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GEOCHEMICAL STUDIES IN THE SURFICIAL ENVIRONMENT OF THE BEAVERLODGE AREA, SASKATCHEWAN

Part A. The geochemistry of U, Ra, Zn, Cu, Pb and Ni.

Part B. A comparison of geochemical exploration methods—lake versus stream sampling

WILLY DYCK

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PART A
THE GEOCHEMISTRY OF U, Ra, Zn, Cu, Pb and Ni
IN THE SURFICIAL ENVIRONMENT OF THE BEAVERLODGE AREA, SASKATCHEWAN

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ABSTRACT

Stream sediments and stream waters collected at a sampling density of one sample per square mile from 500 square miles in the Beaverlodge area of Saskatchewan were analyzed for a number of trace and minor elements. Raw data of U, Ra, Zn, Cu, Pb and Ni presented in a set of contour maps show increased levels of elements near uranium deposits with regional background values (geometric means) of 5.1, 0.7 (pc/g), 24.6, 11.4, 4.5, and 11.2, ppm, respectively. Multiple regression analysis of the data shows that from one quarter to one half of the variance of the trace element content is due to the organic matter, Fe, and Mn contents of the sediments. Removing the effect of these variables from the data does not change the distribution patterns of the trace elements but reduces the areal size of some anomalies.

Due to occurrence of uranium deposits in the area and the complexing action of carbonates and bicarbonates, U is the most abundant of the trace elements studied in the surface waters of the area.

The analyses of 96 rocks from the area show than Zn, Cu, Pb and Ni are closely associated with hornblende and biotite, whereas U and Ra are not. The concentration of Ra, Zn, Cu, Pb and Ni is slightly higher in rocks than in the minus 60 mesh fraction of the stream sediments, whereas the U concentration is considerably lower.

An extreme case of radioactive disequilibrium is exhibited by the stream sediments and the rocks of the area. Whereas stream sediments contain over twice as much U determined fluorimetrically as U determined radiometrically, the rocks contain nearly four times as much radiometric U as total U determined fluorimetrically.

RÉSUMÉ

On a prélevé pour effectuer l'analyse des éléments à l'état de trace et des éléments mineurs des échantillons de sédiments et d'eau de cours d'eau recueillis à raison d'un échantillon au mille carré dans une zone de 500 milles carrés de la région de Beaverlodge, Saskatchewan. Les premières données en ce qui concerne U, Ra, Zn, Cu, Pb et Ni, présentées sous forme d'un ensemble de cartes en courbes, indiquent des teneurs en éléments plus élevées, près des dépôts d'uranium, tandis que les concentrations normales dans la région (moyennes géométriques) sont respectivement de 5.1, 0.76 (pc/g), 24.6, 11.4, 4.5 et 11.2 ppm. L'analyse des données par régression multiple montre que du quart à la moitié de la variation de la teneur en élément à l'état de trace est attribuable à la matière organique et au Fe et Mn contenus dans les sédiments. Si l'on élimine l'effet de ces variables on ne modifie pas la répartition des éléments à l'état de trace mais réduit celle de certaines anomalies.

A cause de la présence de dépôts d'uranium dans la région et de l'action combinée des carbonates et des bicarbonates, l'uranium est le plus abondant des éléments a l'état de trace observés dans les eaux de surface de cette région.

L'analyse de 96 roches recueillies dans cette région démontre que, Zn, Cu, Pb et Ni sont en relation directe avec la hornblende et la biotite contrairement à U et Ra. Les concentrations en Ra, Zn, Cu, Pb et Ni sont légèrement plus élevées dans les roches que dans la partie des sédiments de cours d'eau qui traverse le tamis de 60 mailles. La concentration en uranium est au contraire beaucoup plus faible.

INTRODUCTION

During the 1969 field season a comparison study of geochemical methods of exploration for uranium was carried out in the Beaverlodge area of Saskatchewan (Dyck et al., 1971). Samples from this area were subsequently analyzed for a number of trace elements to determine their relationship to uranium and to each other. This report summarizes the results of these analyses and attempts to explain the observed relationships. The behaviour of radon and uranium in lake and stream waters has been described previously (Dyck et al., 1971) and will therefore not be repeated here except in reference.

Acknowledgments

I would like to acknowledge the assistance of and thank the following persons: (a) Dr. E. E. N. Smith and Dr. A. Sauerbrei and other members of Eldorado Nuclear in matters concerning the Beaverlodge field work area, the setting up of the field laboratory, and the accommodation of the field party. (b) Mr. C. C. Durham, Geological Survey of Canada; Dr. A. S. Dass, Geological Survey of India; Students J. H. Galbraith, M. Saunders, B. Deslaurier, and P. Fobel for carrying out the field work. (c) Mr. J. J. Lynch and his staff, Geological Survey of Canada, for the analyses of the sediments and rocks. (d) Mr. J. C. Pelchat, Geological Survey of Canada, for chemical field tests, uranium analyses, and compiling of analytical data. (e) Mr. J. D. Hobbs, Geological Survey of Canada, for computer processing of the analytical data. (f) Mr. W. Traversy and his staff, Department of the Environment, for the analyses of the water samples.

GENERAL GEOLOGY AND TOPOGRAPHY

The topography of the area is similar to that of most other parts of the Canadian Shield. The southern side of the almost rectangular study area is bounded by the north shore of Lake Athabasca, the northern boundary falls on latitude $59^\circ 45'$ and the eastern and western boundaries on longitudes $107^\circ 50'$ and $108^\circ 30'$ respectively.

Drainage is to the southwest in the northern and eastern sections of the area, following the general slope of the land. The surface is covered with numerous small lakes (nearly two per square mile) which are separated by rock, muskeg and small drift-covered areas. Small streams interconnect many of the lakes and form extended drainage channels. In detail the country is rugged. Ridges commonly rise 100 to 300 feet above the level of the adjacent lakes. In the southern part of the field area rock outcrop exceeds 50 per cent and overburden is thin or absent. In the north, rock outcrops form about 10 per cent of the surface. Vegetation is moderate but persistent, making helicopter landings on land difficult. Spruce predominates and birch, alder, and willow are usually found along stream beds.

The geology for the base map of this report was taken from reports by Christie (1953), Blake (1955), and Tremblay (1972). The oldest rocks in the area, the Tazin Group, consist of metamorphosed sedimentary strata. In the final stages of metamorphism conformable sheets and masses of granite intruded the area. Thus, granites and granite gneisses containing lenses or bands of amphibolite, biotite - chlorite schist, and other mafic rocks predominate in the area. Highly fractured quartzite bands have been eroded and covered by drift along the bottoms of valleys. Amphibolite, being much more resistant to erosion, forms many of the most prominent ridges.

Metamorphism increases from northwest to southeast. The southwestern corner consists of a complex mixture of quartzite, dolomite, dolomitic-quartzite, amphibolite, biotite schist and granite gneiss. In the eastern and southern part, mafic rocks and garnetiferous gneiss occur more frequently.

Several northeast-trending faults occur in the region. The St. Louis fault cuts across the area. Faults have played an important role in uranium exploration because the major uranium orebodies occur in minor faults associated with the major faults.

MINERALOGY

Iron occurrences near Fishhook Bay were noted as early as 1895. Gold was discovered in 1934 and mined from 1939 to 1942 but uranium discovered in 1936 is the only metal mined at the present time. Pitchblende is the dominant uranium mineral in almost all deposits. Associated with the uranium minerals are smaller amounts of pyrite, chalcopyrite, nolanite, and several selenides. Some of the more complex uranium deposits contain lesser amounts of Cu, Co, Ni, Pb, Zn, V, Hg, Pt and Au. Calcite, chlorite, and quartz are the principal gangue minerals in the uranium deposits. For more details on the natural history and mineralogy of the Beaverlodge area the reader may consult Tremblay (1972), Lang et al. (1962), Beck (1969), Koeppel (1968), Johns (1970), Dawson (1956) and Robinson (1955).

GEOCHEMISTRY

Mineralogical investigations of the uranium ore deposits by Dawson (1956) and Robinson (1955) have shown that in certain deposits there are small amounts of native Cu, Ag, Au, Sn, and graphite as well as a host of oxides, sulphides, selenides, and arsenides of Fe, Cu, Pb, Co, Ni, Zn, Ag, and Hg. The formation and evolution of the uranium deposits took place during six discrete periods covering a time span of more than 2,200 million years (Koeppel, 1968). Beck (1969) has characterized the granites of the area by means of trace element content, and minor and major element constituents. Trace element contents of a number of rock types near ore occurrences has led Tremblay (1970) to

the conclusion that granitization of quartzite may have concentrated the uranium into deposits.

That the distribution of uranium in surface lake waters outlines uranium mineralization in the Beaverlodge area was shown by Macdonald (1969). Dyck et al. (1971) showed that besides uranium in surface lake waters, uranium in stream waters and stream sediments and radon in lake and stream waters also outline uranium mineralization. High sensitivity airborne gamma-ray spectrometry (Darnley, 1972) has given a comprehensive picture of the spatial distribution of U, Th, and K in the surficial environment and demonstrated the high degree of correlation between the ground-geochemical and airborne gamma-ray spectrometer results.

