anomalous quantities of lead definitely indicates that the area is mineralized.

A 1:1 HNO_3 extraction method was used in analyzing these soil samples.

Frisco mine.—The Frisco mine is on the south side of Canyon Creek near Gem (pl. 1). The Frisco vein is in the Prichard and

Burke formations and consists of stringers of galena and sphalerite enclosing many fragments of quartzite. The ore shoot has been mined for a maximum strike length of 1,000 feet and for a width of 10 to 20 feet (Umpleby and Jones, 1923, p. 101).

Part of the outcrop of the Frisco vein lies near a ridge crest with a comparatively undisturbed hillside downslope to the north. These conditions offered an excellent chance to determine the concentration of lead and zinc in the soil associated with the Frisco vein. Figure 5 shows the results of soil sampling on a traverse crossing the outcrop of the Frisco vein. Lead shows a very large concentration above background although the zinc concentrations are only 3 to 4 times background.

The wide variations in lead and zinc concentrations from one sample to the next are probably due to at least two factors: first, the field tests used (1:7 HNO_3 , the solvent in this test) are accurate to 30 to 50 percent of the amount of the element present; second, the probable inclusion of individual pieces of gossan material in the soil sample can cause erratic results when the sample taken for analysis is small. The change from a low concentration of lead at point 4 (fig. 5) to the high concentration at point 5 is an increase by a factor of 15, which, along with the other high samples downslope, indicates a true increase in concentration. Although zinc concentrations do not show the sharp contrast that lead does, the fact that the average zinc concentration from point 3 onward is higher than that from point 1 to point 3 indicates that there is also a true increase in zinc.

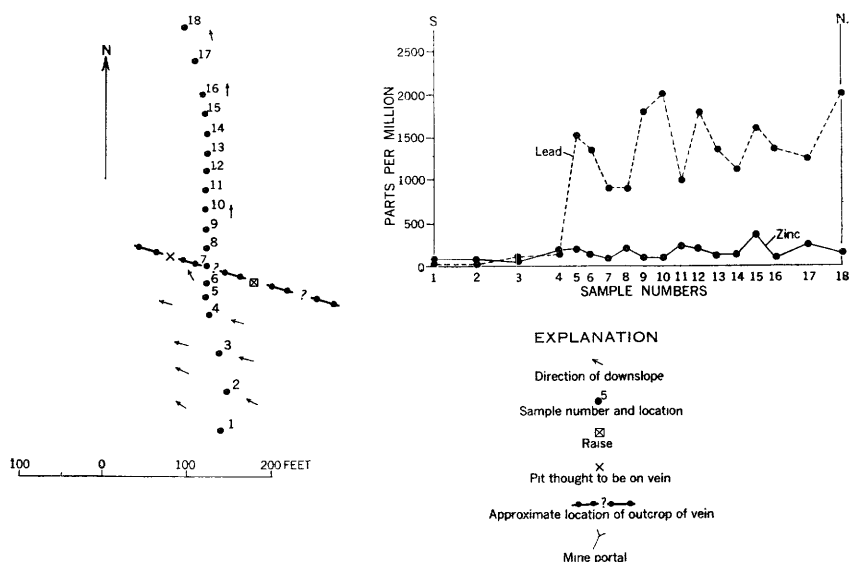


FIGURE 5.—Plan view of soil-sampling traverse, and graph showing the lead and zinc concentration in the soil near the Frisco mine.

The source of lead and zinc between samples 4 and 5 is not near the estimated location of the Frisco vein and must be assumed to be a separate source whose nature is not known.

Star vein.—The Star vein crops out in Grouse Gulch about 2 miles north-northwest of Mullan (pl. 1), where some gossan thrown out from an old prospect pit on the vein contains much cerussite. The ore mined near the surface was predominantly zinc; however, the vein is contributing much more lead than zinc to the soil in the area studied, and it is therefore assumed that the vein contains more lead than zinc at the grass roots. For this study, the vein has been grouped with those having a high concentration of lead.

A series of soil samples was collected beginning about 500 feet upslope from the vein location as projected from the cerussite pit and continuing at about 100-foot intervals to a point about 400 feet downslope from the vein. The traverse was stopped at the edge of an area greatly disturbed by prospecting and bulldozing. Figure 6 shows the location of the sample points and a graph of the concentrations of lead and zinc in the soil.

Although the soil contained anomalous amounts of lead for 500 feet upslope from the vein, the position of the vein was easily located by the sharp increase in lead concentration in the soil just downslope from the vein. Zinc concentrations appeared to increase slightly in the vicinity of, and downslope from, the projected vein outcrop. An additional source of lead and zinc must be present upslope from sample point 2 (fig. 6).

A 1:7 HNO_3 extraction was used in obtaining the lead and zinc concentrations shown.

Gold Hunter vein.—The Gold Hunter mine is in Gold Hunter Gulch about a mile northeast of Mullan (pl. 1). The ore body, now mined out, consisted of a zone of veins and veinlets at least 70 feet wide. The zone strikes N. 75° W. and dips 80° or more to the south (Ransome and Calkins, 1908, p. 169, 170). The ore in the upper part of the vein was valuable mainly for its lead and silver, but some copper, antimony, and zinc were present.

The soil-sampling traverse intersected the vein at a high angle about 150 feet west of the west edge of the glory hole on the vein. No evidence of mining activity was seen beyond a few feet from the glory hole, and it seems probable that contamination of soil samples due to mining activity is negligible. Figure 7 shows the locations of sample points and a graph of the concentrations of lead and zinc in the soil.

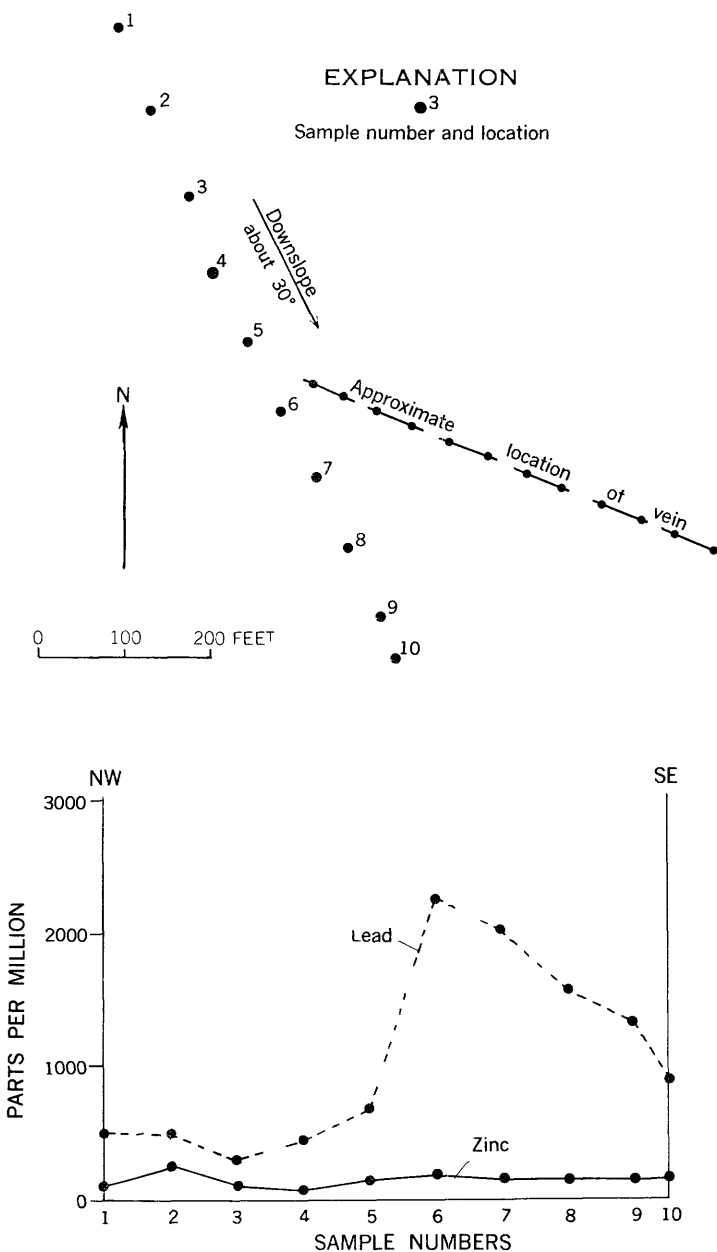


FIGURE 6.—Plan view of soil-sampling traverse and a graph showing the lead and zinc concentrations in the soil near the Star vein.

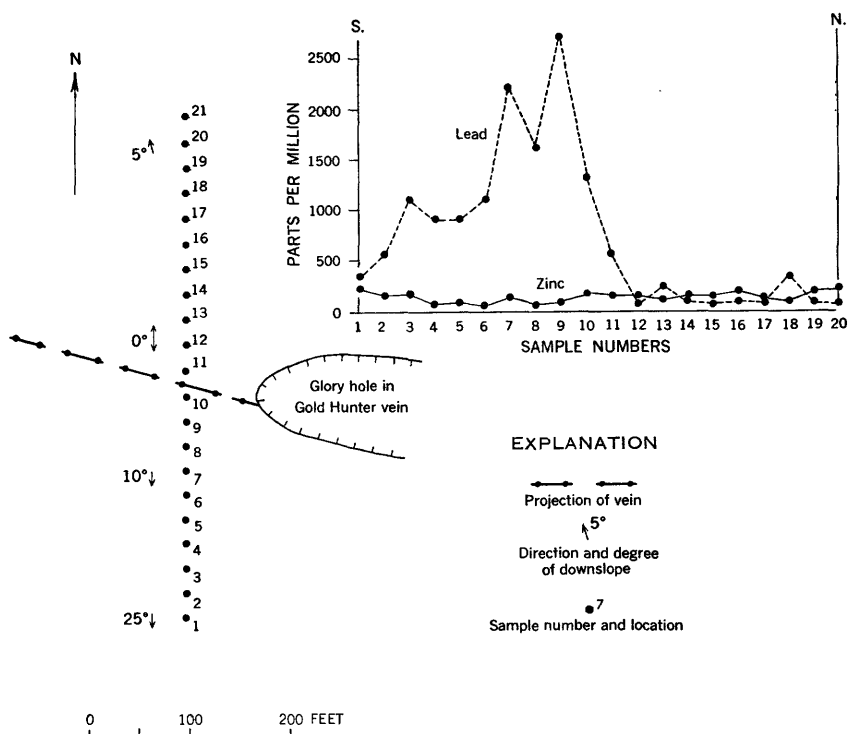


FIGURE 7.—Plan view of soil-sampling traverse and a graph showing concentration of lead and zinc in the soil, Gold Hunter vein.

The concentration of lead in soil near the vein shows great contrast with background, but the concentrations of zinc and copper do not increase. The sharp increase in lead concentration between samples 11 and 12 suggest that the northern boundary of the mineralized zone lies between these two sample points. The southern boundary cannot be detected because of the movement of vein material downslope. Anomalous concentrations of lead in soil extend downslope for a distance of at least 450 feet from the known mineralized zone, and probably extend farther, but bulldozing operations downslope from the location of sample 1 have so disturbed the natural soil distribution that sample data would be meaningless.

In addition to analyzing soil samples for lead, zinc, and copper, analyses were also made for silver and antimony on samples 8 through 10. The silver concentration in these three samples was about 1.0 ppm, and the antimony about 3 ppm. This represents a concentration factor over background of about 10 for silver and 6 for antimony.

The lead, zinc, and copper analyses were made using a 1:7 HNO_3 digestion.

Vindicator vein.—The Vindicator vein crops out on the steep hill slope that bounds the north side of the valley of the South Fork of the Coeur d'Alene River about 1.2 miles east-northeast of Mullan (pl. 1). The vein strikes almost due west and dips about 60° north. A series of shallow prospect pits marks the outcrop, and 2 crosscuts have been driven to the vein; 1 about 100 feet below the outcrop, and 1 slightly above the level of the river at about 380 feet below the outcrop. The main ore mineral is galena which is in a quartz gangue with small amounts of chalcopyrite and sphalerite. Some silver also is present in the ore.

A detailed study was made not only of the soil in the vicinity of the vein but also of the soil in the area to the north and east of the vein. All soil samples were analyzed for both lead and zinc using a 1:1 HNO₃ digestion, and a few samples near the Vindicator vein were analyzed for copper. Plates 2 and 3 show the area studied, the location of the sample points, and the concentrations of lead and zinc in the soil.

