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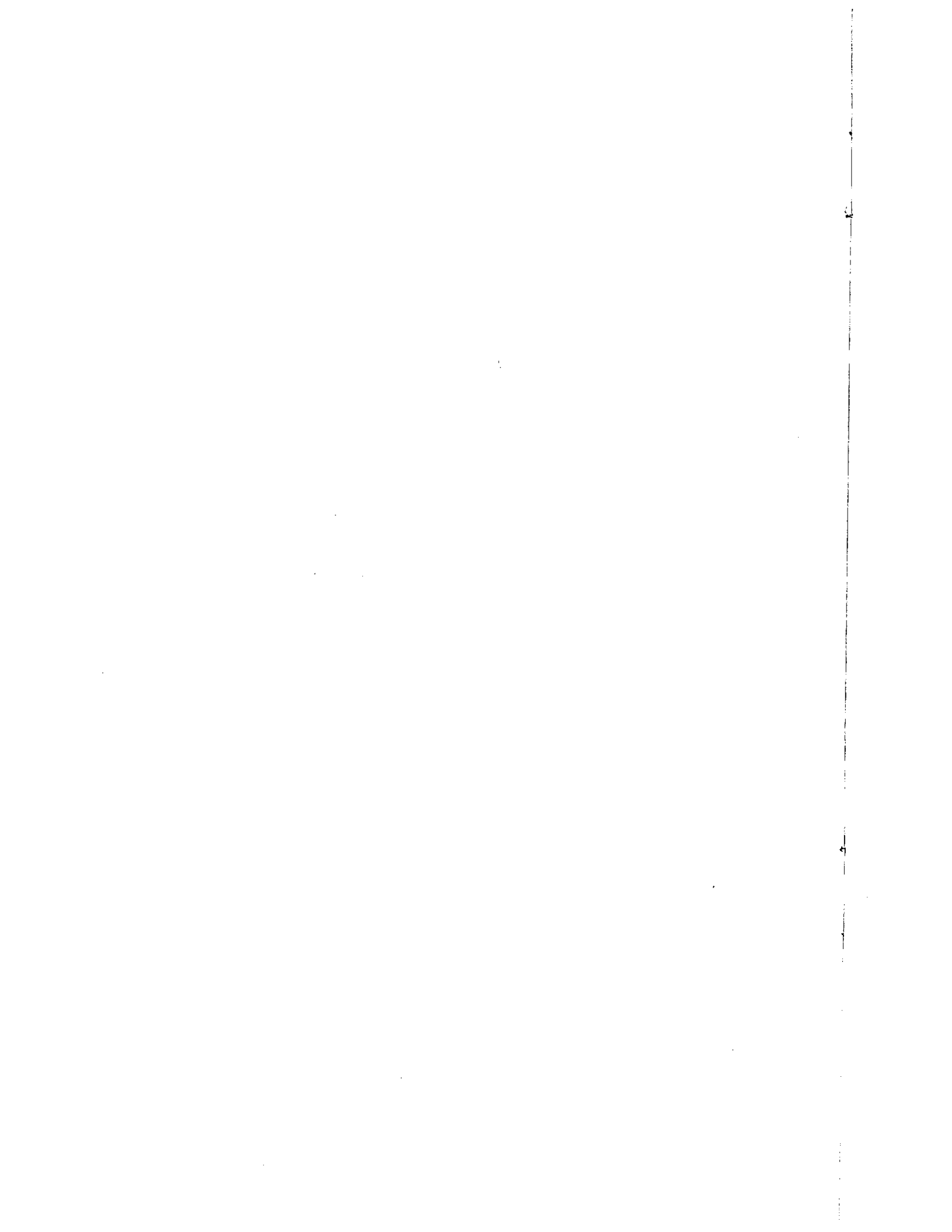
GEOCHEMICAL INVESTIGATION OF THE HEAVY METAL
CONTENT OF STREAM AND SPRING WATERS IN
THE KENO HILL-GALENA HILL AREA,
YUKON TERRITORY

BY

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PREFACE

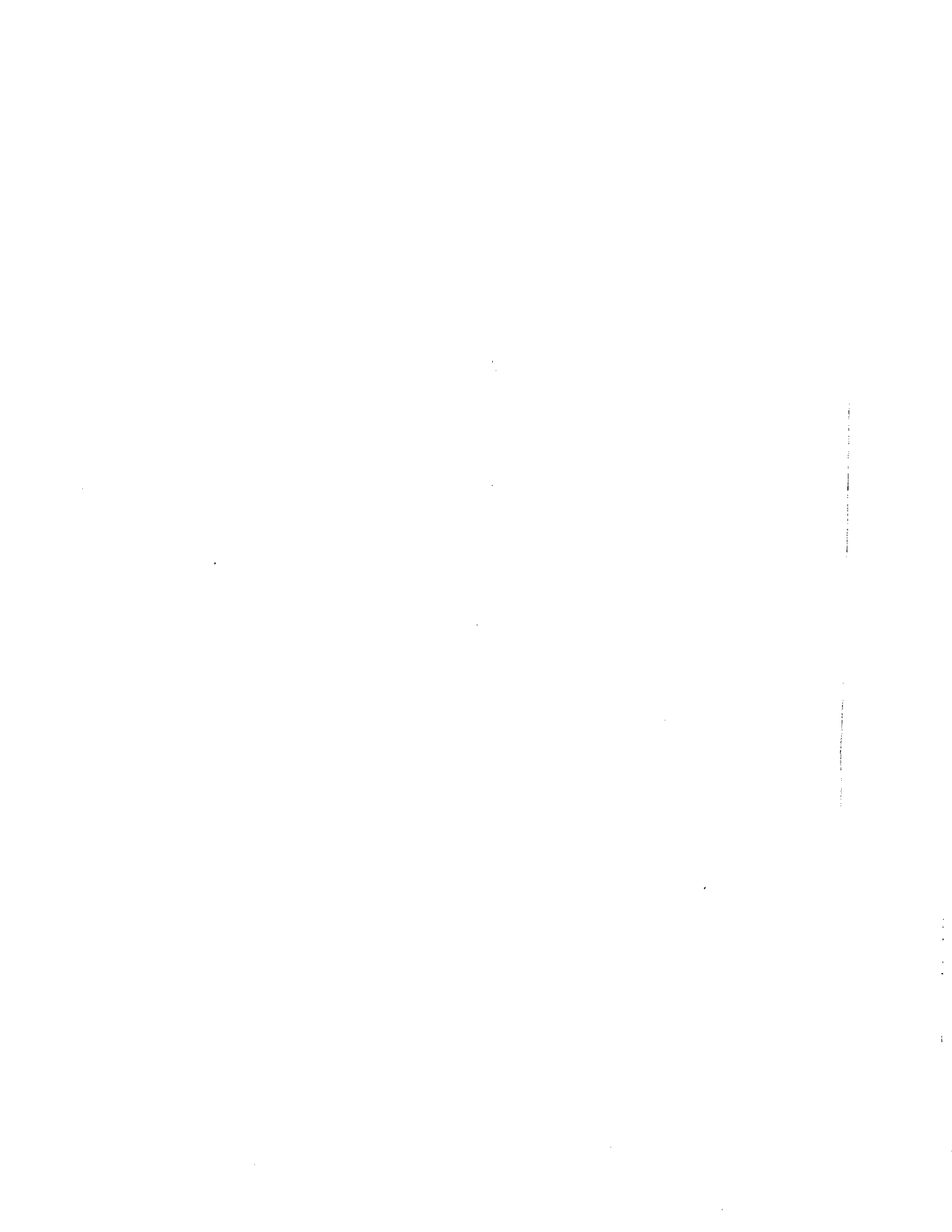
Geochemical prospecting is fast being recognized as a valuable tool in the search for hidden orebodies. One of the methods is to test stream and spring waters for minute amounts of metals and this method has already proved fruitful. The study on which this report is based extends the use of the method into an area of permafrost and demonstrates that the presence of permanently frozen ground does not prevent its successful use.

Attention is drawn to factors that must be considered in prospecting a permafrost area by this method and precautions that must be taken if reliable results are to be obtained.

The procedure found to be successful is given in sufficient detail to serve as a guide to those intending to attempt this type of prospecting.

GEORGE HANSON,
Director, Geological Survey of Canada

OTTAWA, January 24, 1955



**GEOCHEMICAL INVESTIGATION OF THE HEAVY METAL
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INTRODUCTION

This report describes a detailed geochemical investigation of the heavy metal content in the stream and spring waters of the Keno Hill-Galena Hill area in central Yukon. The purpose of the investigation was to determine the applicability of hydrogeochemical prospecting methods in a region containing silver-lead-zinc deposits that occur in the permafrost zone.

The results of the investigation show that heavy metal anomalies occur both in areas that have been extensively prospected by trenching and underground work and those that have been relatively untouched. The abundance of mine and prospect workings, which expose vein material to leaching waters, may be responsible for some of the high anomalies that might not otherwise occur if the areas were undisturbed. As anomalies were found, however, in areas that have been relatively untouched, the authors conclude that hydrogeochemistry can be applied successfully during a limited period of the year. This is the period when the active layer of the permafrost zone has thawed sufficiently to allow spring and stream waters access to veins and mineralized areas from which they can leach heavy metals.

Details of a field testing kit and the chemical procedure used during this investigation are included for the information of those wishing to do similar work.

This investigation is one part of a general geochemical investigation of the silver-lead-zinc deposits of the Keno Hill-Galena Hill area. It is proposed to do further geochemical work on the heavy metal content of soils, rocks, and vegetation, and to test other geochemical prospecting methods and techniques in this extensively mineralized area.

ACKNOWLEDGMENTS

The investigation described was done entirely in the field. Charles Illsley, a student of Pennsylvania State University, organized and carried out the geochemical investigation of the heavy metal content of the stream waters and was responsible for the compilation and correlation of the stream data. The senior author was responsible for the investigation of the springs and for the geological data. Robert Green, a student of McGill University, did the field and laboratory analyses. Donald McLean, the fourth member of the field party, did the draughting and assisted in the compilation of the data.