SAMPLING AND ANALYTICAL METHODS

Sampling of the lakes and streams in the Beaverlodge region was carried out between June 25th and August 25th, 1969. All sites were reached by helicopter from the Eldorado airport. Each two-man party was flown to the mouth of a stream. Because trees extend to the shoreline, the helicopter landed on the lake and taxied to shore. The field party disembarked, proceeded to the stream, and after sampling returned to the shore to be picked up and moved to the next stream by the helicopter. Lake sampling was done directly from the helicopter, which could land on the sample point, by collecting the water samples off the pontoons.

Six hundred and one samples from 550 stream sites, and 813 samples from 740 lake sites were collected. At approximately 10 per cent of the sites, duplicate samples were collected to determine sampling error.

From each stream site two bottles of water and one bag of stream sediment were collected — a 500 ml polyethylene bottle for trace element determinations, and a 250 ml glass jar for radon gas, pH, and total alkalinity determinations. Both bottles were filled at the surface of the water simultaneously with the mouths adjacent to ensure identical sampling. Care was taken not to create bubbling or other turbulence in filling the glass bottle in order to retain the radon gas. Both bottles were completely filled. The stream water samples were taken above any turbulence such as rapids or falls but as far downstream from the lake outflow as possible. The water temperature of the stream was noted in all cases.

A sample of the active stream sediment was collected near the water sample site by scooping up the organic, sand, or silt sediment by hand, and putting it in a paper bag. Sampling density was approximately one sample per square mile.

From the many lakes and ponds in the area two bottles of water were collected at each site in the same manner as the stream samples. Wherever possible the sample was taken at a point near an inflowing stream, approximately 20 feet from shore in the stream delta. Water temperature at the lake surface was recorded. Sampling density of the lakes was approximately 1.3 samples per square mile.

Water samples at four stream and four lake sites were collected for seasonal variation measurements. At each of these, lake shoreline and offshore samples were collected three times a week from June 25th to August 20th. Two bottles of water were collected according to the procedures described above.

A suite of rocks representing the major rock types in the area was also collected. Due to abundant outcropping these specimens were collected in conjunction with the stream sampling operation. Composite samples of fresh unweathered rock chips from the outcrop were collected. At least five samples of each major rock type were taken to provide background information for the water and sediment studies.

Field observations were recorded on cards suitable as a keypunch source document at stream-water and sediment and lake-water sample points. Sample number, U. T. M. location, predominant rock type, and width, depth, flow rate and turbulence of the water, as well as water and sediment colour, precipitates, sediment composition and size fraction, water temperature, contamination, elevation, dominant vegetation and time and date of collection were duly recorded. However, for lake sampling much of this information is not applicable or is unobtainable.

Each day's collection of samples was brought to the base camp laboratory at Eldorado and the water in the polyethylene bottle was acidified with nitric acid. The samples in the glass bottles were then used for radon, pH, and total alkalinity determinations in the field laboratory. Bags containing stream sediment samples were hung up to allow excess water to drain off and were then dried in an oven at 80°C for 36 hours. When dry the sediments were rolled and split in two. One half was stored and the other half was sieved to -60 mesh with stainless steel sieves. The sieved fraction was used for the analyses.

Two factors prompted the choice of -60 rather than the conventional -80 mesh size fraction. Firstly, the majority of samples contained appreciable amounts of organic matter for which size is not important in terms or uranium content. Secondly, inorganic sediments usually contained only small amounts of the -80 mesh size fraction, making it necessary to save coarser fractions in order to get enough sample for analysis.

At the base camp laboratory one technician and a student determined radon in the water samples by degassing 130 ml of the sample with air, transferring this gaseous phase to an evacuated zinc sulphide cell and counting the alpha activity with a photomultiplier and scaler assembly. A detailed description of the apparatus and the method is given by Dyck (1969).

A 50 ml aliquot of the sample was used to measure the pH and total alkalinity. Total alkalinity is expressed in parts per million $CaCO_3$. After the original pH of the sample was measured, sulphuric acid was titrated into the sample to the end point. A description of the method is given by Thomas and Lynch (1960). A Radiometer and a Beckman model N pH meters were used.

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Table 1. Variables determined in this study

Variables	Dimensions or relative scale	Abbreviations of: Variable	Abbreviations of: Dimension	Detect. limit
1. - determined at sample site:				
Depth of lake or stream at site	Feet	Depth	ft	0.5
Width of stream at site	Feet	Width	ft	1.0
Temperature of water	Degrees Centigrade	Temp.	oC	0.5
Colour of water	1=clear; 2=yellow;	Colour	-	-
Turbulance of water	0=still; 1=slight; 2=moderate; 3=strong;	Turb.	-	-
Level of water	1=dry; 2=low; 3=normal; 4=high;	Level	-	-
Flow rate	0=stagnant; 1=slow; 2=moderate; 3=fast;	Flow	-	-
Composition of sediment:	gravel, sand, silt, clay, organic matter.	-	-	-
Boulder fraction in stream bed	Relative scale: 0 to 9.	Bold	-	-
Vegetation, type and intensity	Lettered code with relative scale	-	-	-
2. - determined in field laboratory:				
Radon in water	Picocuries per litre	Rn	pc/l	1.0
Alkalinity of water as CaCO$_3$	Parts per million	Alka.	ppm	0.5
Acidity of water	-	pH	-	0.05
Grain size of rock	1, 2, 3, ... 9=>.004, >.006, >.025, >.5, >1, >2, >5, >20 mm	Grain	-	-
Alteration of rock	0=unweathered; 1=weathered	Alt.	-	-
Hornblende + biotite content of rock	Relative scale: 0 to 9	Hb + Bt	-	-
Biotite content of Hb + Bt	Relative scale: 0 to 9	Biot.	-	-
Co-ordinates of sample site	UTM grid; 1:50,000 scale	-	-	-
Elevation of sample site	Feet	Elev.	ft	20.0
Area of sampled lake	Square kilometres	Area	km2	0.1
Rock type at sample site	Letter codes; e.g. granite=GRNT	-	-	-
3. - determined in the Trace Element Laboratory, Resource Geophysics and Geochemistry Division, Geological Survey of Canada				
Uranium in water	Parts per billion	U(H$_2$O)	ppb	0.5
Uranium in sediment and rock	Parts per million	U(Sed.)	ppm	1.0
Copper in sediment and rock	Parts per million	Cu	ppm	3.0
Lead in sediment and rock	Parts per million	Pb	ppm	3.0
Zinc in sediment and rock	Parts per million	Zn	ppm	3.0
Nickel in sediment and rock	Parts per million	Ni	ppm	3.0
Iron in sediment	Per cent	Fe	%	0.05
Manganese in sediment	Parts per million	Mn	ppm	10.0
Radium in sediment and rock	Picocuries per gram	Ra	pc/g	0.5
Volume of 250 mg of dry (-60 mesh) sediment	Millilitres	Vol.	ml	0.1
4. - determined by Water Quality Division, Dept. of the Environment				
Magnesium in water	Parts per million	Mg	ppm	0.1
Calcium in water	Parts per million	Ca	ppm	0.1
Chlorine in water	Parts per million	Cl	ppm	0.1
Iron in water	Parts per million	Fe	ppm	0.01
Zinc in water	Parts per billion	Zn	ppm	3
Copper in water	Parts per billion	Cu	ppb	10
Cobalt in water	Parts per billion	Co	ppb	30
Nickel in water	Parts per billion	Ni	ppb	10

Table 2.

Variance ratio, F calculated from log transformed data of variables of replicate stream sediments.

Variables	all 50 replicates		25 replicates with similar content of organic matter		25 replicates with dissimilar content of organic matter	
	F*	p**	F*	p**	F*	p**
U	6.58	94	35.4	33	3.55	98
Ra	1.60	35	1.67	88	1.54	90
Zn	4.79	46	8.19	31	3.92	38
Cu	3.26	0	21.8	39	1.67	39
Pb	3.55	34	3.55	8	3.58	54
Ni	4.97	94	19.2	94	3.00	59
Fe	5.99	93	11.1	96	3.96	46
Mn	2.89	40	7.34	64	1.97	11
Vol.	2.08	99	104.8	93	0.89	99

* For 50 replicates F.95 = 1.60, for 25 replicates F.95 = 1.96.

** p = % probability that the replicates come from a different population than the total sample population and is calculated from Student's test.

Uranium in the water, sediment, and rocks was determined by a fluorimetric method, in the Ottawa laboratory. This method involves fusion of the sample with a Na_2CO_3, KNO_3, and NaF flux at a temperature of 650°C, and reading the fluorescence on a Jarrell-Ash fluorimeter. Details of this method are given by Smith and Lynch (1969).

Radium content in the water was also determined in several hundred samples in the field laboratory as follows. After the radon determination the sample was thoroughly degassed, the bottle sealed, left for ten days or longer and then the radon content was measured again. The radium content was calculated from the radon that was generated during the storage time. However, the counts were so low that results of these determinations are in doubt due to the non-reproducibility of successive tests. The radium content of rocks and sediments was determined by dissolving a 1-g powdered rock sample or a 1-g -60 mesh sediment sample in a mixture of nitric and perchloric acid, bottling the solution in tightly sealed glass bottles and measuring the radon build-up in the solution after two weeks of storage. Studies with several radiometric standards suggest that the radium results are ~25% high.

Zn, Cu, Pb, Ni, Fe, and Mn were determined by atomic absorption spectrophotometry. Solid samples were brought into solution with hot 4N HNO_3.