This area was one of two selected for special attention because they presented conditions favorable to a systematic detailed study of the behavior of ore metals in soil. At the Vindicator mine, the location of the outcrop is well defined, the character of the mineralization is known, the soil cover is relatively undisturbed, and the metal content of the vein is rather low. At the other area studied in detail, that near the Little Pittsburg vein, to be described later, the conditions are similar to those at the Vindicator except that the known metal content of the vein is relatively high. Originally, the soil sampling at the Vindicator was intended to cover only the area near the vein; however, in extending the sampling traverses to the north into supposedly nonmineralized country, a second area of soil anomalies was found. After the soil sampling was complete, it was apparent that the area northeast of the Vindicator vein for an unknown distance was covered with soil that contained above-average quantities of lead and zinc. The task of thoroughly outlining the extent of this large anomalous area was beyond the scope of this study.

The concentration of lead in soils as plotted on plate 2 and that of zinc as plotted on plate 3 shows a marked alinement of anomalous soils in a nearly east-west direction along the Vindicator vein and a second less well defined alinement of anomalous soils along a N. 65° W. trend about 600 feet northeast from the east end of the main Vindicator vein. The trend of the N. 65° W. anomaly is in accordance with the strike of a few veinlets found in one of the bulldozed trenches cut into the northeastern part of the mapped area (Robert E. Wallace, oral communication, 1952). It also aligns with some

fracture zones found in the lower Vindicator crosscut north of its intersection with the Vindicator vein.

The fact that small but widespread anomalies in lead and zinc are in the soil over the entire northeastern part of the mapped area suggests that the metals are probably contributed to the soil by many small veinlets scattered over a rather wide area instead of by a single large vein.

Samples were taken along several traverses extending downslope across the Vindicator vein to determine the maximum distance from the vein at which anomalous quantities of lead and zinc could be detected in the soil. Three traverses were extended downslope from the vein for a distance of 500 or more feet, but all cut disturbed and possibly contaminated areas before soils containing background concentrations of lead were found. Zinc concentrations, however, decreased rapidly below the vein, so that soils within 50 to 100 feet downslope from the vein outcrop apparently contained only background amounts of zinc. Lead anomalies could be detected much farther downslope than zinc anomalies probably because the soil over the vein contains lead in quantities 20 to 30 times background, whereas the zinc concentrations are only about 3 times background. After the main vein had been located by the cross traverses and by examination of the prospect pits, a second series of samples was collected along a line 10 to 20 feet downslope from and parallel to the vein outcrop to determine the variations in lead and zinc along the strike of the vein. As expected, the results showed higher concentrations of lead and zinc downslope from areas where the prospectors had found lead, zinc, and copper in the vein and comparatively low lead and zinc concentrations below where the vein material appeared barren.

The effects on analytical results of the depth of the sample and of slight changes in sample location were tested by making three closely spaced traverses downslope across the Vindicator vein. The traverses were spaced 2 feet apart, and samples were collected near the surface and at a depth of 10 to 14 inches at each sample point. Samples were taken at 5-foot intervals along the traverses from a point 50 feet upslope from the vein to a point 50 feet downslope from it and also at points 60, 70, 90, and 110 feet downslope from the vein. A plan view of the sample locations and graphs of the analytical results are presented in figure 8. All traverses, both near the surface and at the 12- to 14-inch depth, show the same general pattern, although the analytical results do not show a smooth curve. Some of this variation from a smooth curve may be due to the semiquantitative nature of the field tests; the rest of the deviation may be due to the presence of small veinlets in the wallrock of the main Vindicator vein. The samples taken at about 12-inch

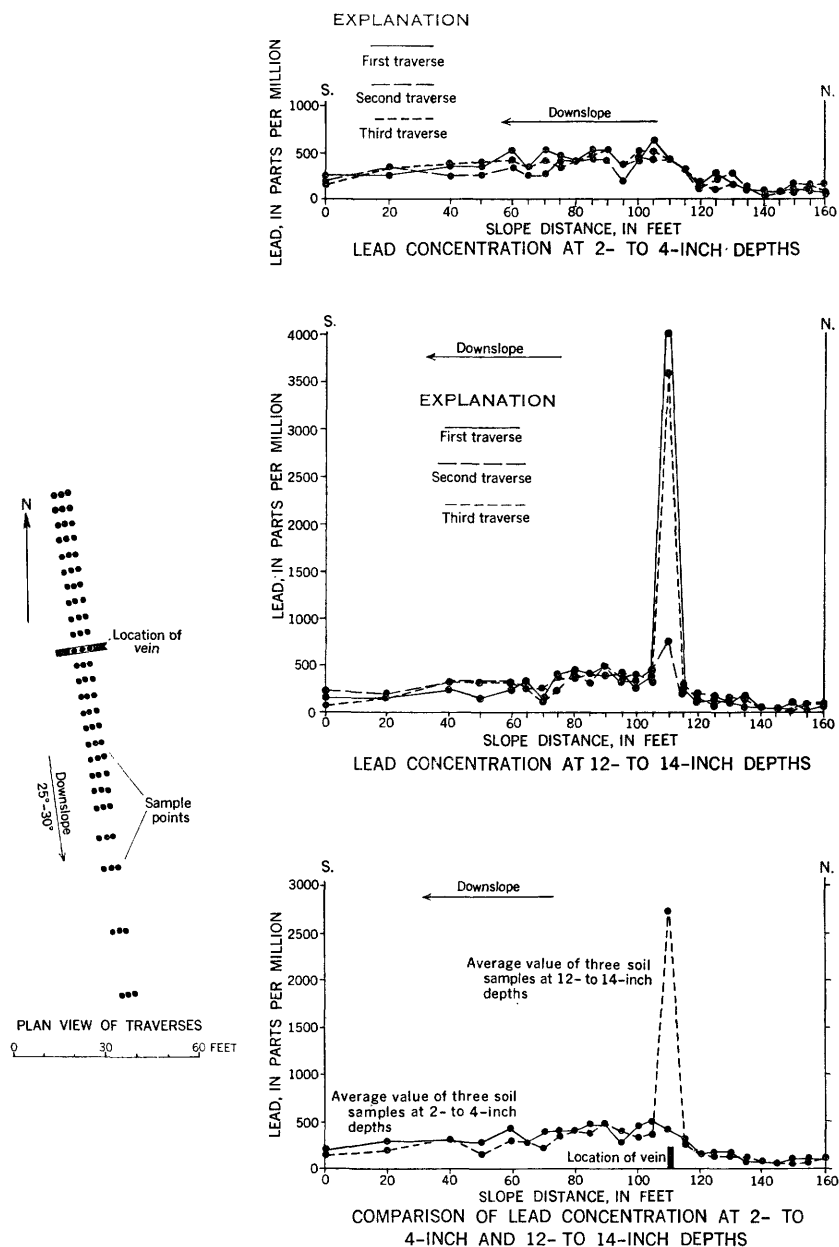


FIGURE 8.—Plan view of three closely spaced soil-sampling traverses, and graphs showing comparison of lead concentration in the soil at 2- to 4-inch and 12- to 14-inch depths, Vindicator vein.

depth show a much larger anomaly at the vein outcrop than do those taken at the surface. This is probably due to the greater dilution of vein material in the upper soil horizons as normal soils move downslope across the vein.

An analysis of the detailed sampling shows two facts that require explanation. The first is an unusual quantity of lead present in the soil upslope from the outcrop of the Vindicator vein; this fact may be explained by the presence of mineral-bearing veinlets in the wall-rock adjacent to the vein. The second is the fact that downslope from the outcrop the lead content of a soil sample taken at a 12-inch depth is about the same as the lead content at the surface. Ideally, the soil creeping downslope from a single source of metal should have a higher concentration in its upper part because the lower soil horizons are diluted by material derived from the adjacent country rock containing only background values. Again the explanation may be the presence of metal-bearing veinlets in the wallrock to the side of the main vein; however, thorough vertical mixing would also produce the effect noted.

In summary, the soil sampling at the Vindicator shows that it is possible to find slightly mineralized veins—particularly lead-bearing ones—and to detect the cumulative effects of many small veinlets which are contributing heavy metals to the soil over a broad zone. In addition, the depth in the soil from which the sample is collected is apparently not critical in this area.

Sidney vein.—The Sidney vein is about 4 miles south-southwest of Smelterville (pl. 1). The vein strikes about due west and crops out in a line running almost directly upslope eastward from the valley of Denver Creek. In the upper levels of the mine, the ores were mainly oxidized lead and silver minerals. Several levels were driven on the vein above the bottom of the valley, but near the ridge crest, between Denver Creek and Red Cloud Creek, the projected outcrop of the vein is comparatively undisturbed. In recent years bulldozer cuts have been made on both sides of the ridge within a few hundred feet of the crest and the Sidney vein outcrop in the two cuts has been approximately located.

A series of six soil samples, spaced 20 feet apart on traverse, were collected along the upper side of the bulldozer cuts on each side of the ridge crest. Because the bulldozer cuts were made along the contour line and the strike of the vein was almost directly downslope, the line of outcrop of the vein was very nearly at right angles to the line of samples.

The analytical results from the soils collected are shown on figure 9. No anomalous quantities of zinc were found in the soil, but the lead concentrations increased to about 45 times background.

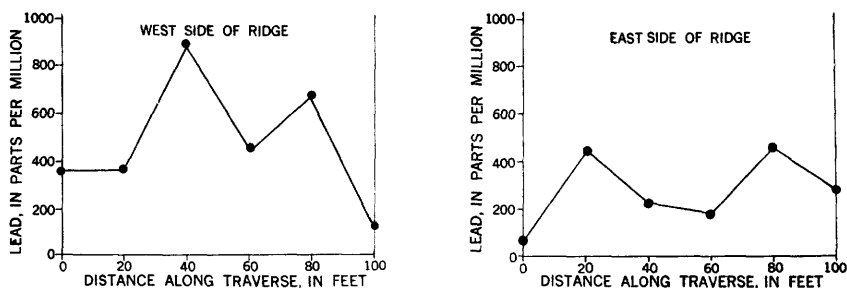


FIGURE 9.—Graphs showing lead concentration in the soil near the Sidney vein.

Apparently the traverses were not of sufficient length to extend beyond the area of high concentration of lead in the soils near the outcrop of the Sidney vein, for none of the samples collected contained less than 3 times the normal concentration of lead in soil.

A 1:7 HNO_3 method of digestion was used in making the analyses.

Little Pittsburg vein.—The Little Pittsburg vein crops out on the west side of Denver Creek about 4 miles south-southwest of Smelterville (pl. 1). The strike of the vein changes gradually from slightly west of north to northwest as it is followed northward. The dip to the southwest changes from about 70° near the surface to 50° or less at depth.

A detailed study of the Little Pittsburg area was made to obtain a better understanding of the behavior of lead and zinc in soil around a vein which contains considerable lead and zinc. Although several prospect pits mark the course of the vein on the surface, large areas of the soil cover are undisturbed, and the samples collected are believed to be uncontaminated. The data resulting from a general heavy-metals test, a zinc test, and a lead test on each sample are shown on plates 4–6. These data are presented in a somewhat different manner from that used at the Vindicator property because the range of lead-zinc concentration is much greater.

Plate 4 shows the results of the general heavy-metals test at the Little Pittsburg mine and is essentially a summary of plates 5 and 6 which show lead and zinc concentrations. Copper concentrations 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 because of different sensitivity of dithizone for different elements, the figure for total heavy metals in parts per million approximately represents the sum of all the zinc, one-half the copper, and one-fourth the lead.

The outcrop of the Little Pittsburg vein, as projected from the underground workings, is shown on plates 4–6. Moderately good correlation of the projected position 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 intensity of mineralization varies along the vein at the surface, for 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 in the area between the two drifts on level 4. This fact is consistent with the small amounts of lead and zinc in the soil at the outcrop of this part of the vein. To the northwest of this barren area the major ore shoot extends toward the surface, but ends at least 300 feet 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 anomalies found during the soil sampling are not explained by the position of the Little Pittsburg vein. The anomaly in lead, zinc, and heavy metals at point *E* (pls. 4-6) cannot be related to an upward extension of the Little Pittsburg vein, and there is a series of unexplained anomalies about 150 feet to the east of the projected outcrop of the Little Pittsburg vein (points *A*, *B*, and *I*). The anomalies are slight to the north of point *I*, but at points *A* and *B* they are very pronounced. The anomalous amounts of lead at point *N* may be part of this same parallel zone. If the mineralized zone diverges from the Little Pittsburg vein, then points *J*, *K*, *L*, and *M* may mark its extension. Some sampling at depths of 12 to 18 inches was done on the east-west traverses lying just south of points *A* and *B*, and a trench about 100 feet long was dug along the traverse near *A*. The analytical results from soil, rock, and vein samples are presented in figures 10 and 11.