The authors wish to thank the mining companies and individuals who assisted in many ways. United Keno Hill Mines Company Limited supplied space for a field laboratory, and Mackeno Mines Company

Limited allowed the use of its balances and other laboratory facilities. McLeod White, A. C. Carmichael, and W. S. Ellis supplied much valuable field information and assisted in other ways. To them the writers are grateful.

GENERAL CHARACTER AND GEOLOGY OF THE AREA

The Keno Hill-Galena Hill area is in central Yukon, 35 miles north-east of Mayo and some 220 miles due north of Whitehorse. The area is served by an all-weather road from Whitehorse and by Canadian Pacific Airlines. The present economic interest in the area centres chiefly about the lead-silver deposits, which have been worked since 1915 and have yielded more than \$50,000,000 in silver, lead, and zinc.

The general geology of the Mayo area was described first by Keele in 1905 (1),¹ by Cairnes in 1915 (2), and by Bostock in 1947 (3). The geology of Keno Hill was described by Cockfield (4) in 1920 and 1923, and Galena Hill by Stockwell (5) in 1925. Recently, McTaggart (6) has restudied the geology of Keno and Galena Hills. The short description that follows is taken principally from the above reports and from data gathered by the senior author.

The area is mountainous with elevations from 6,750 feet (Mount Hinton) to 2,500 feet (Ladue and McQuesten Valley). Areas above 5,500 feet are generally topped by rolling topography. South-facing slopes are steep but relatively smooth, whereas north-facing slopes, especially on Keno and Bunker Hills, are precipitous.

The region was glaciated during Pleistocene time by ice that spread over the area from the east. All but the tops of the high hills and mountains show evidence of glaciation, and glacial debris is widespread on the slopes and in the valleys. In most areas where glacial till and gravel occurs it is 10 to 20 feet thick, but in some areas, as on the southern slope of Keno Hill facing Lightning Creek, the deposits are 30 to 50 feet thick. Valleys exhibit U-shaped cross-sections and are generally floored with glacial sands, gravel, and till, through which the streams in the principal valleys have cut successive channels, forming benches.

Keno and Galena Hills are in the region of permanently frozen ground (permafrost zone). Wernecke (7) has given a short account of the permafrost conditions in the area. The permafrost is patchy in its distribution, depending upon the elevation, hillside exposure, depth of overburden, amount of vegetation, and presence of moving underground and surface waters. Most of the ground on northern slopes is permanently frozen, whereas that on southern slopes may become relatively free of frost each summer. Thus, on Keno Hill, most mine workings on the top of the hill and on the northern slope were coated with frost to a maximum depth of 400 feet below the surface, whereas in the workings of the Mount Keno mine, on the southern slope facing Lightning Creek, no permafrost was encountered. On Sourdough Hill frost and ice veins were encountered in the Bellekeno mine workings to a depth of 250 feet below the surface, and on Galena Hill permafrost has been found to depths of 200 feet and more below the surface.

¹ Numbers in parentheses refer to References at the end of the report.



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Figure 1.

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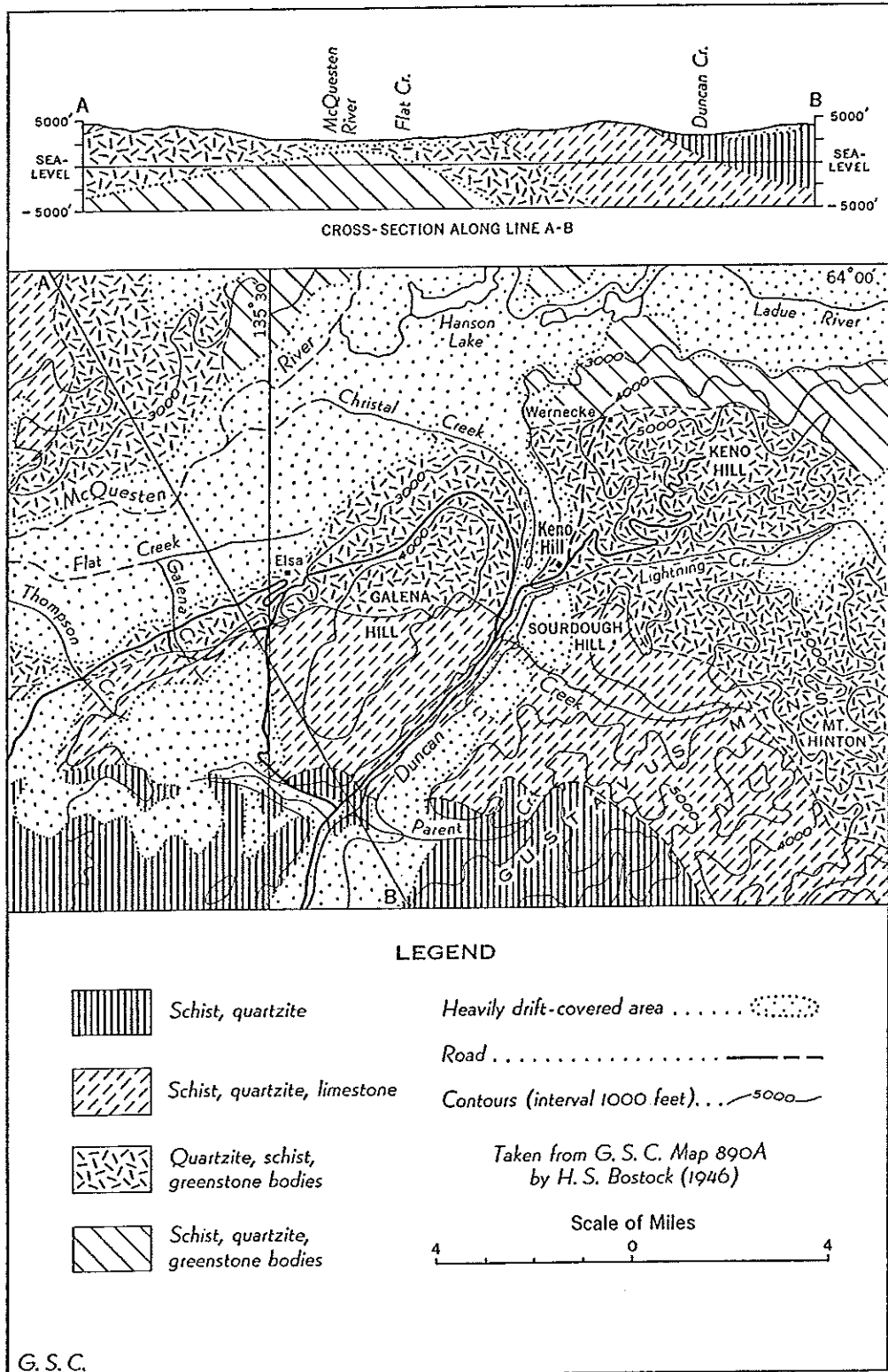


Figure 1. Geological map and cross-section of the Keno Hill-Galena Hill area, Yukon Territory.

Frost action and solifluction have had a marked effect on the rocks in all areas of permafrost. Rock float and in some places vein float are brought to the surface by frost action, and stone rings and stone rivers are widespread results of this phenomenon on the flat-topped parts of the hills. On the steep slopes of hills land creep has moved the outcrops of some veins 20 to 50 feet down the slope.

The consolidated rocks underlying the area belong to the Yukon group and may be Precambrian or Palæozoic in age. They consist of sericitic, chloritic, and graphitic schists and thick- and thin-bedded quartzites (Figure 1). Three formations, a lower schist formation, a central quartzite formation, and an upper schist formation, form the southern limb of a large anticline with an axis along the McQuesten-Ladue Valley. Conformable sills and lenses of greenstone occur in the lower schist and central quartzite formations, and limestone lenses are a common feature in the upper schist formation.

The silver-lead-zinc deposits of Keno, Galena, Sourdough, and Bunker Hills occur in brecciated fault zones where they cut thick-bedded quartzites and greenstones. The various types of schists and the thin-bedded quartzites appear to be unfavourable hosts for ore shoots. Two types of veins are recognized; an early vein type consisting of quartz, pyrite, and arsenopyrite, and a late vein type mineralized with siderite, galena, sphalerite, and freibergite. Both types may occur separately, or the early type may have been fractured and contain minerals of the second type.

The veins near the surface are highly oxidized. The depth reached by oxidation varies, but is rarely less than 50 feet. In some cases, as at the Bellekeno mine, oxidation effects are notable 500 feet below the surface. The minerals developed in the oxidized zone include limonite, various manganese oxides, calcite, gypsum, cerussite, anglesite, smithsonite, quartz, azurite, malachite, and oxides of arsenic and antimony. It is apparent that most of the oxidation in some veins took place prior to the permafrost, because ice veins occupy the solution channels that must have been the courses followed by the ground waters during the period of oxidation. In other veins, notably in the Ladue-Sadie-Friendship, Onek, and Hogan vein of the Mount Keno mine, underground waters are circulating freely. On the lower levels of the Calumet-Hector mine (United Keno Hill Mines) underground waters appear to be circulating below the permafrost. In these situations oxidation is proceeding at the present time.

The ores vary in their metallic content from property to property. The analyses given below are typical bulk analyses of ores from the principal mines.

Mine	Ag	Pb	Zn	Cu	Nature of ore
	oz/ton	%	%	%	
Hector-Calumet ¹	38.4	9.2	8.4	Unoxidized
Mackeno ²	37.03	7.29	5.05	0.04	Unoxidized ore
Bellekeno ³	59.26	7.25	1.51	0.08	Oxidized ore

¹ Analysis of developed ore—Annual Report, United Keno Hill Mines, 1953.

² Analysis supplied by George Esterer, Assayer, Mackeno Mines.

³ Analysis supplied by George Esterer, Assayer, Mackeno Mines.

DESCRIPTION OF STREAMS AND SPRINGS AND FACTORS
AFFECTING THE FLOW OF WATER

An ideal dendritic stream pattern, suited to a hydrogeochemical investigation, is exceptionally well developed (see Map No. 1), and practically the whole area is tapped by tributaries of McQuesten and Ladue Rivers and Duncan and Lightning Creeks. Springs are widespread, as shown by Map No. 2, being most numerous along the bases of the hills and at the heads of all gulches.