An indirect but quick and valuable measure of the relative amounts of organic matter in stream sediments was obtained by measuring the volume of a 250 mg sample in a tapered graduated tube.

All the variables determined in this study, their dimensions, abbreviations, and detection limits are listed in Table 1.

The reader should keep in mind that the analytical methods applied are almost but not quite quantitative. A small uncertainty arises from the fact that the solid samples when digested in various acids do not go into solution completely. The small residue comprising less than 5 per cent of the sample introduces the possibility of occluding a fraction of the trace elements. Occasionally, as in the case of uranium in monazite crystals, more than the proportionate amount will remain in the residue. However, on the whole, tests have shown that the leaching methods employed gives close to 100 per cent recovery of the trace elements, particularly in the case of stream sediments rich in organic matter.

SAMPLING AND ANALYTICAL ERRORS

To measure the reliability of the analytical data, a second sample was collected from every tenth site and processed in the normal manner. In the case of water samples the duplicate sample was taken from the same site as the first sample. In the case of sediments some of the duplicates were taken from the same site (within 2 or 3 feet of each other) for identical pairs. For others, organic-inorganic pairs were collected as close together as possible with one of the pairs predominantly of organic and the other of clastic composition. The results of analyses of these pairs were then subjected to Snedecor's F test and Student's t test. The results of this mathematical treatment are summarized in Table 2. The calculation and application of F to geochemical data of sample pairs has been reported by Garrett (1973). F is the ratio of the data variance to the sampling and analytical error variance. It is a measure of significance of the overall variance compared to the error inherent in the method of collecting and analyzing the sample. As a rule of thumb, F should be 1.6 or greater for a 95% significance level and about 50 replicate pairs. If F is lower than this, complicated treatment of data is not warranted.
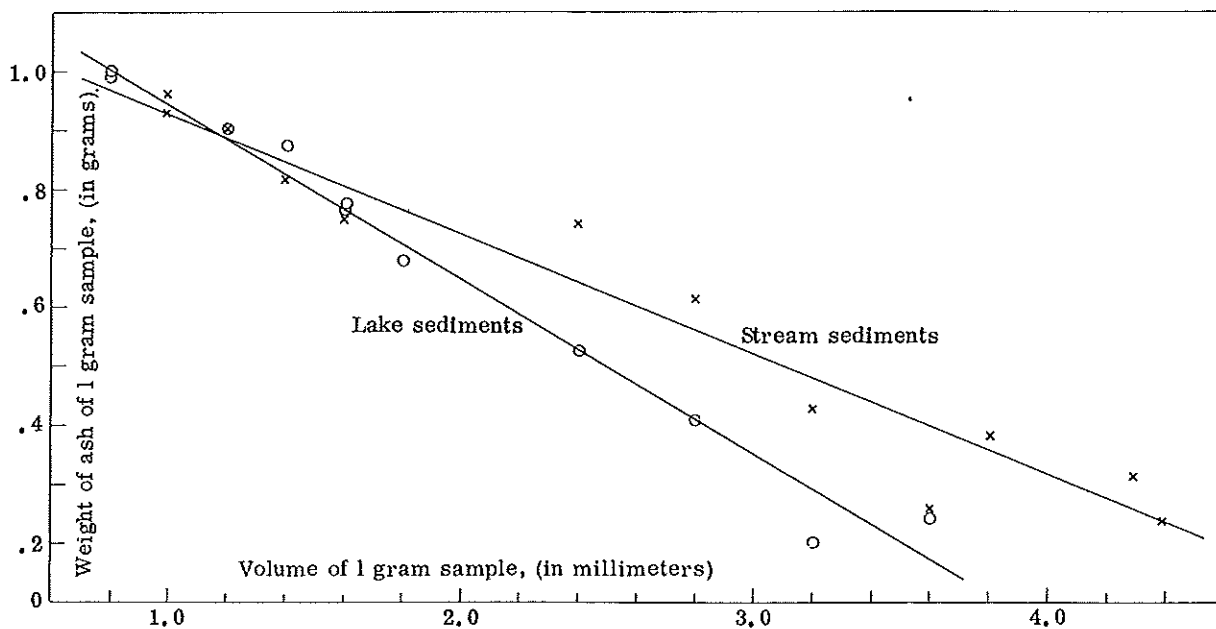
Figure 1.   Relationship between weight of ashed and volume of air-dried minus 60 mesh samples.

The t test gives the per cent probability that the sample pairs are from a different population than the regional sample population. It is a statistical comparison of the mean of pairs to the regional mean and thus gives a measure of reliability to the F test. The per cent probability, p, that the paired samples are from a different population than the regional samples was derived from probability tables.

As shown in Table 2 all elements except Ra exceed the required minimum F of 1.6. Ra is a borderline case most likely on account of the small difference between the average Ra content of the stream sediments and the detection limit of the method, i.e., 0.7 vs 0.5 pc/g, respectively.

Having used organic matter as a basis for dividing the replicate pairs into those with similar and those with dissimilar contents of organic matter, it is not surprising to see that the variable vol. experiences the largest shift in F when the replicates are grouped according to organic matter content. The relatively high probability, p, that the replicates came from a different population than the total sample population (although only vol. is significantly different at the 95% level) appears to be due to a bias in the sampling of the replicates; the average value for vol. for the replicates is 0.43 compared to 0.52 for all the sediment samples.

To ascertain that the variable vol. was a good measure of the organic content of a stream sediment sample, a number of screened and air-dried stream and lake sediment samples, selected so as to cover the full range of volume measurements encountered in the set of samples, were ashed and reweighed to determine the loss of weight on ignition. The loss on ignition should be equal to the organic matter content, ignoring residual free water. The results of this test are illustrated in Figure 1. While this test tends to confirm the relationship

between organic matter and volume of a stream sediment, other tests with powdered inorganic samples show that particle size will also influence the volume of a unit weight of the sample, i.e., the finer the particle size, the larger the volume. In the case of samples rich in organic matter the opposite seems to hold, i.e., the coarser the particles the greater the volume per unit weight of sample. This conclusion can be derived from the slopes of the lines in Figure 1. For example, a stream sediment sample with the same amount of organic matter as a lake sediment sample occupies a larger volume per unit weight even though a physical examination shows that the organic matter in the stream sediment is coarser than in the lake sediment.

There are other factors that influence the element content of the sediment. Hydrous oxides of iron and manganese have long been known to adsorb trace elements from solution but in the stream sediments in the Beaverlodge area neither do so as effectively and as generally as does the organic matter.

RESULTS AND DISCUSSION

1.   Rocks and Stream Sediments

The main field observations and laboratory determinations of stream sediments and rocks are summarized in Tables 3, 4, and 5. Because chi square tests showed that the distribution of the elements in the rocks and sediments tended to be more lognormal than normal, all computations were carried out on log transformed data.

The spatial distribution of U, Ra, Zn, Cu, Pb, and Ni in the stream sediments is portrayed in a set of contoured maps (Figs. 2 to 7). The contour levels of the

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Table 3.

Geometric means and standard deviations of variables of rocks and stream sediments.

Variable	Rocks			Uncontaminated stream sediments			Contaminated stream sediments		
	No. of samples	$\bar{X}$	$\log_{10}S$	No. of samples	$\bar{X}$	$\log_{10}S$	No. of samples	$\bar{X}$	$\log_{10}S$
U, ppm	96	0.59	0.469	483	5.10	0.666	42	7.00	0.544
Ra, pc/1	96	0.86	0.287	483	0.74	0.411	41	1.04	0.510
Zn, ppm	96	41.7	0.349	531	24.6	0.296	47	35.1	0.346
Cu, ppm	96	13.3	0.450	531	11.4	0.401	47	15.0	0.322
Pb, ppm	96	14.1	0.466	531	4.54	0.722	47	6.61	0.676
Ni, ppm	96	26.9	0.378	531	11.2	0.393	47	18.8	0.248
Fe, %	-	-	-	483	1.17	0.405	42	1.75	0.376
Mn, ppm	-	-	-	483	288	0.550	42	630	0.610
Vol., ml/250mg	-	-	-	532	0.515	0.259	47	0.509	0.215
Elev., ft.	-	-	-	544	1129	0.093	57	1050	0.097
Width, ft.	-	-	-	544	4.68	0.440	57	5.49	0.479
Depth, ft.	-	-	-	544	1.22	0.356	56	1.26	0.280

BEAVERLODGE, SASK.