A junction of the projection of the mineralized zone lying east of the Little Pittsburg vein with the southeastern end of level 5 (pls. 4-6) apparently was not detected during mining activity; but, if the zone does cross level 5, it would be difficult to find because level 5 follows the slightly mineralized Crystallite fault for about 300 feet in this area. Several holes were drilled from the Little Pittsburg mine into the area underlying the anomalous soil samples to the east of the Little Pittsburg vein. These holes found no commercial mineralization.

As there appeared to be a mineralized zone to the east of, and approximately parallel to, the Little Pittsburg vein, an effort was made to determine whether the anomaly at point *E* (pls. 4-6) lay 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 *C* and *E* was made to intersect this zone, if present, and additional samples were taken to the north and west of point *E*.

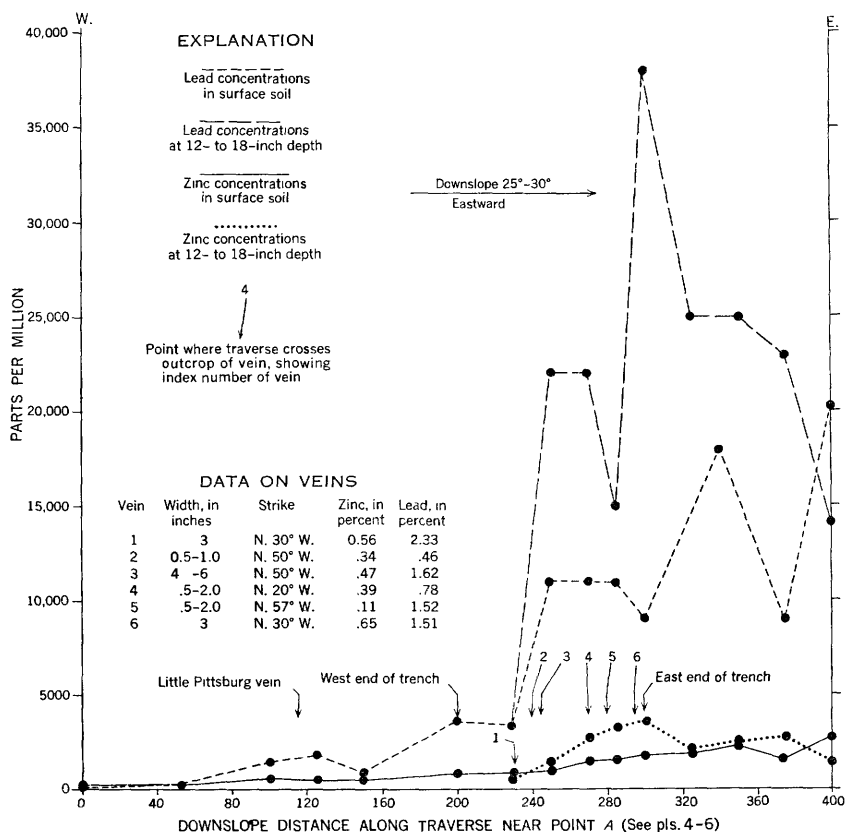


FIGURE 10.—Graph showing concentration of lead and zinc in soil south of point A, Little Pittsburg area.

for the same reason. At point *C* a slight anomaly in zinc and lead was detected, but no connection with the anomaly at point *E* was established. The high concentrations of lead and zinc immediately to the south and east of point *E* can be explained by soil movement downslope from point *E*, but the anomaly in the area lying about 75 feet northwest of point *E* could not be explained on this basis. Therefore, a northwest strike was indicated for the mineralized zone. On the basis of this information a trench 15 feet long was dug to bedrock—about 18 inches below the surface—and a search was made for gossan material at the point where geochemical evidence suggested mineralization. As a result of the trenching, a gossan zone about 3 inches wide was found trending N. 65° W. An assay of the gossan material by D. L. Skinner, of the U.S. Geological Survey, showed 17.26 ounces of silver to the ton. An estimate of the lead content by assay was 45 percent. The gossan contained little or no quartz and crumbled easily. Hence, very little float material from

the vein was seen at the ground surface. The slight anomaly at point *G* is in line with the anomalies near point *E*, but the mineralization has been so slight, if present between *G* and *E*, that it would be difficult to prove a connection between the two points.

A series of closely spaced soil samples was collected on a short traverse across the vein discovered near point *E*. The results are presented in figure 12. Apparently the vein material travels downslope about 4 feet before working its way up to the surface.

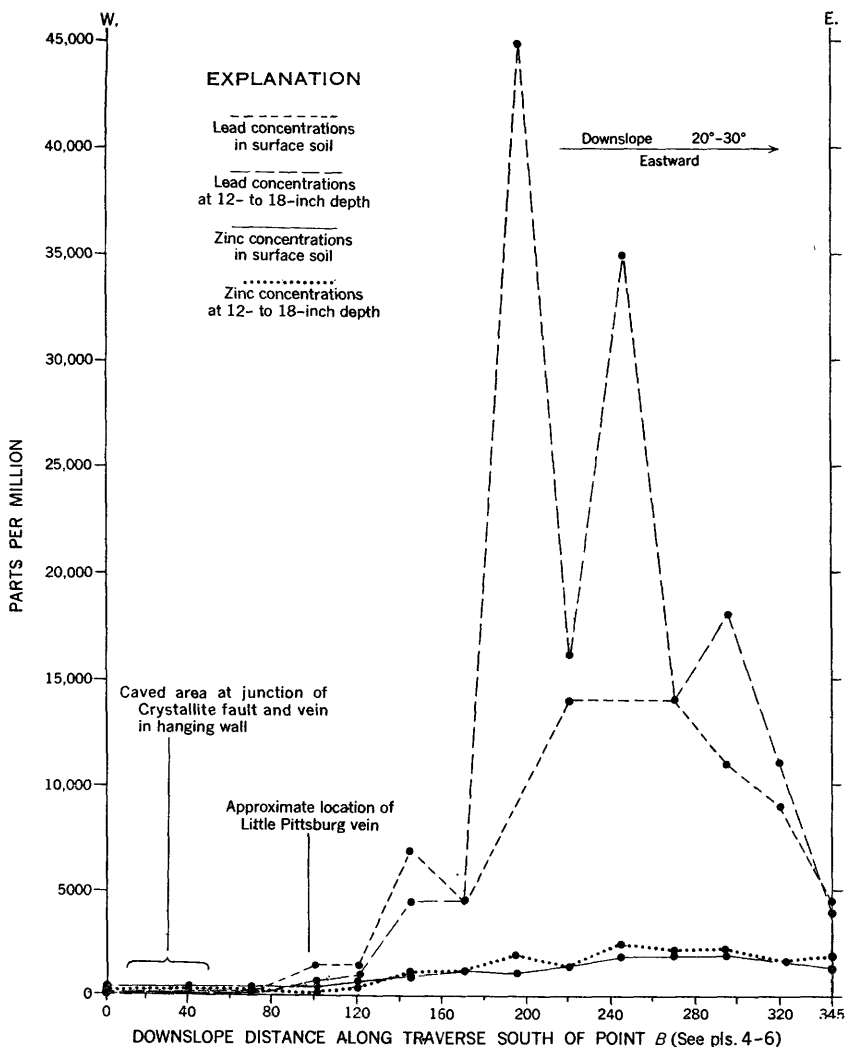


FIGURE 11.—Graph showing concentration of lead and zinc in soil south of point *B*, Little Pittsburg area.

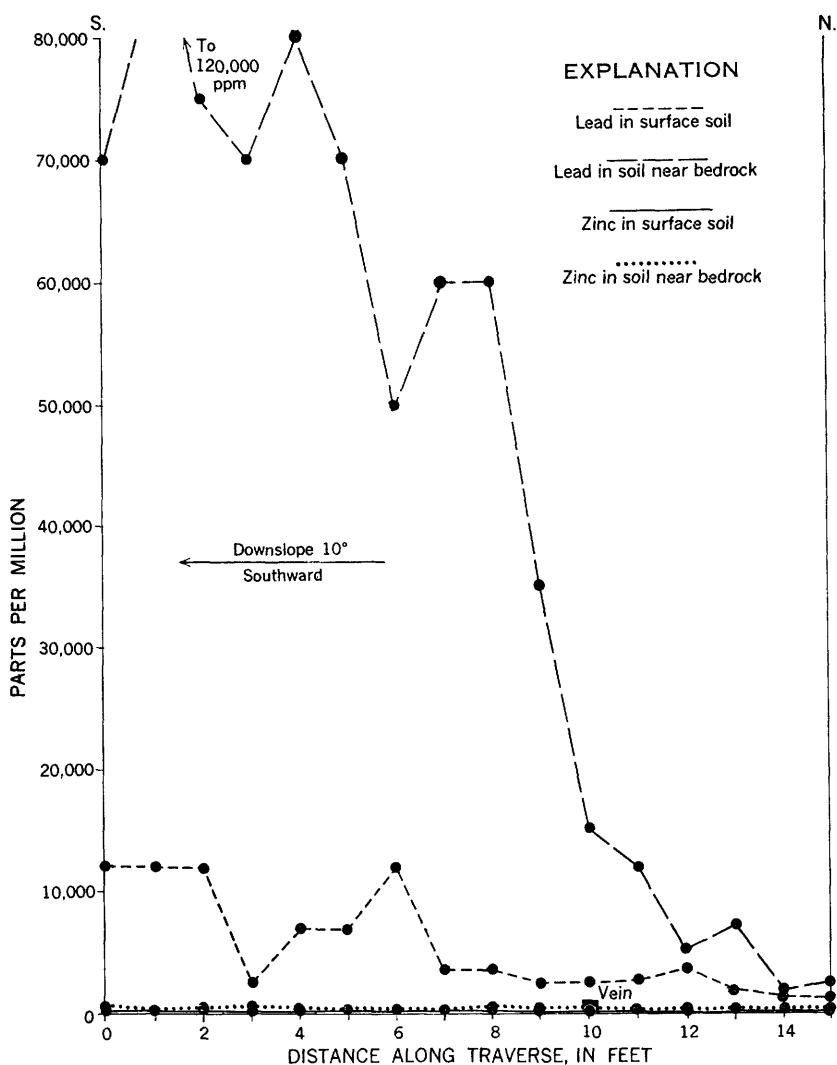


FIGURE 12.—Graph showing concentration of lead and zinc in soil across a vein located 35 feet northwest of point *E* (pls. 4-6), Little Pittsburg area.

A vein in the hanging wall rises almost vertically from the level 4 of the Little Pittsburg vein in the area to the southeast of point *E*. The approximate length and position of this ore shoot is indicated by the short section of level 4. Point *D* is just east of a stope which has broken through to the surface on this vein. If the vein in the hanging wall undergoes an abrupt change in strike, it may account for the anomaly at point *E*, but detailed work would be necessary to establish this. Two faults, paralleling the Crystallite fault and exposed on level 5, lie about 70 and 120 feet, respectively, northeast of

the Crystallite fault. The anomaly at point *E* may be the outcrop of one of these mineralized faults, but again there is no way of checking this other than by considerable surface or underground work. The overall aspect of lead-zinc distribution in the Little Pittsburg area suggests that there are just two main mineralized zones. One of these, with a north-northwest trend, included the Little Pittsburg vein and subparallel structures discovered by geochemical work. The other zone is approximately parallel to the Crystalline fault and trends northwest. The junction of these two trends is indicated by the large lead-zinc anomalies at, and just west of, points *A* and *B*. It is probable that the lead and zinc near points *C*, *E*, and *G*, part of the lead and zinc near points *A* and *B*, and the zinc at point *H* are related to the northwest-trending zone associated with the Crystallite fault. The rest of the lead-zinc mineralization is probably related to the north-northwest-trending zone.

The most pronounced anomalies near the Little Pittsburg vein are in lead. Zinc shows the smallest percentage increase over background, and the results of a heavy-metals test occupies an intermediate position in percentage increase.

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. Mr. Claude E. Nugent, of the Denver Development Co., 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.