The flow and grade of streams differ, as shown by the following field measurements made on August 15, 1954.

Name of stream	Flow in gallons per minute	Grade in feet per mile
Lightning Creek above confluence with Duncan Creek (typical stream with large flow).....	18,600	160
Christal Pup Creek (Erickson Gulch) at road to Wer- necke (typical stream with medium flow).....	3,480	750

The springs also differ in size, some delivering a few gallons per minute, others tens and hundreds of gallons per minute. Some of the smaller streams and springs are intermittent and depend upon seasonal rainfall or melting of snowfields for their source water.

The streams of the area originate in one or other of two ways. Lightning and Christal Creeks have their origin in small lakes that act as reservoirs providing a fairly regular flow throughout the summer months. Both are joined by tributary streams that may produce fluctuations in the flow of the main stream during the spring months. Other creeks, such as Duncan Creek, Parent Creek, Thunder Creek, and the creeks in Faro and Silver Basin Gulches, are fed by a great network of tributaries that derive their water from normal run-off and innumerable springs.

Springs in the area originate in several ways. Some of those at the heads of the tributaries of the main streams are in wet muskeg and grassy areas and consist of a small pool of water fed by seepage from rainwater and the melting of the active layer¹ of the surrounding permafrost. The water in others issues from an orifice at the base of scree areas and accumulations of rock float and is derived from rainwater and the melting of snowfields and the active layer. This water in some places percolates through several hundred feet of loose rock, much of which contains vein float. The water in a few springs issues from fractures and faults in the headwalls of gulches and along rock bluffs. Below the permafrost underground waters issue from veins and faults into most of the mine workings. The origin of the water coming from the faults and fractures is uncertain, but it is probable that it represents surface water that has gained access to the vein and fault systems where permafrost is absent.

¹ The layer of surface soil that is subject to seasonal freeze and thaw is termed the active layer by Muller (Muller, Siemon W.: Permafrost and Related Engineering Problems; J. W. Edwards Inc., Ann Arbor Mich., 1945).

The flow of streams and most springs depends upon three factors: the amount of rainfall, the rate of melting of the snowfields, and the rate of thawing of the active layer. The flow of water in springs issuing from veins and faults is, in most places, remarkably constant, suggesting sources not influenced by the factors noted above. During the spring months and the early part of July the ground is frozen below a few inches from the surface and the rapid run-off after heavy rains that prevail during this period results in marked fluctuations in the flow of nearly all streams. During this period stream testing is not practicable as the sealing of veins by frozen ground does not allow the water to pick up metal and also because of the extreme dilution of any heavy metal that may have been dissolved.

The period from July 20 until September 1 is recommended for stream testing because the rainfall is reduced, the active layer has thawed down to a foot or more, and ice cementing scree and loose rock has thawed sufficiently to allow percolating waters access to vein float and the upper parts of veins. The run-off due to rainfall is also less rapid during this period because the water is retained by vegetation and the thawed ground, and is given up slowly to springs and streams.

FIELD AND LABORATORY METHODS AND PROCEDURE

GENERAL PROCEDURE

The project of water testing for heavy metals was divided into two parts—stream testing and spring testing. The samples of stream water were analysed in the field and those containing significant amounts of heavy metals were brought back and analysed accurately in a field laboratory specifically organized for the project. For the most part, the samples of spring water were collected in the field and analysed in the field laboratory. All samples for laboratory analysis were collected in 130 ml. polyethylene bottles that were washed out three times with the sample water.

SAMPLING PROCEDURE

The preliminary investigation of the stream waters in the southeastern part of the area was carried out by testing the major stream system, Lightning and Duncan Creeks, and then testing each of the tributaries flowing into these streams. The principal streams and tributaries draining the northern slopes of Keno and Galena Hills were tested in a similar manner.

The results of the preliminary investigation were plotted on the stream map of the area and specific areas for more detailed study were outlined. Sample locations on the tributary streams were planned on the topographic map and aerial photographs of the area in advance of field testing. However, during actual field operations it was sometimes necessary to alter the sampling procedure when dry tributaries were encountered or, more important, when a tributary was found that carried more heavy metal than the main stream. In all cases where a high concentration of heavy metal was found, it was traced upstream to its source. Special

attention was paid to points on the streams where known veins or their inferred extensions crossed the streams, and samples for analysis were taken above and below these points.

The springs in the Keno Hill area were located during the detailed investigation of the vein deposits. So far as possible all springs in one general area (e.g., those draining into Charity Gulch) were sampled in a period of one day or two days. Samples were taken from nearly all springs, and special care was taken to obtain samples from springs along known or suspected mineralized zones, veins, and faults. In a few cases samples of water from underground drill-holes and fault fissures were taken and analysed.

METHOD OF ANALYSIS

General Statement, Reagents, and Apparatus

The analytical method employed for testing the waters for heavy metal content was essentially that described by Huff (8). Some minor modifications were taken from Sandell (9) and were checked against standard solutions in the laboratory before being applied in the field. For a method using acetone as an alternative to the method of Huff the reader is referred to publications by Warren and Delavault (10).

The following reagents and apparatus were used in the field laboratory:

Reagents

Dithizone (diphenylthiocarbazone) stock solution, 0.016 per cent (weight/volume), prepared by dissolving 0.08 g. of dithizone in 500 ml. of reagent grade carbon tetrachloride. This solution was stored in amber-coloured, glass-stoppered pyrex bottles and kept cool in an underground storage room.

Dithizone, 0.0016 per cent (weight/volume), prepared as needed from the stock solution by diluting 10 ml. of 0.016 per cent dithizone solution to 100 ml. with reagent-grade carbon tetrachloride.

Metal free water was obtained from several sources. The field laboratory was equipped with a pyrex glass still that supplied pure water for the preparation of all reagents and standard solutions. A nearby stream, which showed no heavy metal detectable by the dithizone reaction, provided a convenient source of wash water. For use in the analytical procedure, the equivalent of triple distilled water was obtained from a Deeminac, Model 16-4, the trade name for a polyethylene bottle and filter containing Deeminite ion exchange resin, manufactured by the Crystal Research Laboratories, Hartford, Conn.

Acetic acid, 2 N, prepared by diluting 28.5 ml. of glacial acetic acid to 250 ml. with metal-free water.

Sodium acetate (2 N solution), obtained by dissolving 164 g. $C_2H_3O_2Na$ in metal-free water and diluting to 1 litre.

Acetate buffer, solution prepared by mixing nine parts 2 N sodium acetate solution and one part 2 N acetic acid. This solution must be purified by shaking with successive portions of the dithizone solution to remove all heavy metals. This buffer has a pH value between 5 and 6.

Ammonium hydroxide, 2 N, prepared by diluting 32 ml. concentrated C. P. NH_4OH with metal-free water to a volume of 250 ml.

Sodium thiosulphate, 1 N, prepared by dissolving 25 g. $Na_2S_2O_3 \cdot 5H_2O$ in metal-free water and diluting to 100 ml. Traces of heavy metals must be extracted with dithizone solution.

Potassium cyanide solution, 2 per cent solution of KCN (2 g. per 100 ml. of metal-free water) made ammoniacal by the addition of 15 ml. of concentrated C.P. NH_4OH per 100 ml. of KCN solution. This solution has a pH of 11. Any traces of heavy metals must be removed by shaking with dithizone solution. Note: this reagent is extremely poisonous. Care must also be taken not to acidify any solution containing KCN as this may produce the lethal gas HCN.

Hydroxylamine hydrochloride, 1 per cent solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in metal-free water prepared by adding 1 g. of reagent to 100 ml. water. The solution should be purified by shaking with dithizone.

Hydrochloric acid, concentrated C.P.

Zinc standard, 0.01 per cent in 0.1 N HCl, prepared by dissolving 0.1 g. reagent grade 30-mesh zinc in 10 ml. concentrated HCl and diluting to 1 litre. One ml. of this solution contains 100 micrograms of zinc (100 gamma, γ)¹. More dilute solutions can be prepared from the standard as needed.

Copper standard, 0.01 per cent, prepared by dissolving 0.2 g. of C.P. $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ in water, adding a few drops of H_2SO_4 and diluting to 500 ml. One ml. of this solution contains 100 micrograms of copper.

Lead standard, 0.01 per cent, prepared by dissolving 0.016 g. dry C.P. PbNO_3 in 100 ml. of metal-free water, containing one drop of concentrated HNO_3 . This solution contains 100 micrograms of lead per ml.

The amounts of reagents required for 1,000 determinations of heavy metals (copper, lead, zinc) in water are given below. These figures provide for the minimum quantity of reagents required and an extra quantity to take care of losses and repeat determinations.

Reagents Required for 1,000 Determinations of Heavy Metals in Water

	<i>Quantity</i>
Acetic acid.....	½ lb.
Ammonium hydroxide.....	½ lb.
Carbon tetrachloride.....	50 lbs.
Dithizone.....	2 g.
Sodium acetate.....	1 lb.
Sodium thiosulphate.....	2 lbs.
Potassium cyanide.....	2 lbs.
Hydroxylamine hydrochloride.....	25 g.
Hydrochloric acid, conc. C.P.....	1 lb.
Zinc metal pellets.....	¼ lb.
Copper sulphate.....	¼ lb.
Sulphuric acid, conc. C.P.....	1 lb.
Lead nitrate.....	¼ lb.
Nitric acid, conc. C.P.....	1 lb.

All the above reagents can be obtained from chemical supply houses.

Apparatus

pH indicator—1 pHyrion roll of test paper in dispenser, plus 3 refills.

5 graduated cylinders, 100 ml. glass-stoppered pyrex.

2 separatory funnels, 125 ml. Squibb type, glass-stoppered pyrex.

2 separatory funnels, 250 ml. Squibb type, glass stoppered pyrex.

4 volumetric flasks, 100 ml., 250 ml., 500 ml., 1,000 ml.

5 volumetric pipettes 5 ml.