BASAL CONGLOMERATE

GRANITE, GRANITE-GNEISS

AMPHIBOLITE

METASEDIMENTS

QUARTZITE

MIGMATITE

LIMESTONE
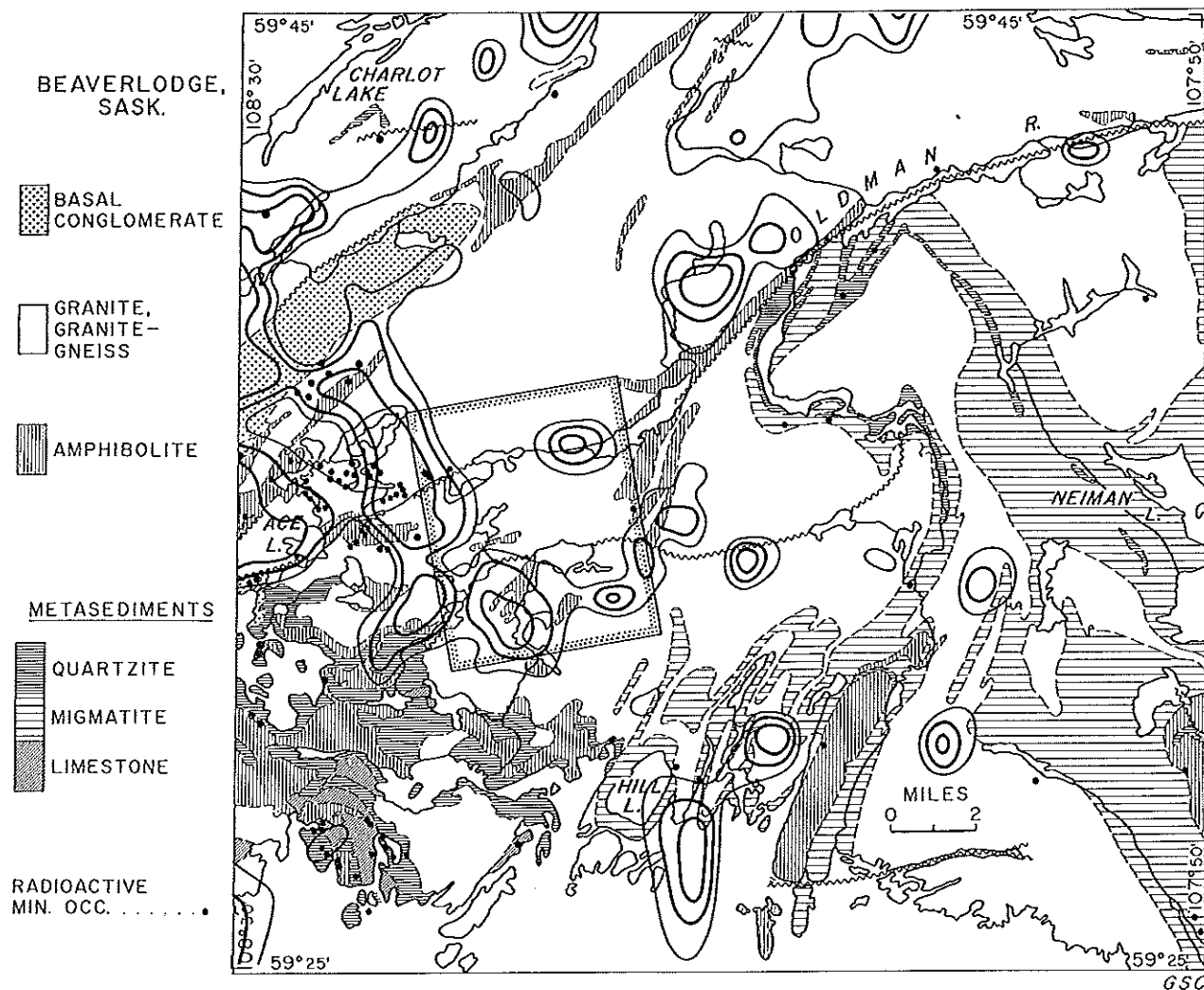
RADIOACTIVE MIN. OCC. . . . . . . ●

GSC

Figure 2. Uranium in stream sediments.

Table 4.

Geometric means of rock and stream sediment variables grouped according to rock type.
For each rock type the first row refers to rock and the second to sediment analyses.

Rock Type and Number of Samples	Ra, pc/g	U, ppm	Zn, ppm	Cu, ppm	Pb, ppm	Ni, ppm
All types						
96	0.9	0.6	41.7	13.3	14.1	26.9
483	0.7	5.1	24.6	11.4	4.5	11.2
Amphibolite						
13	0.9	0.4	81.2	43.8	8.5	58.1
44	0.8	4.4	21.8	13.9	3.0	11.0
Arkose						
6	0.9	1.1	28.8	7.7	13.9	22.9
NS*						
Biotite gneiss						
7	1.0	0.6	70.5	17.2	15.5	⋮..0
NS*						
Conglomerate						
5	1.4	1.8	26.5	6.3	19.5	20.7
1	0.2	37.0	32.0	61.0	6.0	13.0
Chlorite schist						
1	0.9	0.8	160.0	42.0	13.0	170.0
NS						
Dolomite						
5	0.7	0.3	21.6	13.6	18.2	34.3
6	0.7	3.9	15.7	6.9	3.0	10.3
Diabase						
5	0.9	1.2	95.5	34.0	16.8	71.4
NS						
Biotite gneiss						
4	1.1	0.4	46.8	18.6	19.3	47.2
NS						
Granite gneiss						
13	0.9	0.5	41.7	10.3	14.0	20.2
70	0.7	9.3	27.2	10.9	6.1	9.2
Granite						
14	1.3	1.1	36.0	8.8	17.8	19.2
165	0.8	7.3	23.2	10.7	3.2	10.1
Migmatite						
5	0.7	0.5	40.0	8.4	22.5	24.9
85	0.7	3.0	28.3	14.1	8.4	14.8
Paragneiss						
9	0.7	0.5	55.8	17.2	24.1	31.6
77	0.6	2.7	23.7	9.7	5.8	11.5
Quartzite						
7	0.5	0.3	9.7	5.3	3.2	4.9
34	0.8	4.9	23.7	11.4	2.7	13.2

*NS = No samples coded under this rock type.

elements are given in Table 6. Two main features can be read from the maps; (1) a positive correlation in the spatial distribution of the elements (this positive correlation is also evident from correlation matrices not shown here); and (2) a general rise in the concentration of the elements in the western part of the area. The Ra map has no distinct areas of high concentration. Two factors could account for this: (1) the detection limit of the method; and (2) the generally low mobility of Ra in the surficial environment of the Beaverlodge area. Ra in stream sediments in the Bancroft area has been found to give useful results (Morse, 1969) using large samples for Ra analysis (Morse, 1970).

From the similarities of the element distribution maps and the correlation coefficients the impression might be gained that a similar element association exists in the rocks from which the sediments are ultimately derived. However, the rock data show a strong positive correlation between Zn, Cu, Pb, and Ni probably as a result of the concentration of these elements in minerals such as hornblende and biotite, and strong positive correlation between U, Ra, and Pb probably as a result of their close relationship in the uranium decay series and

similar ionic radii but a weak negative correlation between U and Ra on the one hand and Zn, Cu, and Ni on the other. Only Pb is found to associate with U and Ra as well as with Zn, Cu, and Ni. This indicates that hornblende and biotite are not the source of uranium in the rocks. The ease with which uranium appears to go into solution suggests that most of it is only loosely bound in the rocks.

The general rise of the trace element concentration in the western part of the study area must be related to the occurrence of uranium deposits of that area thus showing that the occurrence of these elements in the ore is also reflected in the surficial material. The reasons for this coincidence of trace elements are closely connected with the still only partly understood mechanisms of ore formation. Lithological changes, accompanied by changes in vegetation, as well as mining and exploration activities also influence the trace element content of surficial materials. To eliminate, or at least minimize the effects of mining and exploration, results from sites where such activities were evident were rejected and are not included in the tables and maps. The results in Table 3 show that for the "contaminated" stream sedi-
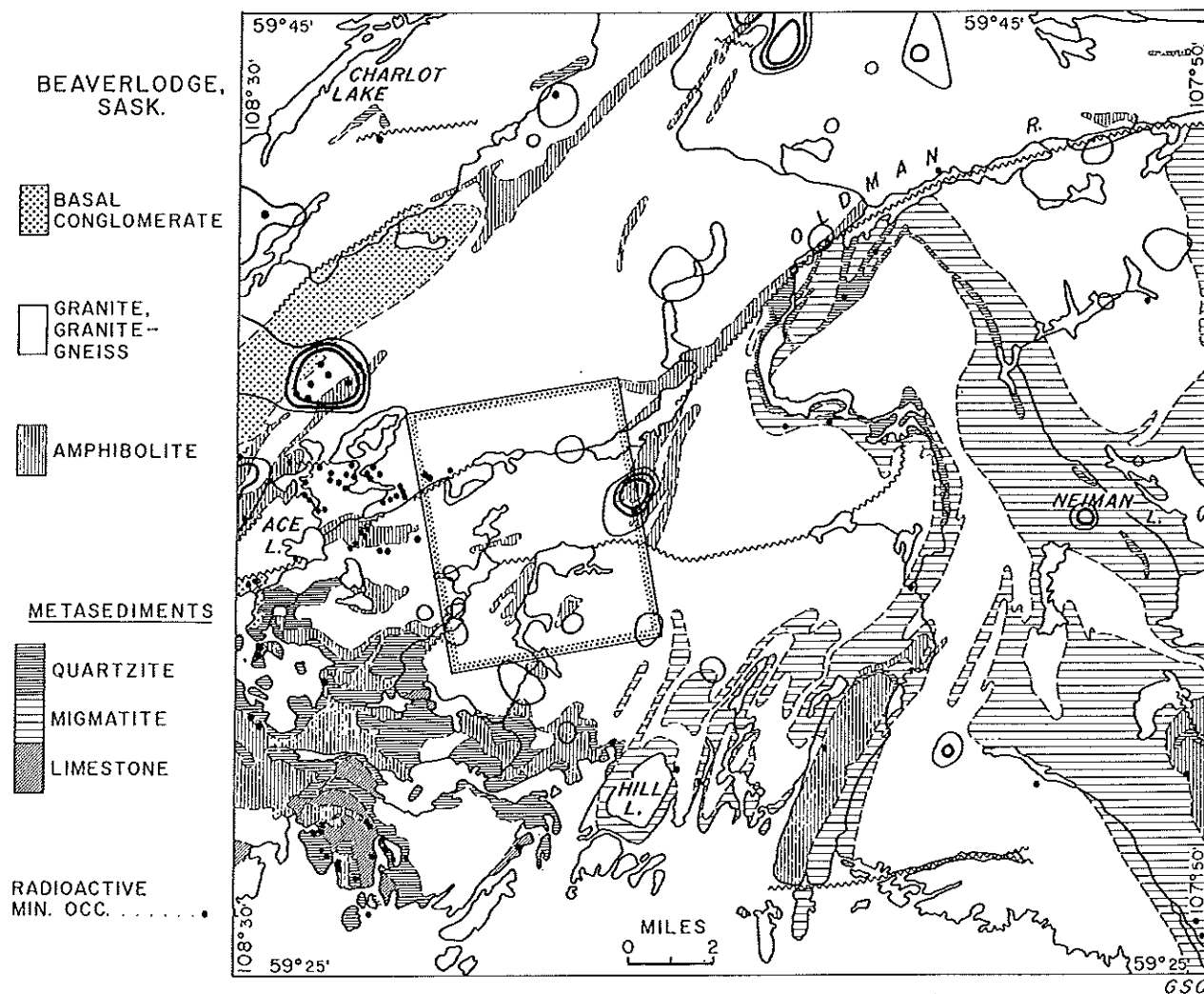