A study of the movement of heavy metals from point *E* was attempted by sampling between points *F* and *E* and by sampling the material in the dry stream bed below point *F*. The anomaly can be detected by lead tests at a distance of 200 to 300 feet from the source, but the zinc and heavy-metals tests do not permit tracing the anomaly so far. This is undoubtedly because of the much higher quantity of lead present at the source.

The relation between size of soil particles and intensity of geochemical anomalies was investigated briefly. A beginning was made on the problem of which size fraction should be analyzed to give the greatest anomaly near lead, zinc, or copper deposits. One sample

representing "local background,"¹ and two samples representing high lead and zinc content were chosen from the vicinity of the Little Pittsburg vein and sieved into seven size fractions. These fractions were analyzed for lead and zinc by using quantitative methods, and the results are shown in table 2. Similarly, three samples were sized and analyzed for copper. No great difference was found in the metal content of different size fractions from the same sample. In practice, the material passing an 80-mesh screen is recommended for general prospecting because the use of a fine-size fraction probably decreases sampling errors.

TABLE 2.—*Relationship of zinc, lead, and copper content to particle size in soils, Little Pittsburg area*

Analyses were made by quantitative methods, H. E. Crowe and Harold Bloom, U.S. Geological Survey, analysts]

| Sieve diameter of soil particles (mm) | Composition (ppm) | | | Ratio | |
|---------------------------------------|--------------------------|-------------------------|--------------|-----------------------------------|-----------------------------------|
| | Local back-ground sample | Anomalous metal content | | Sample No. 1 to local back-ground | Sample No. 2 to local back-ground |
| | | Sample No. 1 | Sample No. 2 | | |
| Zinc | | | | | |
| <0.061----- | 210 | 800 | 1,230 | 3.8 | 5.9 |
| 0.061-0.117----- | 200 | 770 | 1,230 | 3.8 | 6.2 |
| 0.117-0.234----- | 200 | 780 | 1,230 | 3.9 | 6.2 |
| 0.234-0.447----- | 200 | 750 | 1,160 | 3.7 | 5.8 |
| 0.447-0.98----- | 190 | 720 | 1,060 | 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 | | | | | |
| <0.061----- | 40 | 1,200 | 670 | 30.0 | 17.0 |
| 0.061-0.117----- | 40 | 1,850 | 750 | 46.0 | 19.0 |
| 0.117-0.234----- | 60 | 2,150 | 750 | 36.0 | 13.0 |
| 0.234-0.447----- | 70 | 1,830 | 690 | 26.0 | 9.9 |
| 0.447-0.98----- | 40 | 1,260 | 550 | 31.0 | 14.0 |
| 0.98-1.90----- | 30 | 970 | 470 | 32.0 | 16.0 |
| 1.90-4.04----- | 30 | 680 | 420 | 23.0 | 14.0 |
| Copper | | | | | |
| <0.061----- | 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 |

VEINS CONTAINING MAINLY ZINC MINERALS

"Carbonate" vein.—During the bulldozing in Grouse Gulch, about 2 miles north-northwest of Mullan (pl. 1), a zone in the soil was

¹ The term "local background" is used to mean the normal concentration of an element within a restricted area as compared to that for the Coeur d'Alene district as a whole. The concentrations of heavy metals in the local background samples in the Little Pittsburg area are higher than that for the rocks surrounding the Coeur d'Alene district.

uncovered which contained gossan material of a type characteristic of the siderite veins in the area. Some of the gossan material was sampled and contained approximately 30,000 ppm zinc by field test. This mineralized area is about 620 feet N. 58° E. of the portal to the Grouse tunnel. The vein is not named, but for the sake of convenience, it is referred to as the "carbonate" vein in this report.

The vein strikes approximately N. 75° W., and the outcrop extends directly upslope from the bulldozer cut. Soil samples were taken at 10-foot intervals on a traverse which intersects the vein at a high angle; analytical results are presented graphically in figure 13. Small amounts of lead are present near the vein, but zinc is the element showing the greatest contrast with background. No increase in copper was found. A 1:7 HNO_3 digestion was used.

Liberal King vein.—The Liberal King vein crops out high on a southwest-facing slope about 2.5 miles south-southeast of Pinehurst (pl. 1). The vein material, where seen at the surface, consists of quartz, with vugs containing limonite. Underground, according to Umpleby and Jones (1923, p. 108), much of the vein contains small amounts of pyrite, sphalerite, chalcopyrite, and galena, named in order of their abundance. Some stoping has been done on the vein since Umpleby and Jones' work, but most of this has been 1,000 to 1,500 feet below the outcrop.

Soil samples were taken on a traverse across the vein outcrop, but no anomalous concentrations of lead or zinc were found.

Curlew vein near the Page mine.—The Page mine is about one-third of a mile south-southeast of the town of page (pl. 1). A series of soil samples was collected at 50-foot intervals along the east side of the ridge which lies just east of the Page mine buildings. This traverse was laid out across the projected position of the Curlew vein and was extended to the north in an effort to find the outcrop

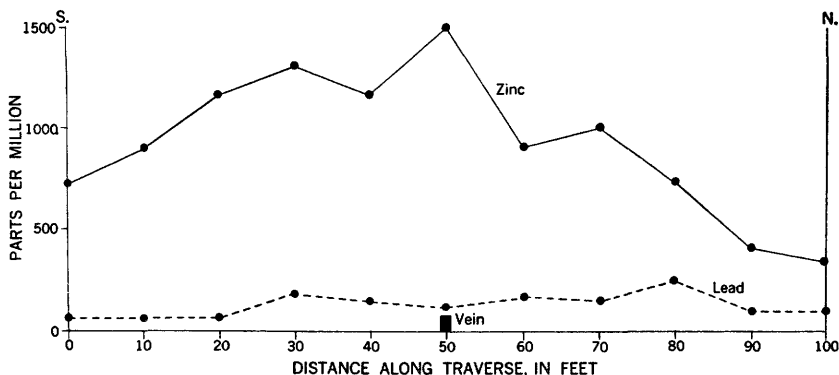


FIGURE 13.—Graph showing concentration of lead and zinc in soil near the "carbonate" vein in Grouse Gulch near Mullan.

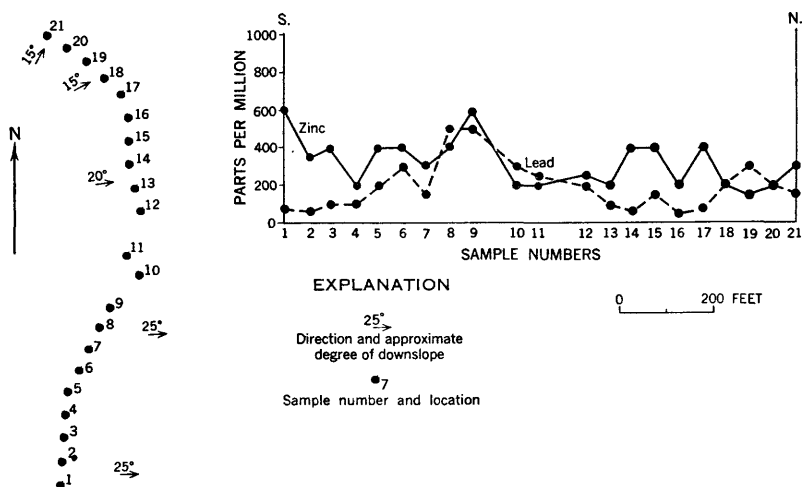


FIGURE 14.—Plan view of soil-sampling traverses and a graph showing the lead and zinc concentration in the soil, Curlew vein near the Page mine.

of the mineralized zone believed to parallel the Curlew vein. The results of this traverse are presented graphically in figure 14. The exact location of the outcrop of the Curlew vein in the sampling area is not known, but it probably lies between sample points 5 and 7. All soil samples contained at least 2 to 3 times the normal concentration of zinc and lead. The dissemination of metals from fumes of the nearby Sullivan lead and zinc smelter probably accounts for the overall high background of lead and zinc; Frank C. Canney's work (written communication, 1956) indicates that lead and zinc contamination is widespread within several miles of the smelter. However, the anomalies of 200 to 500 ppm lead may reflect an increase in the amount of lead in the soil due to underlying rock conditions, if smelter contamination is rather evenly distributed over the area sampled. Correlation between lead and zinc anomalies near sample point 9 (fig. 14) is good, but the reason for the lack of correlation near sample points 1 and 14 is not known.

VEINS CONTAINING COPPER MINERALS

Missoula tunnel copper zone.—The portal of the Missoula tunnel is about 2.5 miles northeast of the town of Mullan, near the head of the east branch of Deadman Gulch (pl. 1). According to Ben Bowyer (written communication, 1952) there are four shear zones in the tunnel which have been replaced by quartz containing some copper and lead minerals. These zones cross the tunnel 200 feet, 680 feet, 1,320 feet, and 2,290 feet from the portal; the one at 1,320 feet contains the most copper and lead. All the veins strike northwest and dip 70° to 80° SW.

The quartz vein which is 680 feet from the portal can be located on the surface, and the soil samples collected were taken near the outcrop of this vein. Figure 15 shows a plan view of the soil sample points in relation to the known vein.

Soil samples were collected along two traverses. One traverse consisted of 6 samples spaced at 5-foot intervals downslope from the outcrop of a zone containing disseminated malachite (fig. 15, samples 1-6). This mineralized zone is not a quartz vein, but is very near the area where a projection of the quartz vein would crop out. The material thrown from a small prospect pit about 50 feet to the northwest of sample point 6 contains malachite-stained quartz, and this is interpreted to mean that the mineralized zone at sample point 6 is associated with an upward extension of the quartz vein found in the tunnel 680 feet from the entrance.

All soil samples taken along this first traverse contained copper concentrations in the range 120 to 200 ppm by field test. The traverse was not continued downslope more than 25 feet because of the presence of a footpath and streambed.

Samples 7 through 18 (fig. 15) were collected in an attempt to cross the quartz vein in an area where the movement of copper downslope could be better studied. The sample collected at point 18 contained 40 ppm copper by field test and all other samples had copper concentrations of 10 to 20 ppm copper. No further work was done in the area. All samples were analyzed using a 1:7 HNO₃ digestion.

Gentle Annie copper zone.—During bulldozer operations by the Bunker Hill Co., a shear zone in bedrock containing small

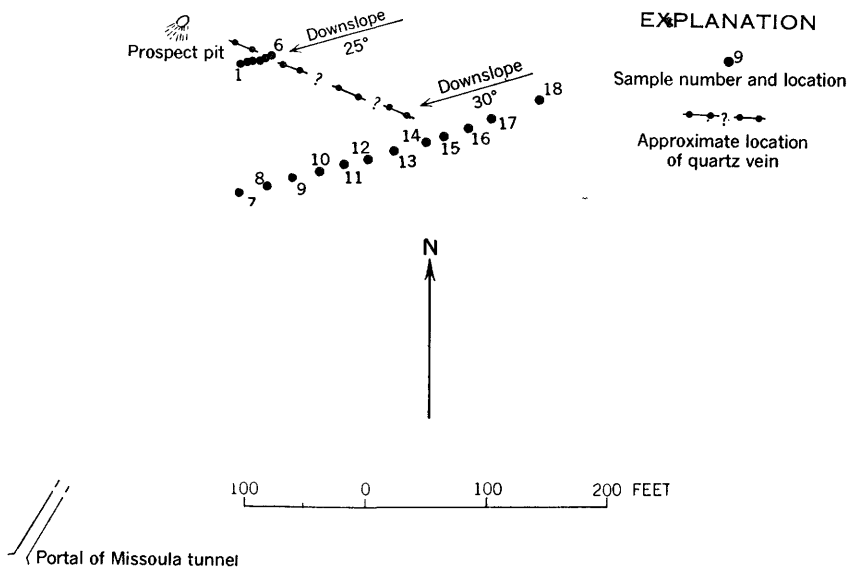


FIGURE 15.—Plan view of soil sampling traverses near the Missoula tunnel.

quantities of disseminated malachite was uncovered about 730 feet N. 82° E. of the portal of the Snowshoe mine. The area is near the head of Gentle Annie Gulch and lies about 2.5 miles northeast of the town of Mullan (pl. 1).

Ten soil samples were taken near the mineralized zone to determine the intensity of the copper anomaly in the soil. A sketch showing the sample points and the copper concentrations in soil is presented in figure 16. Although the copper anomaly present in the soil near this slightly mineralized zone is not large, the copper concentrations are great enough that they can be easily detected. A 1:7 HNO₃ digestion was used.