1 volumetric pipette 25 ml.

2 serological pipettes, 10 ml., graduated in tenths of a ml.

¹ The gamma (γ) is equivalent to 1 microgram, and one gamma per millilitre equals one part per million (ppm.).

- 2 laboratory thermometers, Centigrade.
- 2 thermometers, Fahrenheit, pocket size.
- 12 colorimetric tubes, Nessler, short type.
- 1 Nessler tube rack.
- 2 Coleman gas stoves, pocket size.
- 1 alcohol burner.
- 1 pyrex wash bottle, 500 ml.
- 4 pyrex dropping bottles, 60 ml.
- 1 retort stand and clamp ring.
- 4 funnels and 1 funnel stand.
- Filter paper—15 cm. Whatman No. 42.
- 1 rubber bulb for pipette syringe.
- 2—10 ml. graduated cylinders pyrex, graduated in tenths of a ml.
- 2 Deeminae model 16-4 water purifiers.
- 1 All glass (pyrex) water distilling apparatus.
- 6 polyethylene bottles, 1 litre.
- 50 polyethylene bottles, 130 ml.
- Reagent bottles, beakers, balance, etc.

Laboratory Procedure

A. Determination of total heavy metal content:

The procedure used in the field laboratory for the determination of the total heavy metal content is described briefly below. For details the reader is referred to the three references given above. Dithizone is an extremely sensitive reagent and analyses must be done with the utmost care in order to reduce contamination to a minimum. All apparatus must be kept clean and check determinations should always be made.

1. Prepare three standards in clean Nessler tubes containing respectively 2, 2.5, and 3 micrograms of zinc in 50 ml. by appropriate dilution of the stock zinc standard. The method of reacting the standards with the dithizone is the same as that described in steps 2 and 3. The standards above are given only as an example. In practice the standards are varied to meet specific conditions. New standards should be made up frequently during colour comparisons because the colour of the dithizone layer fades with time.
2. Transfer 50 ml. of the water sample to be tested to a 100 ml. pyrex glass-stoppered graduated cylinder scrupulously cleaned first by washing with distilled water, testing with a few drops of dithizone, and then rinsing three times with the sample water.
3. Add 5 drops of acetate buffer followed by 5 ml. of 0.0016 per cent dithizone solution and shake vigorously for 1 minute, making sure that the reagents and water form a temporary emulsion. After shaking, allow the solutions to settle.
4. If the organic layer (the dithizone plus soluble dithizonates) changes from the initial green colour to red or a mixed colour, the presence of heavy metals is indicated. In this case proceed to step 5. If the organic layer remains apparently unchanged

(still light green) proceed to step 6 (note: a mixed colour is produced by red metal dithizonate plus unreacted green dithizone. This mixed colour varies from blue-green to blue to purple to purplish red depending upon the concentration of heavy metal present in the sample).

5. If heavy metals are indicated, clean the graduated cylinder thoroughly. Repeat step 4 using a sample of water such that when it is diluted to 50 ml. with pure water from the Deeminac, the colour obtained in the organic layer falls within the range of the standards prepared in step 1. Transfer sample and reacted dithizone to a clean 50 ml. Nessler tube and compare accurately with standards prepared in step 1. Report quantity of heavy metals present expressed as zinc in parts per million as outlined in the following example.

Example:

Quantity of water sample—20 ml.

(This water sample was diluted to 50 ml. by pure water from the Deeminac and reacted with dithizone.) The colour of the organic layer of the sample matched the colour of the organic layer of the standard containing 2.0 micrograms zinc after reaction with dithizone.

Total amount of zinc in standard = 2 micrograms.

This amount of zinc is contained in 20 ml.¹ of water sample.

Therefore, the amount of zinc per ml. of water sample = $\frac{2}{20}$ = 0.10 micrograms per ml.

This is equal to 0.10 ppm. heavy metal expressed as zinc (one microgram per ml. equals 1 ppm.).

6. If after completing step 4 the organic layer remains apparently unchanged (still light green), decant off some of the sample water and add more sample until a total volume of 100 ml. has been used. Shake vigorously as before. If the organic layer indicates a mixed colour carry out step 5 above, determining the amount of metal present by comparison with standards. If, however, the organic layer is still light green, proceed to step 7.
7. To the solution prepared in step 6 add two or three drops of 2N NH₄OH. Shake vigorously for 15 seconds and allow to settle. A colourless organic layer indicates that no heavy metal is present in the water. A pink colour indicates the presence of heavy metals; the amount can be estimated from standards or from the following colours.
 - Strong pink—0.02 micrograms per ml. = 0.02 ppm.
 - Weak pink—0.01 micrograms per ml. = 0.01 ppm.
 - Faint pink—0.002 micrograms per ml. = 0.002 ppm.

¹ Note that it is the quantity of sample taken that is used in the calculation and not 50 ml.

B. Supplemental differentiation method:

Copper group

1. Repeat procedure as for determination of total heavy metals, but use 0.5 ml. of concentrated HCl (approximate pH of 1) instead of the acetate buffer. The presence of a mixed colour in the organic layer indicates the presence of the copper group of metals. (Note: this group includes copper, silver, mercury, bismuth, gold, palladium, platinum, and thallium.) Each metal produces a characteristically coloured dithizonate. For details see Sandell and Huff. In the investigation described in this bulletin only the copper was differentiated in some of the samples.
2. Determine the concentration of copper by comparison with standards prepared from the standard copper solution.

Zinc group

1. Repeat the procedure as for the determination of total heavy metals, adding both the acetate buffer and 5 ml. of the 1 N sodium thiosulphate solution. A mixed colour after shaking indicates the presence of the zinc group. (Note: this group includes zinc, cadmium, and tin, each giving a characteristically coloured dithizonate.)
2. Determine the concentration of zinc by comparison with standards prepared from the standard zinc solution.

Lead group

1. Repeat the procedure as for the determination of total heavy metals, but add 5 drops of the 1 per cent hydroxylamine hydrochloride and 5 ml. of the ammoniacal potassium cyanide solution instead of the acetate buffer. Any colour left after shaking for 1 minute, other than a pale yellow dithizone oxidation product can be taken to indicate the presence of the lead group. (This group includes lead, tin, bismuth, and thallium.)
2. Determine the concentration of lead by comparison with standards prepared from the standard lead solution.

It was found that the above procedure worked successfully in the presence of up to 400 γ of zinc. The colours produced were a faint pink for 1 γ of lead and a strong pink for 5 γ of lead.

Field Procedure

For field analyses of total heavy metals a small testing kit was made up that contained the following: 2-100 ml. pyrex glass-stoppered graduated cylinders, 1 Deeminac water purifier, 1 pocket thermometer, 1 roll of pH indicator paper, 2 pyrex culture tubes marked to deliver 5 ml. of dithizone solution, three 250 ml. pyrex reagent bottles containing, respectively, the 0.0016 per cent dithizone solution, acetate buffer, and 2 N ammonium hydroxide, and one 50 ml. pyrex dropping bottle of 2 N ammonium hydroxide.

The method of analysis was the same as that described above for the laboratory determination of total heavy metals except that standards were not used. Graduates were easily cleaned by washing them out several times in the stream water at the point of sampling. The concentration of heavy metals was determined by visual estimation of the mixed colour obtained in an appropriate volume of the sample. The monocolour method was used if no visible colour change had occurred in the dithizone after the addition of 100 ml. of sample. Table I is given as a colour guide, but it is recommended that the operator familiarize himself with the colours by preparing various standard solutions and reacting them with dithizone as outlined above in A.

The heavy metal concentrations were recorded as micrograms per ml. (γ) of original sample and as parts per million of zinc. The temperature and pH of each sample were recorded.

TABLE I
Colours of Organic Layer Obtained with Standard Zinc Solutions

pH of extraction	Micrograms Zn per ml. (ppm.)	Colour of organic layer in strong white transmitted light
Mixed colour range; pH 5.5 obtained by adding acetate buffer.....	1.00	Red
	0.50	Light purplish red
	0.20	Light purplish red
	0.10	Light purplish red
	0.08	Light red-purple
	0.06	Light purple
	0.04	Pale blue-grey
	0.02	Light blue-green
	0	Light green
	Monocolour range; pH 9.0 obtained by addition of ammonium hydroxide to mixed colour test.....	0.02
0.01		Weak pink
0.002		Faint pink
0		Colourless

RESULTS OF THE INVESTIGATION

GENERAL

The heavy metal content of the streams in the area investigated is shown on Map No. 1 and that of the springs and streams on Keno Hill and the surrounding area on Map No. 2. On these maps and on the figures referred to below the heavy metal content is expressed as parts per million of zinc, an acceptable practice as analyses in the field laboratory showed that zinc is the principal heavy metal present in most stream and spring waters.