Figure 3. Radium in stream sediments.

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ments, those collected near mines or prospects (nearly 10 per cent of the total), indeed have a higher trace element content than the "uncontaminated" samples. Whether this increase is due to mining and exploration disturbance or merely to the proximity of the uranium orebodies is open to debate.

The rock type can also have a direct or indirect influence on the trace element content of stream sediments and waters. The direct influence arises from the content of the elements in the rocks and the degree of weathering. The study area provides an excellent example of the indirect influence that a rock type can have on the trace element content of stream sediments. The southwest corner of the sampled area contains a notable proportion of limestone giving rise to high pH – high carbonate waters. Subsequent complexing of uranium, and possibly some of the other elements by the carbonates and bicarbonates, has resulted in near background levels in the sediments in spite of the fact that numerous uranium showings are known in the area. On the other hand the uranium content in the waters from the same area rises to anomalous levels (Dyck et al.,

1971). Unfortunately detection limits for the other trace elements in water were inadequate to give meaningful results for corroboration of the uranium findings.

A clue to the source of the background concentrations of the trace elements can be found in Table 4 where the analytical results of rocks and sediments are listed by rock type. The sediments present a more diffuse picture as a result of the integration of materials from different rock types by the action of flowing streams. Note the decrease in the range of the means in the sediments from different rock types compared to the rocks themselves. Of the four or five major rock types, granite is preponderant and hence is the rock which contributes most to the background level of Ra, Zn, Cu, Pb, and Ni. A rather marked discrepancy is evident in the case of uranium. Although the granites of the area contain more uranium than the other rocks, the mean of 1.1 ppm is considerably lower than the mean value of 3 ppm considered average for acid igneous rocks. Uranium is also the exception in the sense that it occurs in much higher concentrations in the stream sediments than in the rocks, whereas all the other
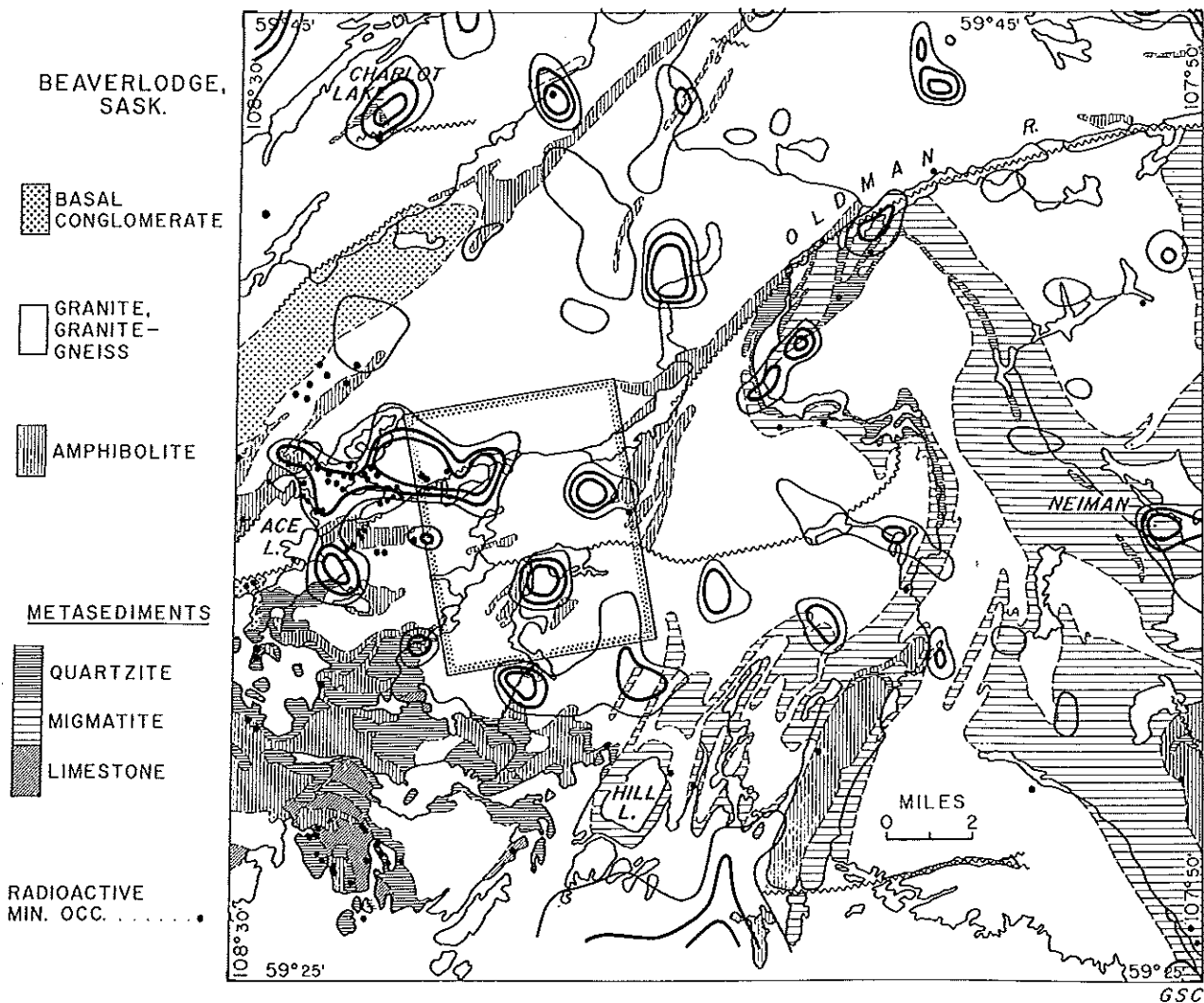

Figure 4. Zinc in stream sediments.

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determined elements occur in higher concentrations in the rocks than in the sediments, perhaps indicating the presence of uranium in epigenetic veins genetically unrelated to the enclosing rocks. Two factors can explain this behaviour of uranium. The evidence available points to the conclusion that the enrichment of uranium in the stream sediments is the result of dissolution of uranium from uranium ore and country rocks and the subsequent adsorption of the uranium on the sediments, particularly on the organic matter in the sediments. There is little doubt that the bulk of the uranium in the sediments is hydromorphic in nature. This is shown below in the section dealing with weathering and disequilibrium of U and Ra. In an attempt to resolve the problem of the source of uranium in the sediments two mathematical techniques were applied to the stream sediment data, namely, factor analysis and linear multiple regression analysis. As indicated earlier, the Snedecor F test had shown that the sampling and analytical error variance was sufficiently small to permit more complex mathematical treatment of the data. However, the F test could not have detected a possible error due to sample site bias which was introduced in an attempt to obtain a