Snowstorm copper mine.—The Snowstorm mine, the only copper property in the northeastern part of the district which has produced much ore, is about 3 miles east-northeast of the town of Mullan near the head of Daisy Gulch (pl. 1). The ore minerals, principally bornite, chalcocite, chalcopyrite, and tetrahedrite in the unoxidized ore, and malachite where the ore is oxidized, are disseminated through a bed about 40 feet thick in the Revett quartzite. The strike of the ore zone is N. 60° W. and dip 65° SW. (Umpleby and Jones, 1923, p. 116).

Soil samples were taken downslope across the projected outcrop of the copper zone at a point a few hundred feet north-northeast of the uppermost portal of the Snowstorm. A plan view of the sample locations showing their approximate relation to the outcrop of the Snowstorm zone is presented in figure 17. The copper concentrations in soil indicate that the mineralized zone probably crosses south of sample point 3. The maximum copper anomaly in soil associated with the Snowstorm copper zone is 180 ppm, but evidence of the zone is shown by slight concentrations of copper for more than 150 feet downslope.

Hansy copper mine.—The Hansy copper mine is 1.5 miles southeast of the town of Adair (pl. 1), on Olentang Creek about a mile

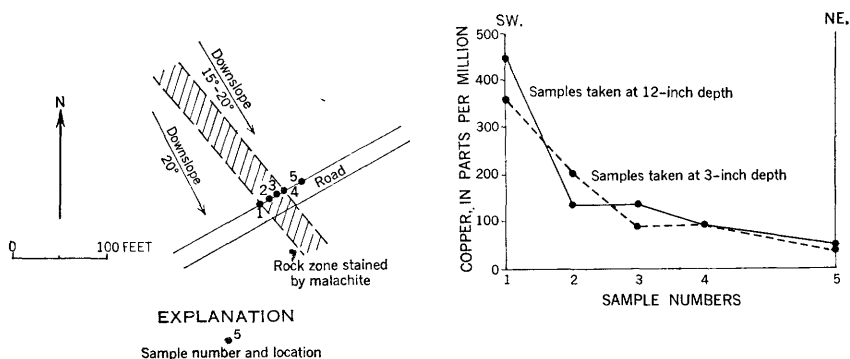


FIGURE 16.—Plan view of soil-sampling traverse near a malachite-stained zone, and a graph showing concentration of copper in the soil, Gentle Annie Gulch.

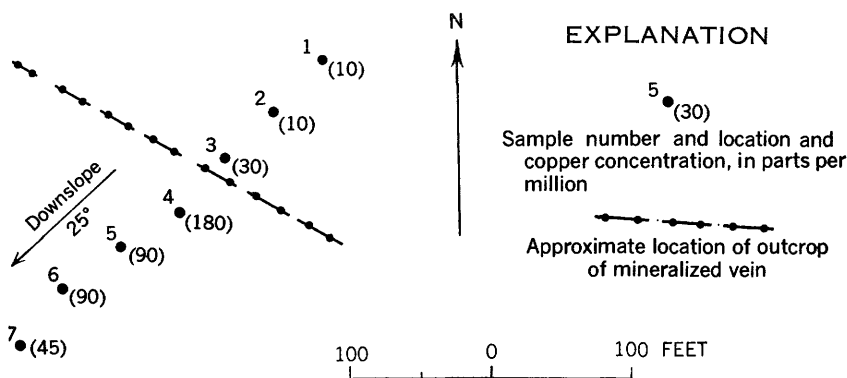


FIGURE 17.—Plan view of soil-sampling traverse near the outcrop of the Snowstorm copper zone.

from its junction with Loop Creek in the extreme southeast part of the Coeur d'Alene district. The copper mineral, as seen underground, is chalcopyrite present as disseminated grains and in small shoots of massive ore.

Soil samples were collected at 25- to 60-foot intervals on a traverse intersecting the projected vein outcrop at an angle of about 60° . A sketch of the sample locations showing their relation to the vein outcrop is shown in figure 18. Only a very small anomaly in copper was found despite the fact that the vein contains copper minerals. Samples were collected at uneven intervals in order to avoid soil disturbed by small prospect pits. A nitric-hydrofluoric acid extraction was used in the analysis.

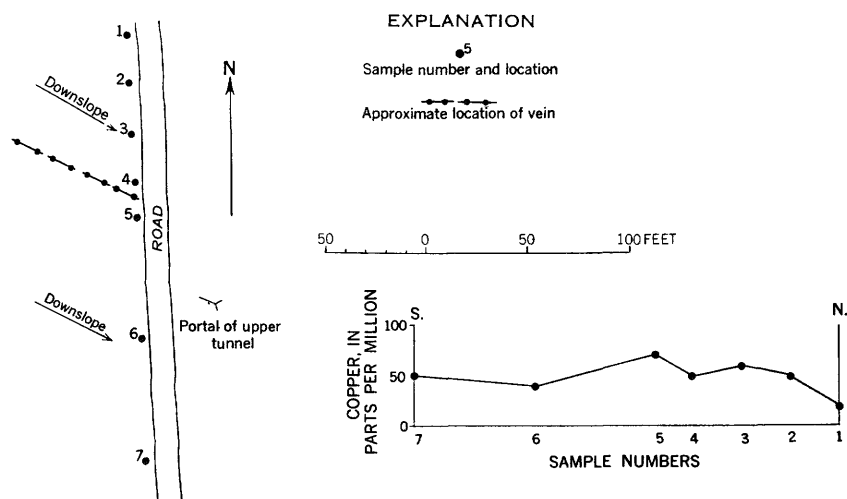


FIGURE 18.—Plan view of soil-sampling traverse and graph showing concentration of copper in soil at the Hansy copper mine.

Richmond mine.—The Richmond mine is at the head of Mineral Creek about 1.5 miles east-northeast of Adair (pl. 1). According to Umpleby and Jones (1923, p. 111) the Richmond mine produced oxidized ore averaging 10 percent copper for a short time in 1916. The vein strikes N. 75° E., dips steeply north, and is from 5 to 10 feet in width. It has been opened by several shafts and one tunnel.

At the Richmond mine a series of soil samples were collected at 50-foot intervals crossing the projected vein outcrop about 100 feet west of the westernmost shaft on the vein. No abnormal concentration of copper was found in any of the soil samples.

VEIN CONTAINING GOLD AND TUNGSTEN

Golden Chest vein.—The Golden Chest vein, in Reeder Gulch about 1.5 miles east of Murray (pl. 1), has been worked extensively underground for gold and tungsten. It is traced by surface pits and shallow workings for more than 1,000 feet along the strike. A sample traverse was run downslope across the vein. The results of analysis of the samples for tungsten are presented graphically in figure 19. Two areas were found where the soil had high concentrations of tungsten. One is related to the outcrop of the main vein; the cause of the other, represented by a high value in sample one, is not known.

VEIN CONTAINING ANTIMONY

Star Antimony.—The Star Antimony property is on the northeast side of the East Fork of Pine Creek and lies on a ridge between Highland and Blue Eagle Creeks about 5.5 miles south-southeast of

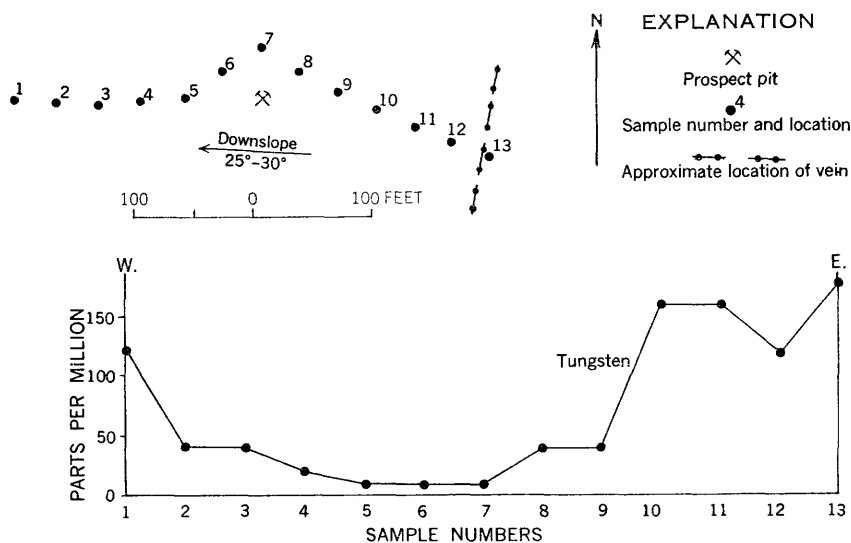


FIGURE 19.—Plan view of soil-sampling traverse, and graph showing concentration of tungsten in soil at the Golden Chest mine.

Pinehurst (pl. 1). The vein (Umpleby and Jones, 1923, p. 122) has been opened by three tunnels and consists of a fault zone 4 to 8 feet in width containing quartz, stibnite, a little pyrite, sphalerite, gold, and much gouge material. The richest stibnite ore occupied a zone ranging from 1 to 28 inches wide, but stibnite was also disseminated in the wallrock. Umpleby and Jones record the strike of the vein as east and the dip 25° to 60° S.; however, in the only adit now open, the largest vein strikes N. 34° E. and dips 65° SE. The enclosing rock is the Prichard formation.

A sketch map of the soil-sample locations, along with the concentration of antimony in soil near the upper tunnel, is shown on figure 26. The results of soil analyses, as well as an examination of the veins underground, indicate that the veins in the open adit probably have a different strike than those in the caved adits described by Umpleby and Jones (1923). Another vein, not observed in the open adit, may be present to the southwest of the portal, for concentrations of antimony in soil approximately 400 times background were found about 50 feet southwest of the upper portal. The westernmost traverse was extended downslope for a distance of several hundred feet in order to determine how far anomalous quantities of antimony could be detected downslope from the main mineralized zone. The results suggest that there may be small additional sources of antimony downslope from the main zone.

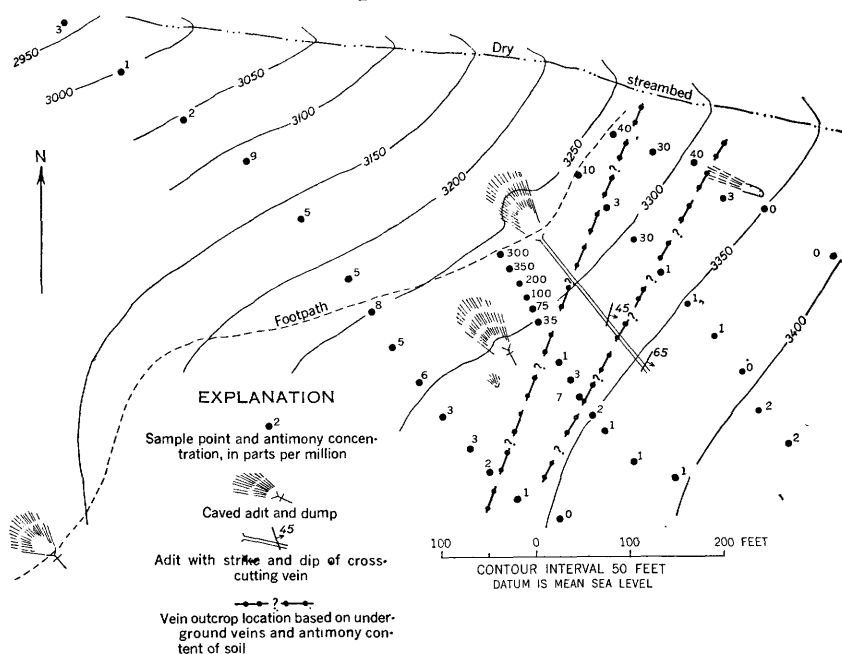


FIGURE 20.—Plan view of soil-sampling traverse near the Star Antimony vein.

PLANT STUDIES

The plant types which were sampled are representative of most of the plants growing in the mining district and are the logical ones to use in prospecting, if widespread sampling is desired. The pines, larches, spruces, and firs make up the largest proportion of the plants in the forested areas; the spirea and tall whortleberry (huckleberry) grow abundantly in the areas where most of the trees have been cut or burned; and beargrass grows at the higher elevations where the conifers and low-growing shrubs are not present.

Plant samples were collected from various places in the mining district where data were available on the lead, zinc, or copper content of the soil. Twigs were cut from several kinds of coniferous trees, and the needles and cones removed for separate analyses. Some low-growing deciduous plants of various kinds were sampled by collecting parts of the plants which appeared to be uncontaminated by dust or soil.