Copper was found in six samples, all of which came from the same area, Basin Creek (Figure 2), and did not exceed 1.00 ppm. Lead was detected in only five samples, from two areas, upper Faro Gulch and Silver Basin. Both lead and copper were detected only in waters with a relatively high heavy metal content as shown by the following table:

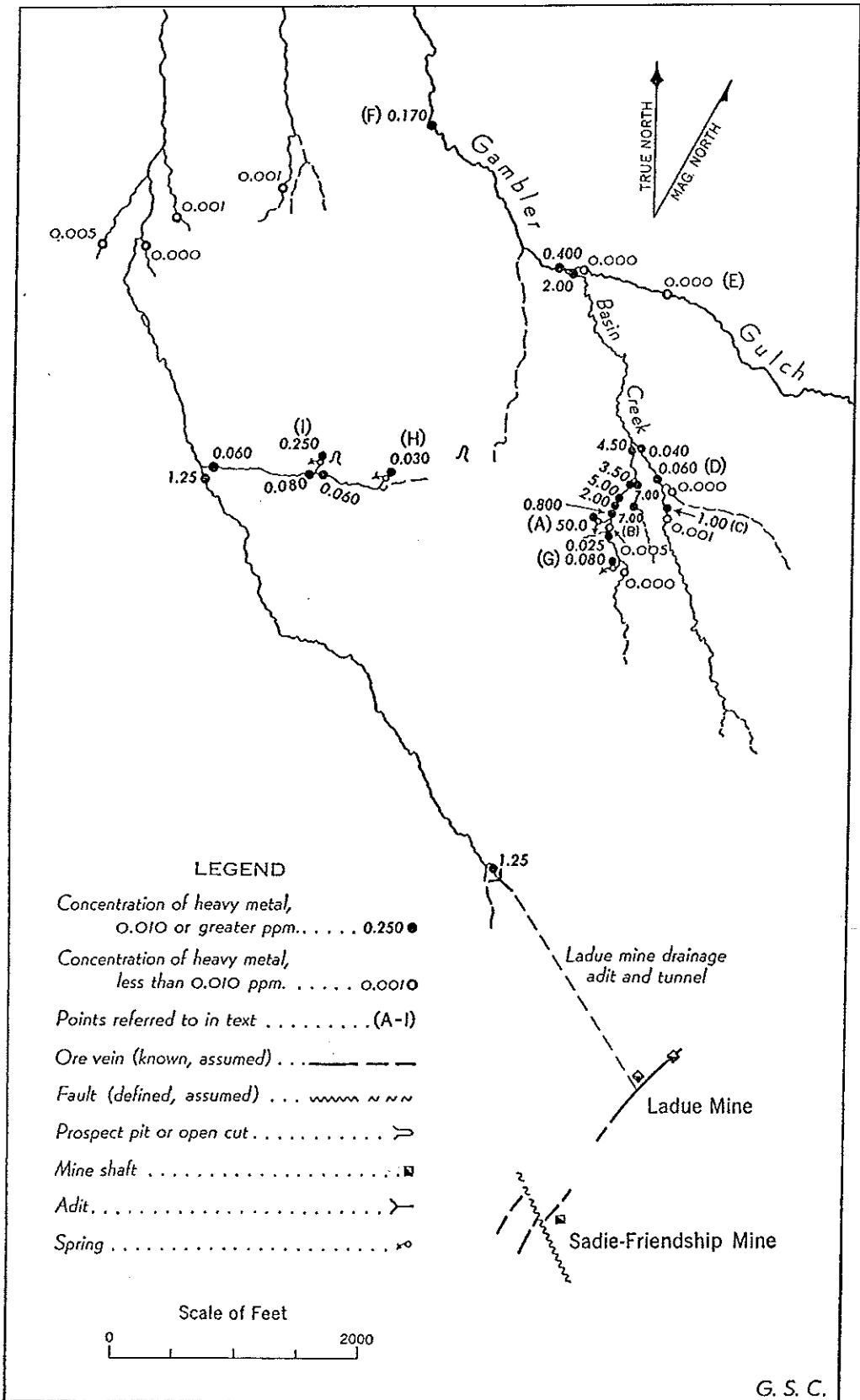


Figure 2. Heavy metal anomalies in the streams in the Gambler Gulch area, Keno Hill, Yukon Territory.

G. S. C.

Analyses of Water for Copper and Lead

Total heavy metal (ppm.)	Copper (ppm.)	Lead (ppm.)
1.25	—	0.05
1.25	—	0.05
4.00	—	0.01
0.20	—	0.02
0.06	—	0.01
1.00	0.08	—
50.00	1.00	—
3.00	0.05	—
0.80	0.03	—
2.00	0.06	—
5.00	0.085	—

The principal cations in the spring waters are Fe, Ca, Mn, Mg, Al, Na, K, Zn, Cu, Pb, Ba, Sr; the anions are SO_4^{2-} and CO_3^{2-} and probably $(\text{SiO}_3)^{2-}$. The concentration of both cations and anions varies over a wide range. In most spring waters, especially those derived from the melting of the active layer and snowfields, only the cations zinc and rarely lead and iron are detectable; the sulphate anion is generally present, but the carbonate and silica anions could not be detected. In some springs where the heavy metal content is high and in the underground waters issuing from faults and fractures into the mine workings, both the cations and anions noted above are readily detected. A partial analysis made by the senior author of a sample of water from a spring in the Basin Creek area is given in the following table.

Partial Analysis of Spring Water, Basin Creek Area

	ppm.
SO_4	258
Cl	None detected
CO_3	Strong trace
NO_3	None detected
Fe	4
Mn	0.92
Zn	2.00
Cu	0.06
pH (at source)	6
Temperature (at source)	3°C.

A spectrographic analysis¹ of the residue from the above sample after evaporation yielded the following results:

Range	100-10%	10-1%	1-0.1%	0.1-0.01%	0.01-0.001%	Not found
	Mg	Al	Fe	B	Co, Cu	Rb, Ag
	Ca	Si	Mn	Zn	Ba, Sr	Pb, Cd
			Ni	K	Cs	Sb, As
			Na	Li		

¹ Analysis by spectrographic laboratory, Geological Survey of Canada.

Analyses of the heavy metal content of the natural precipitate at the orifice of one of the springs of Basin Creek and at 2,000 feet from the orifice are given below.

Sample number	Description	Heavy metal content as zinc in ppm.
6	at orifice	1,000
7	2,000 feet from orifice	600

In the stream waters the cations detectable in normal samples of the water are Zn and rarely Fe; sulphate is the only anion easily detected. Chloride and carbonate were tested for in some stream waters, but could not be determined by ordinary methods.

Most stream waters and a few spring waters contain organic complexes, the composition and nature of which are unknown. In some cases these organic complexes cause minor difficulties in the heavy metal dithizone reactions, probably due to oxidation of the dithizone. Addition of a small amount of ammonium citrate or a drop of nitric acid to complex or destroy the organic compounds seemed to reduce the effect of the interfering compounds.

The temperature of the waters tested varied from 0.5 to 17 degrees Centigrade. The pH of all samples was 5 or 6 with one exception, a spring in Basin Creek had a pH of 4.

HEAVY METAL ANOMALIES IN STREAMS

Significant heavy metal anomalies were found in the following streams: Basin Creek, streams in Faro and Silver Basin Gulches, Duncan Creek, and Parent Creek. These anomalies are discussed in detail below and are followed by a brief discussion of small anomalies found in several other streams.

Basin Creek Area

Basin Creek is on the northwest lower slope of Keno Hill below and north of Wernecke. Its location relative to Gambler Creek is shown on Map No. 2 and on Figure 2. No ore veins are known to occur in the immediate vicinity and the nearest prospect pits, which contain no visible mineralization, are 1,500 feet to the west.

The basin in which the streams occur lies between the main slope of the hill and a long steep ridge about 75 feet high, lying roughly parallel with it. The rocks underlying the basin are graphitic schists and phyllites containing abundant 'blowouts' and lenses of white quartz. Farther west along the ridge, a thin sill of fine-grained rhyolite forms the cap rock. Another prospect was opened up here, but the adit and numerous shafts encountered only rhyolite and barren quartz veins. The abandoned Ladue-Sadie-Friendship mine, formerly a producer of lead and silver, is

located 4,500 feet up slope in a southerly direction from the basin. The drainage adit from this mine empties water into a small creek that passes some 3,000 feet west of the basin.

The investigation of the anomalies in this basin provides an excellent example of finding, by hydrogeochemical methods, the source of the heavy metal content of the water in a stream system. The first indication of possible anomalies in the Basin Creek area was obtained when a water sample from the east branch of Basin Creek was tested during a preliminary survey of a large part of the north slope of Keno Hill. This sample showed a total heavy metal content of 0.060 ppm. (see Figure 2, D), whereas the regional normal background value had been determined as less than 0.005 ppm. The eastern extent of the "anomalous area" was tentatively established after a sample taken from Gambler Gulch at (E) gave negative results. Later work corroborated this assumption when no high values were found along Gambler Gulch and its tributaries upstream from (E).

Following the initial tests, a detailed systematic investigation of the water in Basin Creek, its tributaries, and Gambler Gulch below the confluence of the former, was carried out. From (F) on Gambler Gulch, the heavy metal concentration was found to increase consistently with each sample upstream to three major sources (A), (B), and (C). Beyond these points the heavy metal concentration dropped to the background value except in one stream where low heavy metal concentrations persisted upstream to a possible fourth source in a spring (G). Above this point no metal could be detected in the water.

It was also noticed that water with a high heavy metal content in this stream system is extremely cloudy, due to incipient precipitation of dissolved sulphates and carbonates. Furthermore, the stream bed and nearby banks are coated with yellow to dark reddish brown iron and manganese compounds. This physical 'colour tracer' is pronounced where the crystal clear water of the stream in Gambler Gulch joins the cloudy water from Basin Creek, and the intensity of the cloudiness of the water and the amount of precipitates on the rocks increases markedly upstream to the three sources described above. Furthermore, all the vegetation and trees in a zone 10 feet on each side of the stream and 100 feet below (A) have been killed, presumably by the large concentration of dissolved material in the water. The fact that vegetation once grew in this zone suggests that the spring at this point has only recently broken through the permafrost zone or that it has received a sudden surge of water causing the stream leading away from it to overflow its banks and poison the plants.

An investigation was made of the discontinuous streams draining the west end of the basin and emptying into the relatively large stream rising at the adit referred to on Figure 2 as the Ladue drainage adit. The streams were found to contain significant amounts of heavy metal as shown on Figure 2. The exact location of the source springs was difficult to determine owing to the absence of clearly defined stream channels through the extensive muskeg at this end of the basin. However, two sources were located at points (H) and (I). The relatively high concentration of heavy metal in the water coming from the spring at (I) is

probably the principal source, although other sources farther upstream should not be discounted because of the greater volume of water in the stream than in the spring.

Analyses of the water from the Ladue drainage adit showed 1.25 ppm. heavy metal to be present, an amount one would expect in water coming from a mine still containing zinc minerals. Because of this high heavy metal concentration no further work was done on this stream.

A final traverse of the Basin Creek area was made along the base of the north slope of the ridge forming part of the basin. The three streams tested showed no significant amounts of heavy metal in the water.