uniform sampling density. The rugged, densely forested terrain made it necessary to sample streams by landing on lakes and walking to the stream site. Because there were not enough sample sites near the mouths of streams for a uniform sample density of one sample per square mile, about one quarter of the samples were obtained from streams flowing out of lakes. The analytical data were then grouped to determine the effect of site on element content of the samples. These grouped results are shown in Table 5. They show that the environment at the different sites is similar in most respects. Only temperature and radon in water, and uranium in sediment differ by more than 10 per cent. The radon difference stems mainly from the fact that the water entering the lake is colder and carries a greater proportion of groundwater which has accumulated radon. In the case of uranium it is believed that the slightly higher pH, organic content, and lower alkalinity can account for the somewhat greater difference in content than that observed for the other elements. Factor analysis, however, did not reveal patterns in the data which were not evident from the correlation matrices or the spatial distribution of the elements. In fact, each
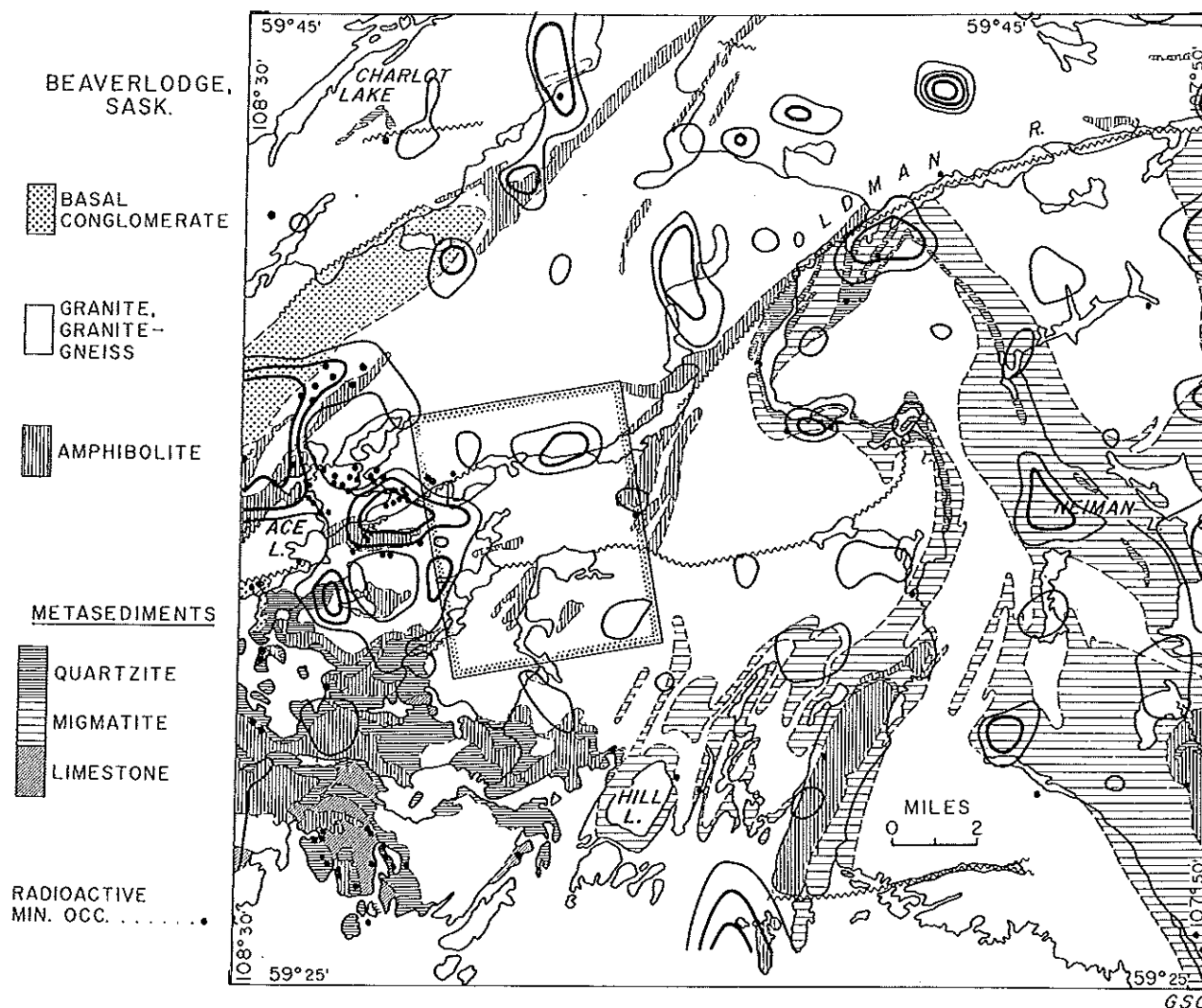

Figure 5. Copper in stream sediments.

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Table 5.

Geometric means and standard deviations of variables of grouped streams.

Variable	Sites of streams flowing into a lake			Sites of streams flowing out of a lake		
	No. of samples	$\bar{X}$	$\log_{10}S$	No. of samples	$\bar{X}$	$\log_{10}S$
1. Stream Sediments:						
U, ppm	366	4.7	.665	117	6.5	.661
Ra, pc/g	366	0.8	.372	117	0.7	.517
Zn, ppm	398	23.9	.291	132	26.8	.309
Cu, ppm	398	11.3	.372	132	11.6	.431
Pb, ppm	398	4.4	.705	132	4.9	.774
Ni, ppm	398	11.4	.392	132	10.5	.398
Fe, %	366	1.2	.392	117	1.1	.443
Mn, ppm	366	281	.544	117	314	.570
Vol., ml/250mg	398	0.50	.256	132	0.57	.263
Elev. ft.	410	1119	.095	131	1163	.087
Width, ft.	410	4.5	.430	133	5.2	.453
Depth, ft.	410	1.2	.359	133	1.3	.350
2. Stream Waters						
U ppb	409	0.5	.375	132	0.5	.355
Rn pc/1	407	15.4	.786	132	4.3	.996
Alka, ppm	408	22.6	.292	132	20.2	.268
pH	408	6.85	.029	132	6.98	.035
Temp., °C	409	11.6	.245	133	14.0	.135

BEAVERLODGE, SASK.

BASAL CONGLOMERATE

GRANITE, GRANITE- GNEISS

AMPHIBOLITE

METASEDIMENTS

QUARTZITE

MIGMATITE

LIMESTONE

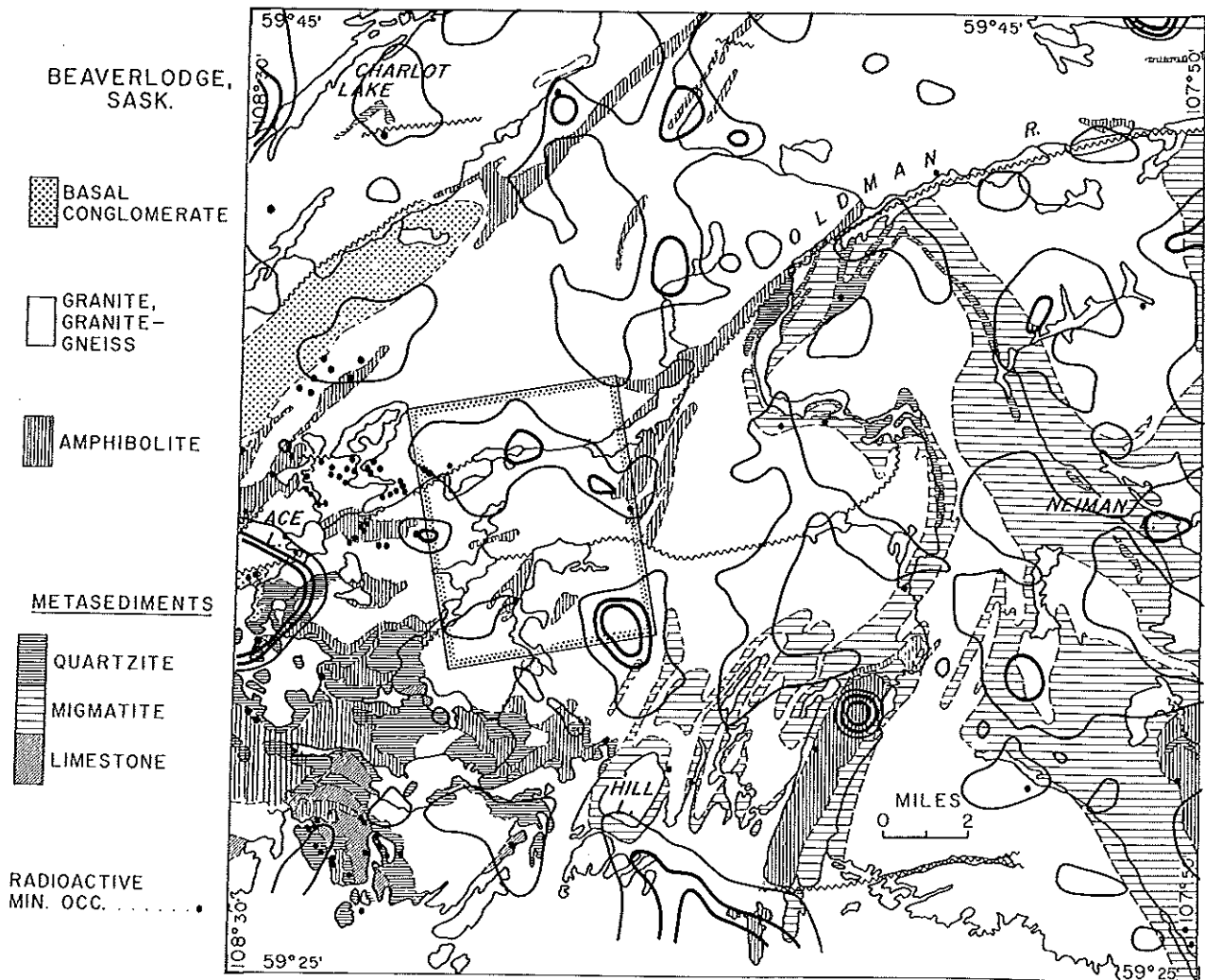RADIOACTIVE MIN. OCC. . . . . ●

Figure 6. Lead in stream sediments.

element gave a specific factor which did not reduce the complexity of the problem. However, it did associate a little more clearly some of the high Ni and Zn values with mafic rocks containing granitic material and low Ni and Zn values with conglomerate and extensive overburden.