In the fall of 1950, samples were collected from 19 trees near the Little Pittsburg vein and analyzed for zinc by the field test of Reichen and Lakin (1949). As the samples were all collected in the area where detailed soil sampling had been done, it was possible to compare the zinc content of the trees with that of the soil nearby. The locations of the trees sampled are shown on plate 6 and the comparison between concentration of zinc in soil and concentration of zinc in needles and twigs is made in table 3.

TABLE 3.—Concentration of zinc in plants and soil in the area near the Little Pittsburg vein

| Plant field No. | Description of plant | | Zinc (ppm) ¹ | | |
|-----------------|--------------------------|---------------------------|-------------------------|-------|------------------------------|
| | Name ² | Approximate height (feet) | Needles | Twigs | Soil within 25 feet 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----- | do----- | 10 | 40 | 60 | 350 |
| P-5----- | Western yellow pine----- | 50 | 40 | 50 | 250 |
| P-6----- | do----- | 12 | 50 | 30 | 150 |
| P-7----- | do----- | 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----- | do----- | 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----- | do----- | 15 | 40 | 40 | 150 |
| P-17----- | Western yellow pine----- | 15 | 40 | 40 | 150 |
| P-18----- | do----- | 25 | 70 | 90 | (³) |
| P-19----- | Douglas-fir----- | 15 | 90 | 140 | (³) |

¹ Semiquantitative plant analyses made on an air-dried basis.

² Identification by G. M. Richmond and V. C. Kennedy.

³ Growing in outcrop of Little Pittsburg vein.

Because the field tests for zinc in plants, like those for zinc in soil, are susceptible to variations in both the extraction and the estimation steps, the concentrations given are probably accurate only to within ± 30 percent of the zinc present. Despite the various sources of possible error, the twigs and needles of both the Western yellow pine and the Douglas-fir show a definite increase in zinc content where growing in soil containing 1,000 ppm or more zinc.

During August 1951, Helen L. Cannon, of the U.S. Geological Survey, visited the field project and, with the author, collected plant samples within the mining district in areas where information was available on the lead, zinc, and copper concentrations in the soil. The samples were identified by H. L. Cannon and analyzed by members of the U.S. Geological Survey using standard quantitative procedures. A few additional samples collected by the author during August 1952 were analyzed by quantitative methods. The copper, lead, and zinc content of the plant parts is compared in table 4 with that of the soil in which the plant was growing.

Despite the reconnaissance nature of the plant study, some tentative conclusions appear warranted from present data. In general, the plants that were sampled showed changes in lead and zinc concentration with changes in the concentration of these elements in the soil in which they were growing. However, lead and zinc anomalies were found to be much greater in the soil than in plants growing in that soil. No soils containing large concentrations of copper were found; so it is not possible to state how high copper concentrations in soil (25 to 500 times background) affect the copper content of the plants growing in such soil. Of the three kinds of plants sampled, both from normal soil and from soil containing 10 times the normal amount of copper, none growing in the high-copper soil showed more than 2.5 times the amount of copper present in the plants growing in normal soil.

WATER STUDIES

Samples of water were collected from springs, streams, and mine drainage in the eastern part of the mining district and analyzed for heavy-metal content. In addition, the pH of many of the samples was measured using a Hellige standard comparator, and a few sulfate analyses were made. When the water was to be analyzed for heavy metals only, it was collected in a 100-milliliter glass-stoppered pyrex graduated cylinder and analyzed at the sampling spot. If sulfate content was also to be measured, a separate sample of the water was placed in a plastic bottle and returned to the field laboratory for analysis. In plate 7 a sketch map of the drainage near Mullan and the results of water analyses are presented. The pH values given are probably accurate to ± 0.2 of a pH unit, and the heavy-metal concentrations are believed to be within 50 percent of the true value.

TABLE 4.—Lead, zinc, and copper analyses of plants and nearby soils, Coeur d'Alene district, Idaho

[Analytical data are reported on an air-dried basis. Soil samples were collected at a depth of 2 to 6 inches. Analyst: H. E. Crowe, U.S. Geological Survey]

| Plant part or associated soil | Concentration of ore metals in plants ¹ and nearby soil (parts per million) | | | | | | | | | | | |
|--|---|-------|-------|-------|-------|---------|---------|---------|--------|--------|-------|-------|
| | Lead | | | | Zinc | | | | Copper | | | |
| | (a) | (b) | (c) | (d) | (a) | (b) | (c) | (d) | (a) | (b) | (c) | (d) |
| Western white pine, <i>Pinus monticola</i> Dougl. | | | | | | | | | | | | |
| Needles ² ---- | 20 | 6 | 6 | ----- | 280 | 110 | 25 | ----- | 5 | 5 | 5 | ----- |
| Twigs----- | 100 | 20 | 22 | ----- | 320 | 95 | 60 | ----- | 5 | 6 | 3 | ----- |
| Cones----- | 5 | 8 | 2 | ----- | 22 | 50 | 25 | ----- | 8 | 7 | 3 | ----- |
| Soil near plant----- | 20,000 | 150 | 20 | ----- | 2,000 | 1,500 | 50 | ----- | 70 | 30 | 25 | ----- |
| Western yellow pine, <i>Pinus ponderosa</i> Laws | | | | | | | | | | | | |
| Needles----- | 24 | 7 | 11 | ----- | 270 | 55 | 32 (34) | ----- | 5 | 8 | 4 | ----- |
| Twigs----- | 73 | 14 | 12 | ----- | 200 | 50 | 40 (29) | ----- | 7 | 6 | 8 | ----- |
| Cones----- | ----- | 1 | 8 | ----- | ----- | 34 | 37 | ----- | ----- | 7 | 10 | ----- |
| Soil near plant----- | 20,000 | 2,000 | 15 | ----- | 2,000 | 400 | 100 | ----- | 70 | 70 | 20 | ----- |
| Common Douglas-fir <i>Pseudotsuga taxifolia</i> Britt. | | | | | | | | | | | | |
| Needles----- | 31 | 18 | 11 | 7 | 140 | 100 | 200 | 50 (24) | 8 | 6 | 6 | 5 (3) |
| Twigs----- | 130 | 73 | 47 | 16 | 130 | 120 | 100 | 82 (40) | 8 | 8 | 6 | 8 (6) |
| Cones----- | ----- | 13 | ----- | 7 | ----- | 50 | ----- | 30 | ----- | 16 | ----- | 10 |
| Soil near plant----- | 20,000 | 5,000 | 150 | 20 | 2,000 | 1,000 | 1,500 | 100 | 70 | 70 | 30 | 20 |
| Alpine fir, <i>Abies, lasiocarpa</i> Nutt. | | | | | | | | | | | | |
| Needles----- | 7 | 10 | ----- | ----- | 70 | 50 (30) | ----- | ----- | 4 | 10 (5) | ----- | ----- |
| Twigs----- | 26 | 12 | ----- | ----- | 50 | 40 (45) | ----- | ----- | 8 | 8 (6) | ----- | ----- |
| Cones----- | 1 | ----- | ----- | ----- | 30 | ----- | ----- | ----- | 12 | ----- | ----- | ----- |
| Soil near plant----- | 100 | 25 | ----- | ----- | 100 | 50 | ----- | ----- | 300 | 25 | ----- | ----- |
| Engelmann spruce, <i>Picea engelmanni</i> Engelm. | | | | | | | | | | | | |
| Needles----- | 5 | 6 | ----- | ----- | 58 | 55 (40) | ----- | ----- | 3 | 12 (4) | ----- | ----- |
| Twigs----- | 56 | 11 | ----- | ----- | 120 | 65 (60) | ----- | ----- | 16 | 11 (9) | ----- | ----- |
| Cones----- | 4 | ----- | ----- | ----- | 38 | ----- | ----- | ----- | 8 | ----- | ----- | ----- |
| Soil near plant----- | 100 | 25 | ----- | ----- | 100 | 100 | ----- | ----- | 300 | 50 | ----- | ----- |
| Lodgepole pine, <i>Pinus contorta</i> var., <i>latifolia</i>, S. Wats | | | | | | | | | | | | |
| Needles----- | 21 | 12 | ----- | ----- | 55 | 75 (38) | ----- | ----- | 3 | 11 (5) | ----- | ----- |
| Twigs----- | 39 | 30 | ----- | ----- | 45 | 65 (36) | ----- | ----- | 5 | 3 (6) | ----- | ----- |
| Cones----- | 9 | 26 | ----- | ----- | 16 | 15 | ----- | ----- | 7 | 3 | ----- | ----- |
| Soil near plant----- | 1,500 | 25 | ----- | ----- | 150 | 200 | ----- | ----- | 20 | 25 | ----- | ----- |
| Western larch, <i>Larix occidentalis</i> Nutt. | | | | | | | | | | | | |
| Needles----- | 47 | 30 | ----- | ----- | 50 | 35 | ----- | ----- | 5 | 8 | ----- | ----- |
| Twigs----- | 100 | 95 | ----- | ----- | 44 | 50 | ----- | ----- | 25 | 10 | ----- | ----- |
| Soil near plant----- | 1,000 | 25 | ----- | ----- | 100 | 100 | ----- | ----- | 20 | 50 | ----- | ----- |
| Creambush rockspirea, <i>Holodiscus discolor</i> (Pursh) Maxim | | | | | | | | | | | | |
| Leaves----- | 77 | 19 | ----- | ----- | 90 | 57 | ----- | ----- | 17 | 6 | ----- | ----- |
| Soil near plant----- | 20,000 | 15 | ----- | ----- | 2,000 | 100 | ----- | ----- | 70 | 20 | ----- | ----- |

See footnotes at end of table.

42 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

TABLE 4.—Lead, zinc, and copper analyses of plants and nearby soils, Coeur d'Alene district, Idaho—Continued

| Plant part or associated soil | Concentration of ore metals in plants ¹ and nearby soil (parts per million) | | | | | | | | | | | |
|--|---|-----|-------|-------|-------|-------|-------|-------|--------|-----|-------|-------|
| | Lead | | | | Zinc | | | | Copper | | | |
| | (a) | (b) | (c) | (d) | (a) | (b) | (c) | (d) | (a) | (b) | (c) | (d) |
| Brachen, <i>Pteridium aquilinum</i> (L.) Kuhn. | | | | | | | | | | | | |
| Stem and fronds..... | 61 | 10 | ----- | ----- | 250 | 27 | ----- | ----- | 16 | 8 | ----- | ----- |
| Soil near plant..... | 20,000 | 25 | ----- | ----- | 2,000 | 100 | ----- | ----- | 70 | 20 | ----- | ----- |
| Big whortleberry (locally huckleberry) <i>Vaccinium membranaceum</i> Dougl. | | | | | | | | | | | | |
| Leaves..... | 23 | 5 | 5 | 4 | 28 | 55 | 21 | 36 | 6 | 6 | 5 | 5 |
| Berries..... | 9 | 8 | 6 | ----- | 12 | 25 | 11 | ----- | 6 | 14 | 5 | ----- |
| Soil near plant..... | 1,500 | 150 | 100 | 25 | 100 | 1,500 | 100 | 100 | 25 | 30 | 300 | 25 |
| American sweetvetch <i>Hedysarum americanum</i> (Michx.) Britt. | | | | | | | | | | | | |
| Leaves..... | 3 | 3 | ----- | ----- | 23 | 15 | ----- | ----- | 14 | 6 | ----- | ----- |
| Soil near plant..... | 100 | 20 | ----- | ----- | 100 | 100 | ----- | ----- | 300 | 30 | ----- | ----- |
| Common beargrass <i>Xerophyllum tenax</i> (Pursh.) Nutt. | | | | | | | | | | | | |
| Leaves..... | 22 | 7 | 6 | 4 | 28 | 38 | 20 | 18 | 7 | 5 | 8 | 6 |
| Soil near plant..... | 1,500 | 150 | 100 | 25 | 150 | 1,500 | 100 | 100 | 40 | 30 | 300 | 40 |

¹ Letters in parentheses indicate plant samples. Plant (a) under lead is the same plant as that listed a plant (a) under zinc and copper.