Faro Gulch Stream System

The testing of streams in Faro Gulch was initiated primarily to determine the applicability of hydrogeochemistry in the Keno Hill-Galena Hill area. The gulch and its headwall have been thoroughly prospected and several veins have been found and investigated by underground workings. Among these veins the No. 9 vein in the headwall was the most important producer of lead and silver during the early history of the camp. The streams in Faro Gulch, therefore, provided an excellent 'standard' by which other stream systems could be compared.

The system provided another clear cut example to illustrate the uniqueness of hydrogeochemistry in tracing metal to its source. The first sample was taken from the main stream 3 miles down from the headwaters in the gulch (*see* Map No. 1) where the heavy metal content was 0.06 ppm. Subsequent sampling showed a steady increase in values up the main stream and into the western sector of the gulch (*see* Figure 3). The streams in the eastern sector did not contain any detectable heavy metal.

The streams in the western sector follow a complex braided pattern probably with several sources, but most of the water feeding the streams comes from two springs relatively high in heavy metals. Some heavy metal in these springs is undoubtedly derived from the numerous veins in the headwall of the basin. The rest has been picked up by water leaching the large amount of rock and vein float that has developed by natural disintegration and mining on the steep slope of the headwall.

Silver Basin Stream System

The results obtained from the stream waters in Silver Basin Gulch were significant but not as striking as those from Faro Gulch. Only the samples taken above the large eastern tributary showed anomalous values; below this tributary the heavy metal was diluted beyond detection by ordinary methods. Heavy metal anomalies in a stream system such as this can only be found by detailed work because they would not be indicated by a general geochemical survey in which tributary streams are tested only at their junction with a main stream system.

The apparent sources of most of the heavy metal in the Silver Basin stream water are the numerous small veins on the western rim and in the headwall of the gulch. Some heavy metal may, however, have been contributed by vein float on the steep slope of the gulch.

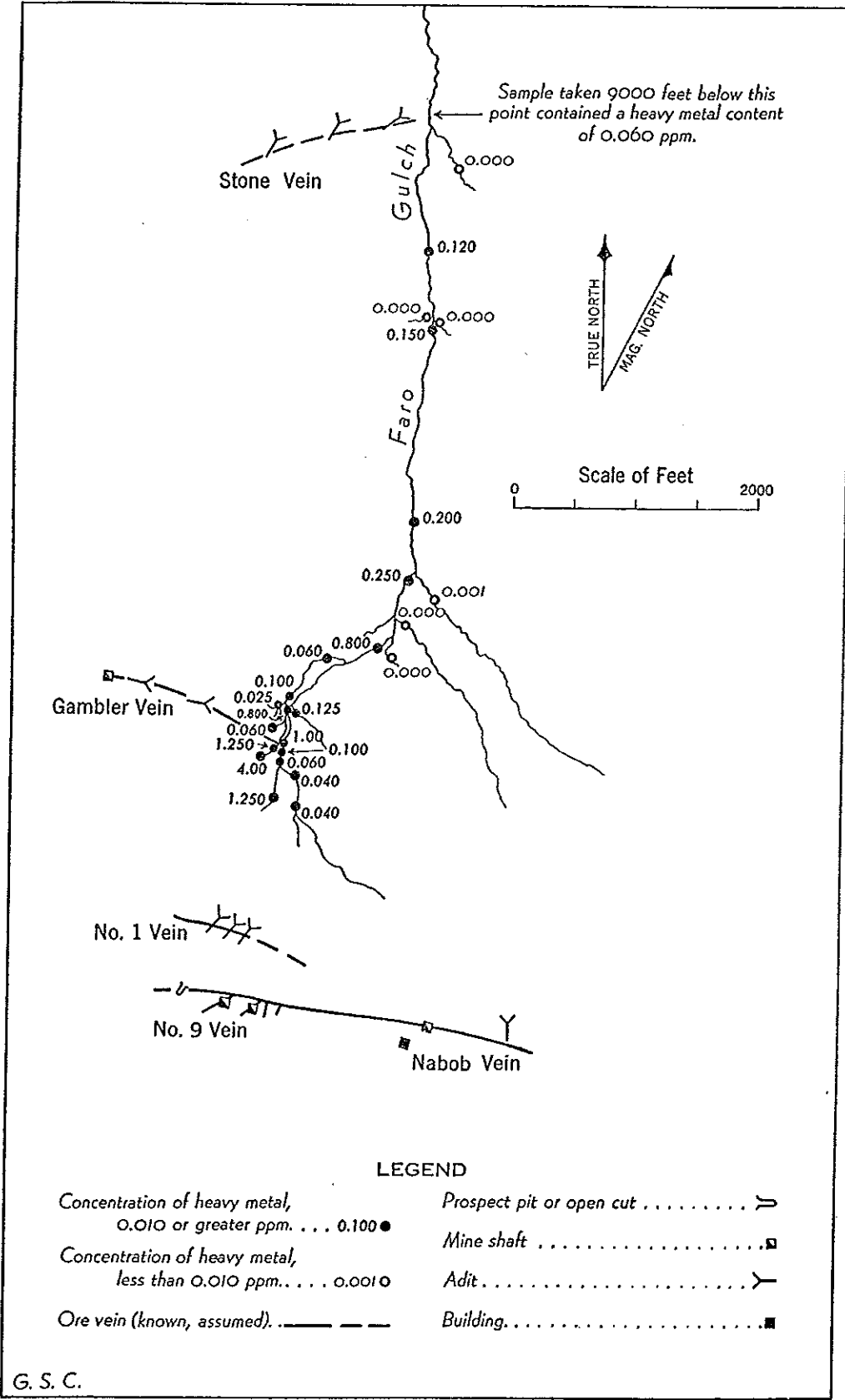


Figure 3. Heavy metal anomalies in the streams in the Faro Gulch area, Keno Hill, Yukon Territory.

Duncan Creek Stream System

A small anomaly was found in Duncan Creek at its junction with Lightning Creek during the preliminary survey. In view of the large volume of water in Duncan Creek at that time, this anomaly appeared significant and the stream was sampled in detail. The results (Map No. 1) show that the heavy metal is most probably contributed to the stream by a pyrite-pyrrhotite-sphalerite vein (property 25) that apparently crosses the stream as shown on the map. Above this point the heavy metal concentration decreased to zero and no anomalies were found in the rest of the stream system.

Parent Creek Stream System

Parent Creek was chosen as one of the best stream systems for hydrogeochemical investigation in an area where no mineralization was known. This drainage system forms a well-developed dendritic pattern of main stream and tributaries, flowing through a geological setting similar in some respects to that in areas known to be mineralized. Furthermore, the area drained by the system has not been extensively prospected and there are no prospect pits, shafts, or adits exposing vein material as are scattered over most of the other areas covered by the watertesting project.

The preliminary survey of Duncan Creek showed no significant anomaly at the mouth of Parent Creek. It was decided, however, to investigate the stream because it was evident that the large volume of water in the creek would dilute any large concentrations of heavy metal beyond detection within short distances from their source.

The first significant sample was collected at Station (R) (*see* Figure 4). The concentration of heavy metal had increased from 0.001 ppm. at the mouth of the creek to 0.010 ppm. at this point. The concentration continued to increase up the main stream to (T), thence up the northeast tributary branch to a spring at (X). No tributary below this point carried any detectable heavy metal. Upstream from the spring at (X), the heavy metal decreased in amount for several hundred feet and then gradually increased again up to point (Z). Beyond this point no metal could be found, and most of the water was coming from a small snowfield.

The physical appearance of the water containing the high heavy metal content was similar to that found in Basin Creek, with some exceptions, suggesting a somewhat different chemical and geological source. The cloudy water was first noted at point (S) and could be traced visually to point (W) with a marked increase in cloudiness after the confluence at (T) was passed. A greyish tan precipitate in the stream bed similar to that found in Basin Creek extended from (U) to a point some 600 feet upstream. Another distinguishing feature was a reddish brown to orange iron stain on the rocks in the stream from the point (V) to the spring at (X). Near point (Y) a body of graphitic schist is cut by the stream. This body has a strike approximately perpendicular to the direction of the stream flow and consists of limonite and schist fragments cemented with limonite. The origin of this fragmental material is uncertain. The topography and lineaments on air photographs suggest a series of faults in the general vicinity.

Other Stream Systems

Several other streams exhibit small local anomalies in their heavy metal content. Some of these streams are either small with an intermittent flow or cannot be traced due to their discontinuous nature. Other streams have so large a flow of water that the heavy metal content is diluted beyond the normal means of detection.

One of the streams flowing north into Gambler Lake and draining the lower slopes of Keno Hill northeast of Gambler Creek was found to contain a slightly higher than normal amount of heavy metal (0.03 ppm.). This anomaly decreased slightly 300 feet upstream and could not be followed farther because of the absence of surface water.

A small stream 2 miles east of Silver Basin Gulch yielded anomalous values in heavy metal probably derived from a mineralized zone not far distant. This stream (called Cascade Creek for identification purposes on the map) drains part of the north slope of Beauvette Hill. It has cut a narrow gorge into the black schist bedrock and drops some 100 to 150 feet in a series of nearly vertical cascades. As Map 2 shows, the heavy metal content increases from 0.005 to 0.040 ppm. The latter value was obtained from a water sample taken from the lowest cascade and appeared to be coming from a fracture in the rock west of the main flow of water. The water above this point gave lower but still relatively high values. The geological environment suggests mineralization, as the schist is heavily iron stained and abundant float of limonite and breccia occur in the vicinity.

Another anomaly in this general area was found in Allen Creek, just above its confluence with Faith Creek. The volume of water flowing in both these creeks is very high and the 0.003 ppm. of heavy metal detected in Allen Creek is probably significant, as no metal could be detected in Faith Creek. The source of the heavy metal in Allen Creek was not investigated, due to lack of time, but it should be noted that this creek drains a favourable area of greenstones and quartzites in which veins might occur.

Tests made up Faith Creek gave negative results until the upper section of Faith Gulch was reached. The significantly high results found in the southern tributary were presumably derived from the three veins shown on Map 2. These same veins were apparently supplying heavy metal to the headwaters of Hope Gulch, as even higher values were determined in the stream flowing down that gulch. This anomaly was not indicated by tests made on this stream just above its confluence with Lightning Creek.