Linear multiple regression analysis proved to be valuable in accounting for data variability. For this purpose a program called Whirlpool, published by Krumbein et al. (1964) and modified for this work by Garrett and Hobbs (pers. comm.), was used. The results of the regression analysis are summarized in Tables 7 and 8. It is at once apparent that out of the 11 independent variables used, five adequately account for the data variability due to the independent variables used. Of these five, organic matter, Fe, and Mn are the most effective and account for one quarter to one half of the data variability. Fe and Mn are usually constituents of the minerals harbouring trace elements and in the hydrous oxide state also adsorb trace elements from solution. It is, therefore, no surprise that they account for a large share of the variance of the data. In the case of U and Cu, organic matter is the largest single variable influencing data variance. Lesser factors in the variance are bicarbonate ions (Alka.) in the case of uranium and manganese in the case of copper. Radium seems to be least affected by organic content and most by manganese. Because of the strong association between Fe and Mn in the sediments, it is not really possible to assign a degree or percentage variance to each of these variables as the multiple regression technique has done. One should rather talk of an "iron-manganese" variable. Laboratory studies have shown that hydrous oxides of manganese are much more effective trace element sorbers than hydrous oxides of iron. However, the much greater abundance of iron in the surficial environment of Beaverlodge (1.2% Fe vs 288 ppm Mn) probably evens out the overall effectiveness of these two elements. Organic matter shows only a weak positive correlation with manganese and no correlation with iron and therefore is an independent variable in its own right. It is interesting to note that clay is often a constituent responsible for trace element adsorption and plays a minor role in this environment, probably because there is very little clay in the sediments. However, since clay determinations were made by visual inspection of the samples in the field, lack of accurate measurements may have masked the effect.
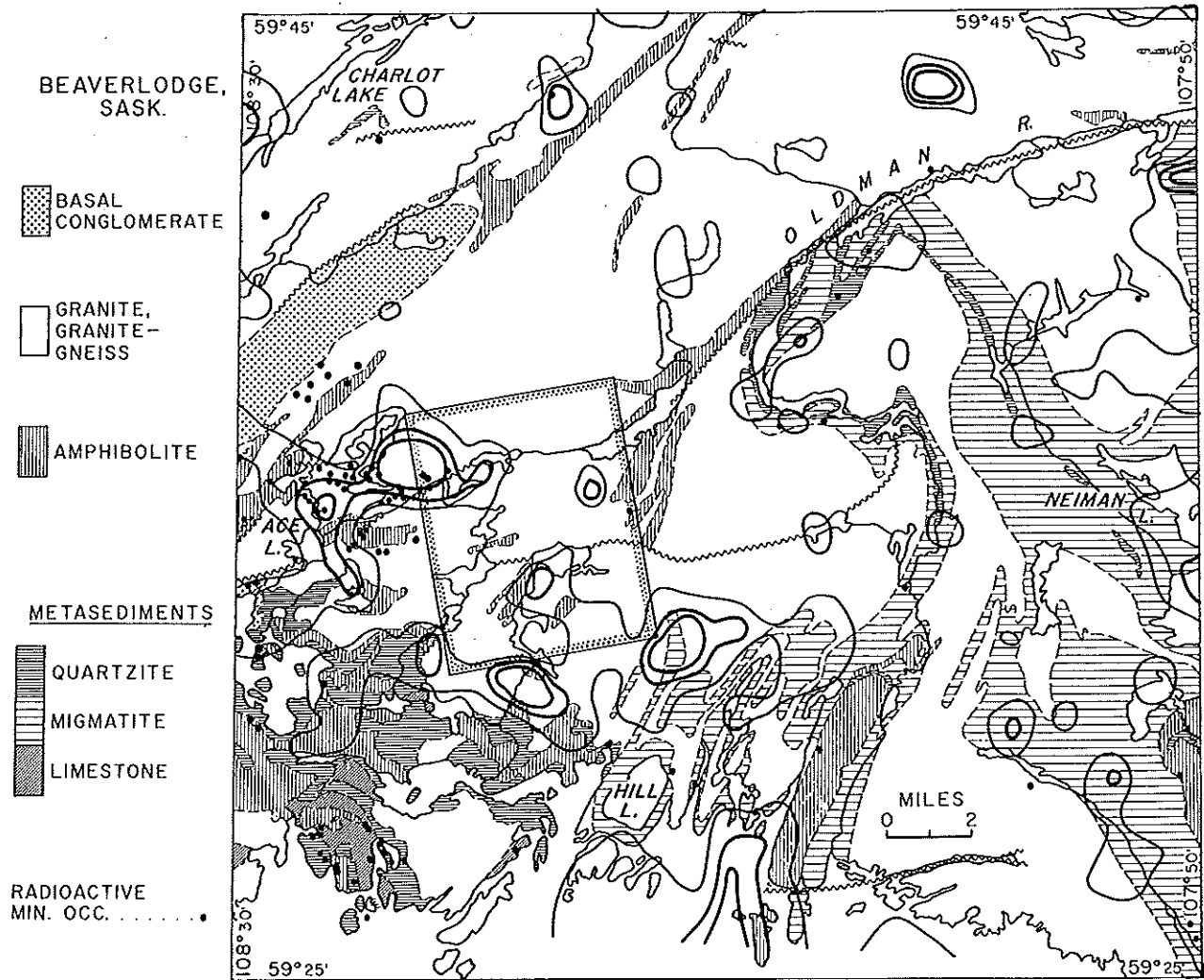

Figure 7. Nickel in stream sediments.

Table 6.

Background and contour levels of plots shown in Figures 2 to 7.

Variable	No. of samples	Background (Geometric mean $\bar{X}$)	Lowest level	Intermediate level	Highest level	Detection limit
Zn, ppm	530	24.6	$\bar{X} + S = 50$	$\bar{X} + \frac{3}{2}S = 75$	$\bar{X} + 2S = 100$	3.0
Cu, ppm	530	11.4	$\bar{X} + S = 25$	$\bar{X} + \frac{3}{2}S = 40$	$\bar{X} + 2S = 60$	3.0
Pb, ppm	530	4.5	$\bar{X} + \frac{1}{2}S = 10$	$\bar{X} + S = 20$	$\bar{X} + \frac{3}{2}S = 30$	3.0
Ni, ppm	530	11.2	$\bar{X} + \frac{3}{4}S = 20$	$\bar{X} + \frac{3}{2}S = 40$	$\bar{X} + 2S = 60$	3.0
U, ppm	483	5.1	$\bar{X} + S = 22$	$\bar{X} + \frac{3}{2}S = 46$	$\bar{X} + 2S = 95$	1.0
Ra, pc/g	483	0.7	$\bar{X} + S = 1.9$	$\bar{X} + \frac{3}{2}S = 3.1$	$\bar{X} + 2S = 4.9$	0.5

Table 7.

Percentage variance of dependent variable accounted for by individual independent variables as determined by multiple regression analysis of log-transformed stream sediment data.

Dependent variable	Independent variable										
	Vol.	Fe	Mn	Alka.	Elev.	pH	Temp.	Flow	Width	Depth	Clay
U	13	0	2	7	3	1	0	1	1	0	0
Ra	3	13	17	3	0	0	0	0	2	1	0
Zn	12	28	27	0	1	0	2	1	0	0	3
Cu	43	9	16	0	2	0	0	1	3	1	1
Pb	22	14	17	2	2	0	0	0	1	0	1
Ni	10	24	21	0	1	0	0	1	2	3	6

Table 8.

Summary of regression analysis of log-transformed data of stream sediments.
(Correlation coefficient, $\gamma.99 = .12$)

Dependent variable	% variance accounted for using all independent variables	% variance accounted for using the 5 most prominent independent variables *	Correlation coefficients of the five independent variables with most prominence										
			Vol.	Fe	Mn	Alka.	Elev.	pH	Temp.	Flow	Width	Depth	Clay
U	28	27	+.39			+.26	+.18	+.15			-.09		
Ra	23	22	+.15	+.33	+.37	+.17		+.02					
Zn	43	42	+.25	+.58	+.57				+.16		+.07		
Cu	53	52	+.55	+.31	+.41	+.08				-.08			
Pb	35	35	+.37	+.34	+.38	-.10			+.02				
Ni	43	42	+.20	+.48	+.45		-.12						-.22

*The criterion for selecting the "most prominent independent variables" was based on the frequency with which the variables occurred in the various combinations of five variables.

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The variables flow, width, and depth give a measure of the volume rate of flow water and are closely related to elevation. Even pH is affected by elevation but in an indirect way. Field observations showed that the higher streams contained larger amounts of organic matter, giving rise to a lower pH as a result of the formation of humic acids.

The results of the multiple regression analysis leads to the conclusion that up to about one quarter of the variance in uranium and up to one third to one half of the variance in Zn, Cu, Pb, and Ni may be due to factors other than mineralization. Combining this knowledge with the overall variance of these elements (see the standard deviations in Table 3), one reaches the same conclusion as was reached earlier from the disproportionation of the means of the elements in rocks and sediments. Namely, the greater overall variance in uranium is due to near surface uranium ore occurrences.