² Field and laboratory serial numbers are given below:

Western white pine:

Needles: a, H.C. 1-85, 513807; b, H.C. 1-123, 513845; c, 67N, 52-3632

Twigs: a, H.C. 1-86, 513808; b, H.C. 1-124, 513846; c, 67T, 52-3633

Cones: a, H.C. 1-87, 513809; b, H.C. 1-150, 513847; c, 67C, 52-3634

Western yellow pine:

Needles: a, H.C. 1-88, 513810; b, H.C. 1-98, 513820; c, H.C. 1-106, 513828

Twigs: a, H.C. 1-89, 513811; b, H.C. 1-99, 513821; c, H.C. 1-107, 513829

Cones: b, H.C. 1-100, 513822; c, H.C. 1-108, 513830

Common Douglas-fir:

Needles: a, H.C. 1-92, 513814; b, H.C. 1-94, 513816; c, H.C. 1-129, 513851, d, H.C. 1-107, 513825

Twigs: a, H.C. 1-93, 513815; b, H.C. 1-95, 513817; c, H.C. 1-130, 513852, d, H.C. 1-104, 513826

Cones: b, H.C. 1-96, 513818; d, H.C. 1-105, 513827

Alpine fir:

Needles: a, H.C. 1-112, 513834; b, 64N, 52-3626

Twigs: a, H.C. 1-113, 513835; b, 64T, 52-3627

Cones: a, H.C. 1-114, 513836

Englemann spruce:

Needles: a, H.C. 1-115, 513837; b, 65N, 52-3628

Twigs: a, H.C. 1-116, 513838; b, 65T, 52-3629

Cones: a, H.C. 1-117, 513839

Lodgepole pine:

Needles: a, H.C. 1-132, 513854; b, 68N, 52-3635

Twigs: a, H.C. 1-133, 513855; b, 68T, 52-3636

Cones: a, H.C. 1-134, 513856; b, 68C, 52-3637

Western larch:

Needles: a, H.C. 1-137, 513859; b, 66N, 52-3630

Twigs: a, H.C. 1-138, 513860; b, 66T, 52-3631

Creambush rockspirea:

Leaves: a, H.C. 1-91, 513813; b, H.C. 1-101, 513823

Brachen:

Stem and

fronds: a, H.C. 1-90, 512812; b, H.C. 1-102, 513824

Big whortleberry:

Leaves: a, H.C. 1-135, 513857; b, H.C. 1-127, 512849; c, H.C. 1-110, 513832; d, H.C. 1-121, 513844

Berries: a, H.C. 1-139, 513861; b, H.C. 1-128, 51385; c, H.C. 1-111, 513833

American sweetvetch:

Leaves: a, H.C. 1-119, 513841; b, H.C. 1-120, 512842

Common beargrass:

Leaves: a, H.C. 1-136, 513858; b, H.C. 1-131, 513853; c, H.C. 1-118, 513840; d, H.C. 1-122, 513844

³ The numbers in parentheses are the concentrations suggested as being normal for the same kind of plant in British Columbia (Warren and others, 1952). The plant part denoted as "twig" here is not strictly comparable to Warren's "stems," for the twigs constituted all of the first year's growth including the tip, whereas, the term "stem" apparently does not include the tip.

Most of the water containing an abnormal concentration of heavy metals comes at least in part from mine workings. The highest concentration of heavy metals found was 5 ppm in mine drainage about 1,600 feet east-northeast of the Star mine in Grouse Gulch. This water, along with the large volume of water draining from the Star, causes the heavy-metal concentration to remain near 1.0 ppm in Grouse Creek until it joins the South Fork of the Coeur d'Alene River. In Mill Creek, as in Grouse Creek, mine drainage causes anomalous concentrations of heavy metals in the water, although dilution from the east branch of the stream is responsible for decreasing the heavy-metal concentration to 0.04 ppm near Mullan. The heavy-metal concentration in Gold Hunter Gulch is slightly higher than the normal background of about 0.002 ppm, probably owing to the presence of the Gold Hunter mine. Similarly, mine drainage contaminates Daisy Creek. In Deadman Gulch, water from the Copper King mine and also from the National mine mingles with the normal stream waters, but the water leaving the mouth of the gulch has a normal concentration of heavy metals. Dilution of the mine water undoubtedly accounts for some of the decrease, and precipitation from solution may account for the rest. In Gentle Annie Gulch, mine drainage is believed responsible for the value of 0.01 ppm heavy metals found near the mouth of the stream. South of the Coeur d'Alene River, water samples were collected from several tributaries; but none, except Dry Creek, contained unusual quantities of heavy metals. The reason for the anomalous amounts of heavy metals in solution in Dry Creek is not known.

A study of copper concentrations in waters of a mine adit up Willow Creek in the southeastern part of the map area about 1,600 feet northeast of the Reindeer Queen mine (pl. 7) indicated a nearly complete removal of copper from mine drainage by a slight change in chemical conditions. Small quantities of copper were known to be disseminated in the enclosing rock; yet the waters draining from the mine were low in copper. Investigation disclosed the presence of light-green stalactites, 1 to 2 inches in length, hanging from the roof of the drift at a distance of about 200 feet from the portal. Water was slowly seeping down from above and dropping from the stalactites. Analysis of the water dripping from the stalactites showed an average copper content of approximately 1 ppm. Splashes of light-green carbonate were deposited where some of this water struck the walls in falling. Analysis of water in small pools under these stalactites showed a copper content of about 0.02 ppm. This decrease in copper concentration probably results from the combined effects of precipitation and of dilution by water containing little copper. The small amount of water trickling along the floor of the drift in

the area of stalactite formation contained less than 0.01 ppm copper. Although dilution of the copper-bearing solutions undoubtedly helped decrease the copper concentration in the drainage from the drift, precipitation is believed to be the major factor. The pH of the water dripping from the stalactites ranged from 7.0 to 7.3, and the water draining from the drift had a pH of 7.3. Although a slight rise in pH may account for the copper precipitation where the water is exposed to air, the evidence for this is not conclusive.

Coprecipitation with hydrous ferric oxide may also cause a nearly complete removal of heavy metals from drainage. At the portal of the Midnight mine, water samples contained about 0.1 ppm heavy metals and had a pH of 7.2 in August 1951. A year later, the heavy-metal concentration was 0.08 ppm and pH was 6.4. At a distance of about 175 feet outside the portal, water samples collected in 1951 contained 0.003 ppm heavy metals and had a pH of 7.2, and samples collected in 1952 had a heavy-metal concentration of 0.007 ppm and a pH of 7.3. Between these two sample points, the mine water flowed in a broad shallow stream from which hydrous ferric oxide apparently was precipitating because a layer of red-brown flocculent material covers the streambed to a thickness of $\frac{1}{8}$ to $\frac{1}{2}$ inch. Very probably, ferrous iron in solution is oxidized on exposure to air, and the ferric iron thus formed then precipitates. No dilution of the mine water by other sources was noted; so the decrease in heavy-metal concentration is believed to be due to coprecipitation.

The water draining from another mine tunnel, about 800 feet west-northwest of the Midnight mine, was also studied. The data are presented as follows:

| Location | Concentration | |
|-----------------------------|---------------|-----------------------|
| | pH | of heavy metals (ppm) |
| At portal | 7.2 | 0.1 |
| 150 ft outside portal | 7.4 | .05 |
| 220 ft outside portal | 7.4 | .04 |

Between the portal and the point 150 feet downstream, much hydrous ferric oxide covered the streambed, but from 150 to 200 feet very little ferric oxide was seen.

These data are also interpreted as an indication that precipitation of hydrous ferric oxide, associated with aeration of the water and rise in pH, may be responsible for the removal of heavy metals from solution.

In Daisy Gulch, water draining from a shear zone 100 feet or more wide was analyzed and found to contain about 0.004 ppm heavy metals. The pH was 8.6. A few quartz veinlets an inch or so in width were found throughout the shear zone, and enough zinc was present so that the soil overlying the sheared area contained 400 to 600 ppm zinc. This is the only locality examined in which the water

analyzed was draining from mineralized ground undisturbed by mining activity.

The comparatively few sulfate determinations which were made suggest that mine water in the Coeur d'Alene district contains several hundred times as much sulfate as does normal surface water. However, many of the samples of surface water contained sulfate in quantities too low to be measured accurately by the equipment used, and the only conclusion to be drawn regarding sulfate analysis is that more work seems worthwhile.

SIGNIFICANCE OF ANALYTICAL RESULTS

SOILS

The results of studying 13 lead- and zinc-bearing veins (table 5) show that, near 11 of the 13, lead has been concentrated over background to a greater extent than zinc. Because lead background is about 20 ppm and zinc background about 100 ppm, the actual percentage of zinc may be greater than that of lead and yet not be shown in the table as having a greater ratio to background. The ratio of anomalous concentration to background concentration is shown in the table because it permits a better evaluation of the correct metal to use in prospecting than does the absolute concentration of the elements.

TABLE 5.—*Summary of lead and zinc soil anomalies found near veins*

| Name of area | Ratio of highest lead concentration found to background concentration ¹ | Ratio of highest zinc concentration found to background concentration ¹ |
|-----------------------|--|--|
| Jack Waite..... | 20 | 1 |
| Hercules..... | 45 | 2.2 |
| Custer Peak..... | 125 | 2.5 |
| Standard-Mammoth..... | 50 | 2.7 |
| Frisco..... | 100 | 3.5 |
| Star..... | 110 | 1.8 |
| Gold Hunter..... | 135 | 3.0 |
| Vindicator..... | 32 | 6.0 |
| Sidney..... | 45 | 1 |
| Little Pittsburg..... | 1500 | 36 |
| "Carbonate" vein..... | 12 | 15 |
| Liberal King..... | 1 | 1 |
| Page..... | 25 | 6 |

¹ Background lead is taken as 20 ppm and background zinc as 100 ppm.

In general, the analytical data resulting from the study of these 13 veins strongly suggest that successful prospecting for new lead-zinc veins could be done using soil analysis for lead. Where low or questionable lead anomalies are detected, a specific test for zinc could be used to check the lead data.

At the Liberal King vein there are no lead or zinc minerals known to be in the vein for a depth of several hundred feet from the surface

where the samples were collected, and this probably accounts for the lack of anomalous amounts of lead or zinc in the soil.

Of the 5 copper-bearing veins studied, 4 contributed enough copper to the soil to be detected by the soil test for copper. The highest concentration of copper found was 450 ppm at the area in Gentle Annie Gulch. Despite the presence of considerable malachite staining in the bedrock near the Missoula tunnel, at the Snowstorm mine, and in Gentle Annie Gulch, relatively low copper anomalies were found in soil. One possible explanation for this is that copper ore minerals may be leached during soil formation. The very slight copper anomaly near the Hansy copper mine, where chalcopyrite ore is known to be a few tens of feet below the surface, is further evidence suggesting removal of copper during soil formation. In contrast to these data, studies of nonmineralized rock and overlying soil suggest that copper may be somewhat concentrated in soil during soil formation. The explanation for this apparent contradiction of data is not known.

Although the data available do not permit drawing definite conclusions regarding geochemical prospecting for copper by soil analysis, the work thus far does suggest that in the Coeur d'Alene district, copper anomalies are relatively small near known copper deposits. There is a possibility, which cannot be ignored—that each of the sample traverses near copper veins crossed the veins in an area of rather low copper content. This would account for the low amounts of copper in the soil.

The analysis of soils for antimony and tungsten as a means to prospecting for veins containing these elements is probably worthwhile, but further work is necessary before recommendations can be made. The southern vein seen in the crosscut at the Star Antimony mine is about 2 feet wide and contains perhaps 1 to 3 percent crushed and broken stibnite in a gangue which is primarily quartz. If such a vein contained 1 to 3 percent galena instead of stibnite, the soil downslope from its outcrop would very probably contain several thousand parts per million lead. The relatively low concentrations of antimony found in the soil near the projected outcrop of the southern vein suggest that either the vein seen underground is greatly different in antimony content at the surface or else the antimony is removed in solution during weathering and soil formation. The concentration of tungsten in the Golden Chest vein is not known at the point where the soil-sampling traverse crossed it. Hence, the sensitivity of soil analysis as a prospecting tool for tungsten cannot be evaluated. However, the fact that anomalous amounts of tungsten were found in the soil indicates that soil analysis should be considered when prospecting for tungsten.

PLANTS

The analysis of plants growing in normal and in high lead-zinc soils indicates a positive correlation between the concentration of lead and zinc in plants and the concentration of lead and zinc in soil in which the plants are growing. In general, a given percentage increase in lead or zinc in soil will result in a corresponding, but smaller, increase in plants growing in that soil. Thus, in prospecting, a larger anomaly should be detected by sampling residual soil than by sampling plants.