Despite the relative abundance of known veins above the headwaters of Charity Gulch, only one small tributary stream was found to contain a significant amount of heavy metal. This low concentration was diluted beyond detection downstream, so that preliminary testing of the water in Charity Creek at its junction with Lightning Creek found no metal present.

Almost identical results were obtained from the water analyses in Erickson Gulch. No heavy metal was detected in the stream from its junction with Christal Creek upstream to within 1,500 feet of the head-

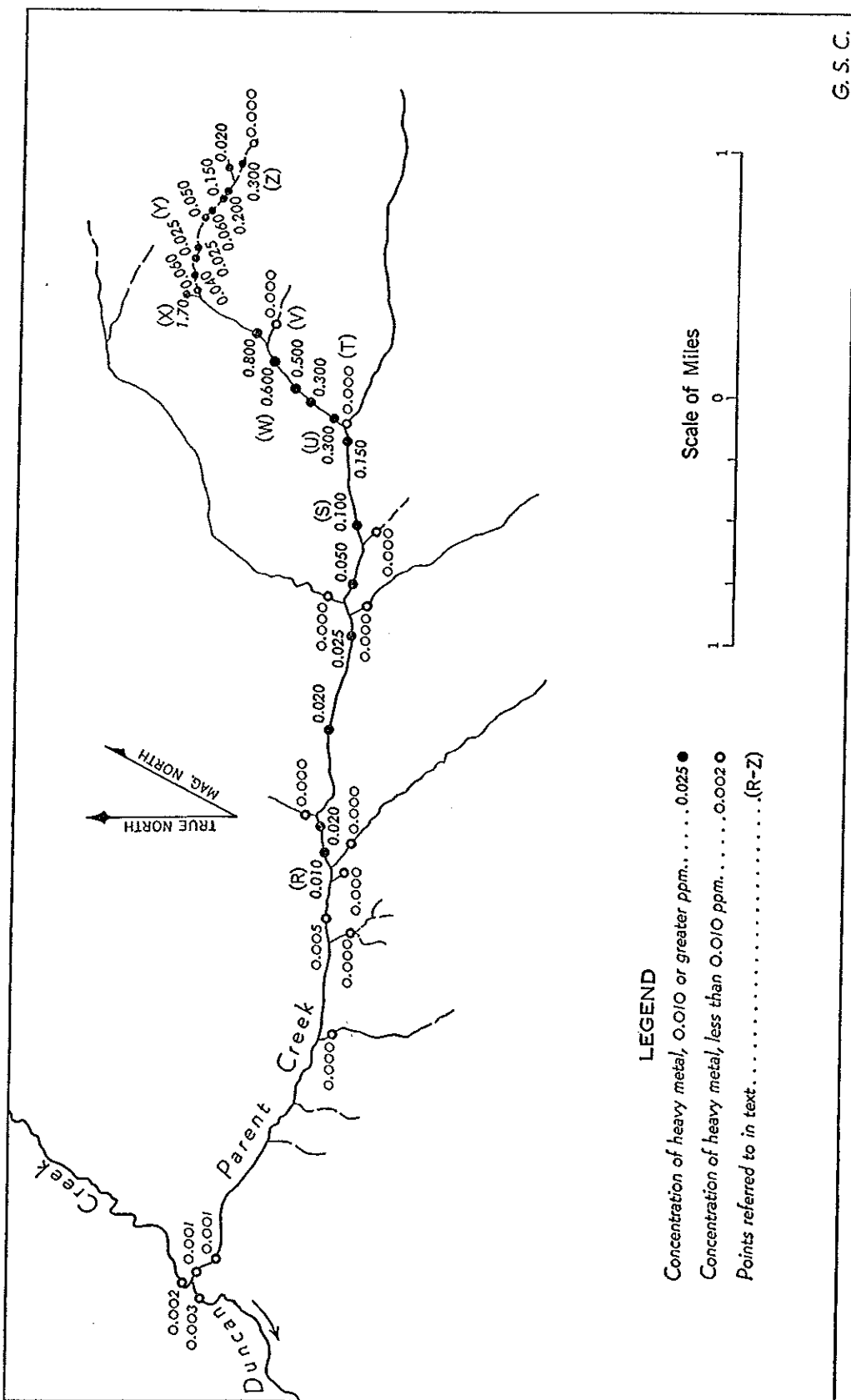


Figure 4. Heavy metal anomalies in the Parent Creek stream system, Yukon Territory.

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waters. From this point upstream the position of concentrations of heavy metal indicates that the metal in the northeastern tributary came from the Shamrock vein and that in the eastern tributary possibly from the inferred southwestern extension of the same vein. However, in the eastern tributary another source is probable as the concentration of heavy metal drops only slightly above the point where the vein extension should cross the stream. A high heavy metal content was found for 1,000 feet upstream from this vein extension; beyond there no heavy metal was detected.

The effect of severe dilution on the heavy metal content is well illustrated by results obtained from water testing on Lightning Creek a mile downstream from the town of Keno Hill. At this point the assumed extension of the pyrite-sphalerite vein investigated at the Moth (property No. 16) crosses Lightning Creek. The heavy metal content of the main stream is not appreciably increased below the vein (0.001 ppm., as against 0.000 ppm. above). However, a small tributary crossing the vein on the west side of the main stream was found to contain 0.08 ppm. heavy metal.

HEAVY METAL ANOMALIES IN SPRINGS

The springs contributing significant amounts of heavy metal to the stream systems of Basin Creek, Faro and Silver Basin Gulches, Parent Creek, and Cascade Creek have been described in the previous section. Several other springs on Keno Hill (Map 2) contribute anomalous amounts of heavy metal to the stream systems. Some of these are the points where surface waters issue after leaching extensive accumulations of scree, much of which contains vein float derived from nearby veins; others mark the orifices of underground channels and are generally located in fractures, veins, or faults.

Near Wernecke two springs were contributing anomalous amounts of heavy metals to a small stream. One of these, 1,000 feet southwest of the Sadie-Friendship shaft along the Keno Hill-Wernecke Road, contained 0.040 ppm. heavy metal and issued from an underground channel probably following a fault. The source of the metal is undoubtedly the old Sadie-Friendship vein system. The other spring, 1,500 feet southeast of Wernecke, contained 0.013 ppm. heavy metal and showed little variation during the month of August. The water issuing from this spring leaches a large volume of quartzite scree below a prominent rock bluff. A detailed study of the geology suggests that this bluff may mark a vein from which the spring may derive its heavy metal. Three caved adits, showing some massive siderite on their dumps, have been driven in the bluff above the spring and appear to have explored a fracture or fault above the suggested vein. When the water samples were taken, these adits were visited to ascertain if they were contributing metal, but they were found to be dry, and it is unlikely that any metal was coming from this source.

On the Wernecke Road some 2,000 feet north of Keno Hill townsite, a pool of water apparently fed by springs from a muskeg area showed 0.015 ppm. heavy metal. The only visible spring in this area tested negative, however, and the source of the metal is unknown.

Two springs in the Bellekeno area showed anomalies in heavy metal content. One, midway between Keno Hill townsite and the Bellekeno mine, issues from a schist area along the road and contained 0.040 ppm. heavy metal. The source of the metal is unknown. The other, 400 feet below the lower adit of the Bellekeno mine, probably derives its heavy metal from the principal Bellekeno vein.

Numerous springs and water issuing from adits on the top of Keno Hill showed anomalous values, as shown on Map 2. Some of the springs indicate the presence of nearby veins. One spring northwest of the junction of the roads leading to the Shamrock and No. 9 contained 0.017 ppm. heavy metal and may indicate a possible extension of the No. 1 vein.

Northeast of the Nabob adit a spring issues from beneath a large accumulation of quartzite scree and contained 0.125 ppm. heavy metal, probably derived from an extension of the Nabob vein.

A spring and small stream some 2,800 feet southeast of the Stone vein (property No. 13) was found to contain 2.00 ppm. heavy metal. The source of the metal in this area is unknown for ore veins have not been found in the immediate vicinity. The area should be investigated, however, because the small stream crosses a favourable greenstone body and lineaments on air photos suggest the presence of northeast faults.

Several springs issuing from faults into the underground workings of the mines were analysed for heavy metals. The following table gives the heavy metal content of these springs and a short description of each.

Heavy Metal Content of Underground Springs

Sample number	Heavy metal content as zinc in ppm.	pH	Temperature °C.
1	0.06	5	3
2	0.30	—	—
3	0.01	6	2
4	0.10	6	2
5	0.02	6	2

Notes:

- 1 Spring in fault at end of eastern crosscut, Klondike-Keno adit. Fault may intersect southern extension of Sadie-Friendship vein system. Abundant iron precipitates on crosscut walls.
- 2 Spring in highly fractured quartzite marking fault at northeast end of Onek drift. Abundant iron precipitates on drift walls.
- 3 Water issuing from drill-hole at end of 3,900 crosscut, Runer vein, Mount Keno mine.
- 4 Water issuing from drill-hole cutting Hogan vein, Mount Keno mine. Abundant iron precipitates on crosscut walls.
- 5 Drill-hole, northeast crosscut, 3,300 level Mount Keno mine. Abundant iron precipitates on crosscut walls.

These underground springs show conclusively that considerable amounts of heavy metal are moving in the underground waters in both the veins and faults. They also indicate that iron and other elements are moving in the waters. The precipitates at their orifices are almost identical with those found in Basin Creek, Silver Basin, Cascade Creek, and Parent Creek, suggesting similar origins for all springs of this nature in the area.

DISCUSSION OF RESULTS WITH NOTES ON THE CHEMISTRY OF THE SPRING WATERS

Springs in the area fall into two distinct types, on the basis of their heavy metal content and general characteristics. One type contains an abundance of dissolved salts, a general high heavy metal content, and forms a characteristic iron and manganese precipitate near the orifice. This type contributes heavy metal to Basin Creek, Parent Creek, Cascade Creek, and Silver Basin, and occurs in the underground workings of the mines.¹ Those in the mines occur in faults and fractures in or near ore veins and have undoubtedly derived their dissolved load from these veins. The origin of those at the surface is uncertain, but they show identical characteristics with those found underground, and it seems highly probable that they represent the surface outlet of underground waters that follow faults and veins. These springs are manifestations of the underground waters that are circulating in fault and fracture systems below the permafrost zone.