Plant sampling may be of value in the Coeur d'Alene district when prospecting in areas covered by alluvium or terrace gravels. However, such areas represent a very small percentage of the total area in the Coeur d'Alene mining district; so no effort was made to investigate the feasibility of prospecting through such deposits.

WATER

The normal concentration of heavy metals in stream water is approximately 0.002 ppm and the normal pH is about 7.1. Mine waters range in heavy-metal concentration from 0.002 ppm to 5.0 ppm and the pH ranges from 6.0 to 8.6. The pH variations do not correlate with variations in heavy-metal concentrations although oxidation of pyrite associated with most ores would be expected to depress the pH with an increase of heavy metals in solution.

Because of the difficulty of determining the localities from which spring water may have obtained anomalous quantities of heavy metals, the analysis of such waters is essentially a tool for reconnaissance prospecting in areas which have been little disturbed by mining activity. Where there are many known veins in an area, as in the Coeur d'Alene, the surface water and much of the ground water may be contaminated by solutions from the rapidly oxidizing ore which has been exposed by mining; this contamination complicates the interpretation of water analysis data. With such limitations in mind, however, analysis of surface water and springs or seepages might prove helpful. During the author's study, relatively few springs were found, and many of the streams were contaminated by mine drainage; hence the conclusion that the water-analysis method of prospecting was of limited usefulness in the mining district.

CONCLUSIONS

Three methods of prospecting by geochemical techniques were used in the study of the Coeur d'Alene district. These methods were, in order of decreasing time expended on them, analyses of soils for lead, zinc, copper, antimony, and tungsten; analyses of plants for

zinc, lead, and copper; and analyses of surface, mine, and spring water for total heavy metals. The conclusions regarding each method are presented in the following paragraphs.

SOILS

1. Soil analysis as a means of prospecting is feasible in the Coeur d'Alene.

2. The concentration of lead in soil should be measured when prospecting for ore bodies having a zinc to lead ratio of about 3:1 or less.

3. Analyses for zinc are valuable when looking for ore bodies in which the zinc to lead ratio is high.

4. Analysis of soil for copper has yielded relatively poor results. Therefore, if neither lead nor zinc in quantity is associated with the copper, soil samples should not be spaced more than 50 feet apart and concentrations of 50 to 100 ppm copper should be checked.

5. Present results for antimony and tungsten are encouraging, but neither has been studied in sufficient detail to permit definite recommendations.

6. Normal concentrations of lead, zinc, and copper in soil are 20 ppm, 100 ppm, and 25 ppm, respectively. The normal concentration of antimony in soil is about 0.5 ppm, and that of tungsten is apparently less than 10 ppm.

7. In the process of formation of soil from unmineralized bedrock, lead, zinc, and copper seem to be concentrated, but this may be only an apparent concentration due to the method of sampling.

8. When using the field tests described, soil samples should be considered probably anomalous if the ore-metal concentration is 2 to 4 times the normal concentration and almost certainly anomalous if the concentration is more than 4 times background.

9. In general, depth of soil sampling is not critical in detecting an anomaly in areas where the soil is a foot or less in thickness. Sharp changes in ore-metal concentrations between consecutive, closely spaced samples should not be found except in the immediate vicinity of a vein outcrop. However, sample-digestion methods resulting in partial extraction of heavy metals may cause a greater apparent variation in heavy-metal concentration than is actually present.

10. Sample spacing will vary with the type or strength of mineralization being sought and with the accuracy of the chemical test being used, but, in general, a spacing of 50 feet should be suitable when searching for small veins and 200 feet when searching for large veins—topography being taken into account.

11. In this mining district, when making analyses for lead, zinc, or copper, the soil which passes an 80-mesh sieve is satisfactory as a sample.

12. Soil analysis as used in this study is sufficiently quantitative so that two parallel veins, one above the other on a slope, can be distinguished with suitable sample spacing.

13. Because a wide zone of tiny veinlets can produce an anomaly as large as that produced by one large vein, soil analysis should be helpful in searching for ore bodies represented at the land surface by only a series of veinlets.

14. Soil analysis is preferable to plant or water analysis if only one method of prospecting is to be used. However, under favorable circumstances, plant and water sampling also might be of value.

PLANTS

1. In general, above-normal concentrations of copper, lead, and zinc in soil will be reflected in above-normal concentrations of these metals in plants growing in the abnormal soil. However, the percentage increase over background in the plants will not be so great as in the soil.

2. The work done thus far suggests that western white pine, western yellow pine, and Douglas-fir show lead anomalies best in the twigs and that zinc anomalies are best shown in the needles. Many more samples should be analyzed before drawing definite conclusions.

WATER

1. Normal concentrations of heavy metals in stream and spring water is about 0.002 ppm, and the normal pH is about 7.1.

2. Water sampling within the mining district may be feasible under favorable conditions as a method of prospecting, but present data indicate that contamination of surface drainage is a major problem in any water analysis program. It is very probable, however, that reconnaissance prospecting by water analysis outside the mining district would be of value.

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APPENDIX
METHODS OF ANALYSIS
SOIL

The method of analysis to be used for soil samples from this area posed several problems. These problems fell into essentially two groups: first, those dealing with the completeness of extraction of the heavy metals from the sample and the accuracy of estimating heavy metals in solution; and second, those dealing with the choice of the element or elements for which analyses should be made. Some information regarding these problems was obtained, and this information should be of help in determining appropriate methods of prospecting in the Coeur d'Alene district.

A general heavy-metals test of the type described by Huff (1951) was used on some of the soil 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 other than copper, lead, and zinc which react with dithizone are present in negligible quantities in most soils and usually may be disregarded as was done in the Coeur d'Alene area.

Briefly, the heavy-metals test is performed by shaking a buffered aqueous solution of pH about 5.5 (obtained by adding buffer solution to an aliquot of the acid extract from a soil sample) with a carbon tetrachloride solution of dithizone. Prior to shaking, the carbon tetrachloride layer is clear green, but, after shaking, the color will be some shade of green, blue, purple, or red, depending upon the quantity of heavy metals originally present in the aqueous phase. If essentially no heavy metals are present the color remains green upon shaking; as the amount of heavy metals is increased the carbon tetrachloride layer becomes blue, then purple, then red. When the carbon tetrachloride layer is a clear red, no further color change will take place regardless of the amount of heavy metals present. The metal content of the aliquot is determined from the color of the dithizone layer by comparison with standard series of dithizone solutions whose heavy-metal content is known. The amount of heavy metals in the aliquot and the size of the aliquot are used to calculate the heavy-metal content of the original sample.

The sensitivity of dithizone is different for each of the heavy metals. This fact is important and must be taken into account in interpreting the heavy-metals test. To match the color produced by any given weight of zinc, approximately twice as much copper or

4 times as much lead by weight is required. Therefore, anomalies in parts per million (ppm) of copper and lead must be greater than those in zinc in order to give comparable results.

Specific tests for lead, zinc, and copper were made using the soil solutions prepared for the heavy-metals test. The test for zinc described by Lakin and others (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. It is possible to make specific tests using any of the three methods of digestion described below, but standard heavy-metals tests should not be made when using the 1:1 HNO_3 digestion, for this digestion leaves an undesirably high concentration of acid in the final solution.

The methods of analysis for tungsten, antimony, and silver have been described, respectively by Ward (1951), Ward and Lakin (1954), and Almond and others (1953).

During the summer of 1950, the only method used for putting the sample into solution for a total heavy-metals test was Huff's (1951) method B. This method consists of an hour-long 1:7 nitric acid digestion. The extraction of zinc and lead was found to vary rather widely when this digestion was used on Coeur d'Alene soil samples; therefore, at the end of the 1950 field season, a more intense digestion using HF and HNO_3 , Huff's (1951) method D, was tried, resulting in more consistent extraction of zinc. As a consequence, the nitric-hydrofluoric acid digestion was used during the 1951 field season even though the lead extraction by this method was not all that was desired. In the spring of 1952, a third method of digestion (0.33 gram of soil digested for an hour in 2 milliliters of 1:1 HNO_3) was tried. A comparison of the three methods was made under the direction of Harold Bloom, and the results are shown in table 6.

TABLE 6.—Comparison of the various analytical methods used for soil samples

[Analysts: H. E. Crowe, A. P. Marranzino, and J. H. McCarthy, U.S. Geological Survey]

| | Huff's method B (1951) 1:7 HNO_3 digestion | | | | Huff's method D (1951) HF- HNO_3 digestion, nitric-hydrofluoric acid | | | | 1:1 HNO_3 digestion | | | |
|---|--|------|------|-------------|---|------|------|-------------|------------------------------|------|------|-------------|
| | Heavy metals | Lead | Zinc | Cop- per | Heavy metals | Lead | Zinc | Cop- per | Heavy metals | Lead | Zinc | Cop- per |
| Number of samples analyzed..... | 50 | 47 | 47 | 10 | 50 | 52 | 47 | 10 | ----- | 31 | 31 | ----- |
| Percent of semi-quantitative (field) analyses agreeing within ± 25 percent of quantitative value..... | 36 | 65 | 19 | 40 | 70 | 38 | 60 | 50 | ----- | 77 | 65 | ----- |
| Percent of semi-quantitative analyses agreeing within ± 50 percent of the quantitative value..... | 78 | 91 | 70 | 50 | 94 | 71 | 94 | 80 | ----- | 90 | 100 | ----- |

Each of the three methods of sample extraction has its advantages when used on soil samples from the Coeur d'Alene area. Although the 1:7 HNO_3 method yields rather poor results for zinc, the reagents used are relatively mild (a desirable feature in a field test), and the lead extraction is good enough for general prospecting. If zinc were the main ore metal, the 1:7 HNO_3 method would be less desirable than one of the other two methods. The nitric-hydrofluoric acid method is suitable for use when general heavy metals, zinc, or copper tests are to be made. The disadvantages are the relatively poor lead extraction and the need for both platinum ware and standard laboratory facilities. The 1:1 HNO_3 method does not require platinum or the use of standard laboratory facilities and yields satisfactory extraction of lead and zinc. The disadvantage is that the general heavy-metals test cannot be made unless a large amount of buffer is used to counteract the higher acid concentration.

In describing the results of soil studies, reference is made to the methods of extraction as follows: 1:7 HNO_3 , nitric-hydrofluoric acid, and 1:1 HNO_3 .

PLANTS

Plant samples collected in 1950 from near the Little Pittsburg mine were analyzed for zinc only, using the semiquantitative field method of Reichen and Lakin (1949). Plant samples collected in 1951 from various parts of the mining district were analyzed by the quantitative method used by Reichen and Lakin (1949). The latter method consists of a wet oxidation of the dried plant parts by nitric and perchloric acids (Piper, 1944) followed by estimation of the lead, zinc, and copper in the manner described by Holmes (1945).

No data were obtained on the accuracy or precision of the results for zinc in plants using the field semiquantitative method, but some information was obtained on the precision of the quantitative method used. The data are presented in table 7, shown on the following page. As the precision of the results from separate determinations was as good as that from repeat estimations of the lead, zinc, or copper in the same solution the percentage extraction must be very consistent and is probably near 100 percent.

WATER

Analyses of water were made for zinc alone and for total heavy metals using the technique described by Huff (1948). Determinations of pH were made by means of a Hellige standard comparator and sulfate analyses were done using a Hellige turbidimeter.

TABLE 7.—*Precision of quantitative plant analyses.*

[Analyses were made by H. E. Crowe, U.S. Geological Survey]

| Zinc (ppm) | | Lead (ppm) | | Copper (ppm) | |
|--|-----------------|----------------|-----------------|----------------|-----------------|
| First analysis | Repeat analysis | First analysis | Repeat analysis | First analysis | Repeat analysis |
| Results of repeat analyses | | | | | |
| 320 | 320 | 103 | 98 | 6 | 6 |
| 35 | 30 | 1 | 2 | 7 | 8 |
| 30 | 25 | 1 | 1 | 12 | 13 |
| 110 | 110 | 6 | 6 | 5 | 6 |
| Results of repeat estimations from same sample solution | | | | | |
| 65 | 60 | 13.0 | 14 | 6 | 8 |
| 50 | 45 | 34.0 | 35 | 5 | 6 |
| 40 | 35 | 6.0 | 6 | 6 | 7 |
| | | 20.0 | 20 | | |
| | | 8.5 | 7 | | |
| | | 10.0 | 4 | | |
| | | 15.0 | 14 | | |
| | | 1.5 | 1 | | |

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