The second type of spring contains very small amounts of dissolved salts, a low heavy metal content, except locally, and forms no characteristic precipitate. These springs occur in wet areas and at the bases of scree accumulations. They appear to derive their heavy metal content by leaching the near surface parts of ore veins and from vein float in scree areas. They originate from near surface waters that are moving above the permafrost zone.

The stream map shows that some ore veins produce anomalies in the heavy metal content in the streams in their vicinity. Other ore veins do not produce anomalies in the heavy metal content of nearby streams. An example is the failure of the Calumet-Hector, Elsa, and No Cash veins to produce anomalies in the streams draining the northwestern slope of Galena Hill. Dilution or precipitation of the heavy metal may be the reason for these failures. Further work is required in this area.

In the case of the Calumet-Hector vein cited above, springs tested in the vicinity of the deposit contain high values. The distance from these springs to the headwaters of streams downhill is a mile or so, however, and opportunity for precipitation of the heavy metal or dilution by other surface water is so great that the concentration of heavy metal is too low to detect in the streams. The reasons why the Elsa and No Cash veins do not produce anomalies are unknown.

In other places dilution undoubtedly causes the absence of any anomaly. Neither the Bellekeno nor Mount Keno systems of veins show up in Lightning Creek because the volume of water flowing in this

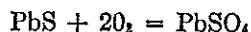
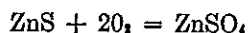
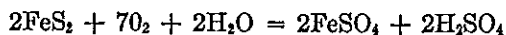
¹ L. H. Green, Geological Survey of Canada (personal communication) has found similar springs in quartzites in the Scougale Creek area, northeast of the area covered in this investigation.

creek is so great that the effect of any small stream or spring contributing heavy metal is lost. Another cause in many places is the lack of both surface and underground water to leach the vein systems. This may occur during periods of dry weather or in areas where underground circulation of water is prohibited by permafrost.

The chemical results show that zinc is the principal heavy metal cation carried in the water and sulphate the main anion. The presence of zinc is to be expected because zinc is the only heavy metal with a soluble sulphate present in sufficient quantities in the deposits. (Solubility of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ —117.5 gms. per 100 ml. at 40°C .) Copper sulphate is also soluble (14.3 gms. per 100 ml. at 0°C .), but copper is present in only small amounts (0.04 per cent) in the deposits and is unlikely to be present in most waters in detectable amounts. Lead is present in larger amounts than zinc in the deposits, but owing to the low solubility of PbSO_4 (0.00425 gms. per 100 ml. at 25°C .) it would be present in most water in only infinitesimal amounts.

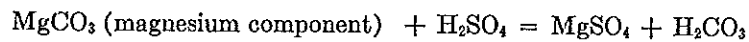
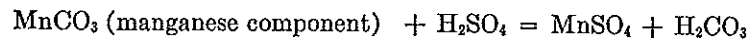
The chemical and spectrographic analyses of the spring water heavily charged with salts show that magnesium, calcium, alumina, silica, the alkalis, iron, cobalt, nickel, boron, barium, strontium, and the heavy metals zinc and copper are moving in the underground waters. All these elements are present in the vein minerals or crushed rock in the fault zones, and it seems probable that they were picked up by the underground waters during the oxidation processes outlined below. The presence of nickel in the evaporated precipitate is to be expected as the siderite gangue of the veins, from preliminary spectrographic analyses, is known to contain nickel and probably also cobalt. The presence of these elements in carbonates is normal, Ni^{2+} and Co^{2+} substituting for Fe^{2+} in the siderite structure.

The oxidation phenomena in the veins and the chemistry of the underground waters may be briefly summarized for the purposes of this report. The details remain to be worked out, but the general process appears to be clear. The primary ore veins contain manganiferous siderite, galena, sphalerite, pyrite, and freibergite. The sulphides in the veins are attacked by the oxygen-bearing waters, producing soluble sulphates in the case of sphalerite, pyrite, and freibergite. Some free sulphuric acid is liberated during the reactions. The equations illustrating the oxidation process for pyrite, sphalerite, and galena are given below:



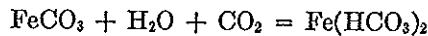
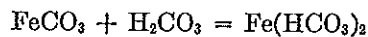
The iron and zinc sulphates formed during the oxidation processes are soluble and move with the circulating water. Any copper sulphate formed during the oxidation of freibergite will do likewise. The lead sulphate is, however, immobilized by its low solubility and forms anglesite, which is common in the oxidized parts of the veins.

The free H_2SO_4 attacks the siderite according to the following reactions:



All the sulphates formed in the above reactions are soluble and migrate with the underground waters.

The carbonic acid produced during the acid attack on the siderite plus atmospheric carbon dioxide dissolved in the percolating waters is responsible for the solution and transport of some Fe, Mn, Mg, and Ca by forming soluble hydrogen carbonates. The reactions for the iron component in the siderite is relatively simple:



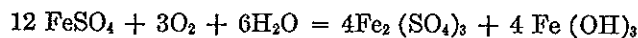
Similar reactions would occur for the manganese, magnesium, and calcium components.

The presence of H_2SO_4 and H_2CO_3 in the underground waters would facilitate the chemical breakdown of the numerous silicate minerals in the wall-rock and gouge of the faults and veins. Sodium, potassium, and alumina would be taken into solution and transported as either the sulphate or carbonate; silica is probably transported as the $(\text{SiO}_3)^{2-}$ anion in solution (11).

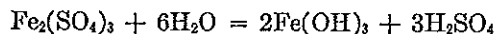
The effects of pressure, temperature, pH, and the formation of complexes have not been discussed in any of the above reactions, principally because the variations in the factors and types of complexes formed are unknown. In most cases the temperature and pH of the underground waters were constant; in nearly all localities the pH was 5 to 6 and the temperatures varied from 0.5 to 5°C. The pressure would rarely exceed 75 atmospheres in any vein system (pressure equal to a water column 2,500 feet in height). The relatively low temperature and moderate pressure compared to surface conditions would promote the solubility of CO_2 and hence the solubility of carbonates.

The iron and manganese precipitates at the orifices of the underground springs are composed of hydroxides, sulphates, and oxides (probably limonite). Precipitation near the orifices is due to a change in conditions; the pressure is reduced thus allowing the escape of CO_2 , with consequent precipitation of CaCO_3 , MgCO_3 , etc.; furthermore, the solutions have access to the free oxygen of the atmosphere.

Ferrous sulphate in the presence of oxygen is oxidized to ferric sulphate and ferric hydroxide, as shown by the following reaction:



According to Mellor (12), ferric sulphate is hydrolyzed in aqueous solution, forming first basic salts, which are ultimately converted into ferric hydroxide. The final reaction would be:



The insoluble ferric hydroxide is probably responsible in part for the turbidity of the water near the orifices of the springs and constitutes part of the precipitate found on the rocks and vegetation. The remainder of the precipitate is composed of sulphates of iron and calcium together with other compounds. These may have been precipitated by evaporation or during the reactions discussed above.

One of the final processes is the conversion of the ferric hydroxide to limonite by dehydration of the hydroxide.

As shown by the heavy metal analyses of the natural precipitate a part of the heavy metal content of the water is precipitated at the orifice of springs with the various compounds, and downstream from the springs still more appears to be precipitated. However, heavy metal cations remain in solution in sufficient concentration to be detected by normal methods several thousand feet from the source springs.

CONCLUSIONS

The investigation of the heavy metal content of streams and springs demonstrates the applicability of geochemical prospecting for heavy metal deposits in the Keno Hill-Galena Hill district. The fact that the method proved satisfactory for tracing the heavy metal to its source in areas of known mineralization, as well as in undeveloped areas, points to a possible twofold utilization. First, and perhaps the more important, new areas of mineralization can be located and delineated, and second, possible extensions of known ore veins can be located.

It must be borne in mind that hydrogeochemical prospecting will not lead directly to an orebody, nor will it give any indication of the grade or type of orebody. The immediate source of the heavy metal may be a spring at the head of a tributary stream, but the actual source of the metal is usually a vein or series of veins some distance from the spring. Only rarely is the ore vein exposed to the stream water and supplying heavy metal directly to it.

The investigation in this area indicated that it is not always possible to detect an anomaly in a stream with a large flow unless the heavy metal concentration of its springs or tributaries is greater than 0.05 ppm. The proper conditions were fulfilled in the Faro Gulch and Basin Creek-Gambler Creek systems, but as previously noted, in such streams as Silver Basin and Parent Creek the volume of water downstream is too great and hence the dilution excessive for the detection of the heavy metal known to be present at the streams' headwaters. These conditions dictate the necessity of searching assiduously for and testing all the small tributaries of any stream system to their sources.

Records of the amount of rainfall and the normal water level in the streams show that any hydrogeochemical prospecting program in this area should be planned for the period between July 20 and August 31. Before and after these dates, the high water level tends to give erroneous results. Furthermore, the flooding of the extensive muskeg areas makes traversing many areas physically impossible. Another reason for planning a late summer program is that until the active layer of the permafrost and the ice cementing scree areas thaw, water circulation is greatly inhibited.

The presence of permafrost in the area does not appear to affect the common oxidation phenomena and the production of soluble salts of the heavy metals in most areas tested, although in some areas the veins appear to be sealed and do not contribute heavy metal. The patchy distribution of the permafrost allows the oxygen-bearing waters to enter the veins and faults at higher elevations and to issue at lower elevations with their dissolved heavy metal. Even in areas known to be underlain by permafrost there is usually sufficient thawing of the upper part to expose veins and vein float to circulating near-surface waters that carry away traces of the heavy metals.

Certain areas merit further investigation by both ordinary prospecting methods and soil analyses or biogeochemical methods. The most promising areas are Basin Creek, Parent Creek, Allen Creek, Cascade Creek, and southeast of Wernecke.

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