2. Stream and Lake Waters

The waters collected for the comparison study of uranium exploration methods were analyzed for a number of elements. These analytical results are listed in Tables 9 and 10. Direct analysis by atomic absorption spectroscopy proved to be unsatisfactory; very few samples had trace element contents above the detection limits. Analyses with preconcentration by liquid-liquid extraction proved too costly for the large number of samples involved. As was shown elsewhere (Dyck et al., 1971) the uranium results gave useful information even though only one third of the samples contained uranium concentrations above the detection limit of the analytical method. The results in Table 10 indicate that Zn, Cu, and Ni would also give useful information if 100-ml to 200-ml samples were preconcentrated for analysis. The results in Tables 9 and 10 also show that

Table 9.

Log-transformed data of surface waters.

| Variable	Lake waters			Stream waters		
	No. of samples	$\bar{X}_G$	$\log_{10}S$	No. of samples	$\bar{X}_G$	$\log_{10}S$
U, ppb	681	0.40	0.270	542	0.50	0.370
Rn, pc/1	681	1.16	0.649	540	11.2	0.875
pH	679	7.40	0.040	543	6.88	0.031
Alkalinity, ppm	680	17.33	0.267	541	21.98	0.287
Mg*, ppm	540	2.81	0.293	300	2.37	0.319
Ca*, ppm	540	8.65	0.317	300	7.44	0.282
Cl*, ppm	540	0.83	0.439	300	0.56	0.408
Fe*, ppm	540	0.065	0.357	300	0.16	0.376
Temp., °C	681	19.1	0.080	543	12.2	0.226
Level, relative scale	–	–	–	544	2.1	0.15
Flow " "	–	–	–	544	1.0	0.40
Turbulence " "	–	–	–	544	0.4	0.59
Colour " "	–	–	–	544	0.2	0.51'

*These analyses were carried out by the Department of the Environment, Inland Waters Branch.

Table 10.

Summary of water analyses by atomic absorption spectroscopy for Zn, Cu, and Ni, and by fluorimetry for U.

Element	No preconcentration of sample					100 ml sample preconcentrated by liquid-liquid extraction				
	Detection limit	No. of samples analyzed		% of samples above detection limit		Detection limit	No. of samples analyzed		% of samples above detection limit	
		stream	lake	stream	lake		stream	lake	stream	lake
Co	30 ppb	118	120	0	0	1.0 ppb	12	18	0	0
Zn	3 ppb	130	220	23	12	1.0 ppb	37	52	68	69
Cu	10 ppb	130	220	0	0	1.0 ppb	37	52	24	8
Ni	10 ppb	130	220	0	0	1.0 ppb	14	17	21	6
U	0.5 ppb	597	813	38	30					

the trace elements occur in slightly higher concentrations in streams than in lakes. The difference could be due to slightly lower pH (less adsorption on sediments) and/or slightly more suspended matter in streams (the water samples were not filtered prior to analysis) which when acidified would release trace elements into solution. The notably higher iron content in streams is no doubt due to the sluggish, pH-dependent process of coagulation of hydrous iron oxides in nearly neutral waters; the correlation coefficients between pH and iron were -.30 for streams and -.39 for lakes. This fact may also be partially responsible for the lower concentration levels of U, Zn, Cu, and Ni in lake waters. The rise in pH and drop in alkalinity that takes place as the stream water becomes lake water must result from the loss of CO_2 in accordance with the reaction

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$
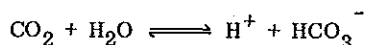
The strongest positive correlations in waters were observed between pH and alkalinity, alkalinity and calcium, calcium and magnesium, uranium and calcium, and uranium and alkalinity. Although the UO_2^{2+} ion does form bicarbonate and carbonate complexes, explaining the uranium alkalinity correlation; the correlation of uranium with calcium points out another association — the presence of calcite in the gangue material of the uranium ore.

3. Radioactive Disequilibrium and Chemical Weathering

A discrepancy between uranium determined fluorimetrically and uranium determined radiometrically, assuming radioactive equilibrium between uranium and radium, became quite evident early in this study. Whereas stream sediments showed an excess of fluorimetric uranium, rocks showed an excess of radiometric uranium. In Table 11 the results of stream sediment data from the regional study area and lake and stream sediment data from a detailed study are listed. The secondary nature of uranium in the sediments is quite apparent, especially in anomalous samples. These have the smallest ratio of radiometric to fluorimetric uranium ($\bar{X}_{eU}/\bar{X}_U$). Next in order of decreasing disequilibrium are the lake and stream sediments from the detailed study area. This 30-square-mile area (see rectangle on Figs. 2 to 7) was sampled in order to determine the relationship of trace elements between lake and stream sediments. Details of this study are described in Part B. Only sediments with below average fluorimetric uranium show a slight excess of radiometric uranium. The results of the rock analyses shown in Table 12 can easily account for the imbalance observed in the stream sediments. In Table 12 two sets of rocks are listed, each set broken into four rock types. The detailed rocks were obtained from Dr. L. P. Tremblay

Table 11.

Degree of uranium - radium disequilibrium in active stream and lake sediments.

	No. of samples	Sample density g/ml	Fluorimetric uranium $\bar{X}_U$, ppm	Radiometric uranium $\bar{X}_{eU}*$, ppm	$\bar{X}_{eU}/\bar{X}_U$
All stream sediments from regional survey	483	0.49	5.10	2.15	0.44
Stream sediments from regional survey with high U content as determined by fluorimetry	38	0.47	71.9	4.67	0.064
Stream sediments from regional survey with low U content as determined by fluorimetry	52	0.56	2.38	2.62	1.10
All stream sediments from detailed survey**	125	0.40	23.1	3.58	0.16
All lake sediments from detailed survey**	125	0.57	17.1	2.72	0.16

* $\bar{X}_{eU}$ (ppm) = 2.91 x $\bar{X}_{Ra}$ (pc/g) assuming radioactive equilibrium.

** These results are taken from a lake-stream comparison study described in Part B.

Rock Type	No. of samples	$\bar{X}_U$, ppm	$\bar{X}_{Ra}$, pc/1	$\bar{X}_{eU}$*, ppm	$\bar{X}_{eU}/\bar{X}_U$
1. Detailed Rocks					
Amphibolite	15	0.42	0.78	2.27	5.4
Quartzite	15	0.89	1.61	4.69	5.3
Granite gneiss	15	2.04	1.68	4.90	2.4
Granite	15	3.20	2.75	8.01	2.5
All types	60	1.25	1.55	4.52	3.6
2. Regional Rocks					
Quartzite	7	0.25	0.52	1.52	6.1
Amphibolite	13	0.39	0.70	2.04	5.2
Granite gneiss	13	0.51	0.88	2.56	5.0
Granite	14	1.14	1.26	3.67	3.2
All types	47	0.59	0.86	2.51	4.2

$*\bar{X}_{eU}$(ppm) $= 2.91$ x $\bar{X}_{Ra}$(pc/g) assuming radioactive equilibrium.

and come from the vicinity of the town of Eldorado and the active uranium mines (Tremblay, 1970). The regional set was collected during the 1969 field season from the same 500-square-mile area as the stream sediments with proportional representation by area and abundance. The most striking result is the large disequilibrium between uranium and radium in both sets of rocks. The detailed set was actually analyzed after the regional set in order to test whether another set of rocks collected by a different person for a different purpose would reveal the same discrepancy in radioactive disequilibrium. As can be seen, only the granite gneisses show a notable shift in the degree of disequilibrium and quartzite and amphibolite exchange positions in the order of content of uranium and radium. The generally higher uranium and radium levels in the detailed rocks relative to the regional rocks may be due to their proximity to the known uranium deposits. Earlier, it was concluded that the disproportionate enrichment of uranium in the stream sediments was due to the chemical weathering of uranium deposits with subsequent adsorption of this uranium on the sediments. The loss of uranium from country rocks can now be seen to be partially responsible for the gain of uranium by the sediments. One wonders how such a large difference can come about; to the naked eye, near-surface rock chips look unweathered. Part of the answer may lie in the fact that the perchloric-hydrofluoric acid attack did not dissolve the rocks completely. A fraction of the uranium could have stayed in the residue in such hard to decompose minerals as monazite. However, the fact that radium was determined on the same solutions should cancel any such effects, except for generally lower levels of concentration. Hence, one has to postulate that radium was leached from the samples more efficiently than uranium — an unlikely proposition. Studies with several radioactive standards suggest that the radium results are ~25% high. To solve the riddle of the large radioactive disequilibrium observed in the surface rocks of the Beaverlodge area a quantitative method of sample

dissolution is required. There is no doubt that disequilibrium exists, only its degree is in some doubt.

The striking similarity of the stream sediment U map to the Bi^{214} map produced by airborne gamma-ray spectrometry (Darnley, 1972) and the nearly identical lake sediment U and radiometric Bi^{214} patterns obtained from another area of the northwestern Canadian Shield (Allan and Richardson, 1973) seem to confirm radioactive equilibrium in the surficial materials of these areas. But more detailed work shows clearly that on a small scale severe radioactive disequilibrium prevails, at least in the Beaverlodge area. The reason the U and Bi^{214} maps look alike is the fact that the dispersion of chemically weathered U is limited to about 1 to 2 miles in the surficial environment. As the results of this study show, stream sediments with background levels of Ra and U are essentially in equilibrium. However, none of the surface rocks are. One can therefore assume that the clastic fraction of the stream sediments would also be deficient in U but because of the presence of organic matter are enriched in U as a result of U adsorption from solution. In the presence of U mineralization the leaching of U from the minerals and subsequent enrichment in the sediments becomes more pronounced.

CONCLUSIONS

The correlations between U, Ra, Zn, Cu, Pb and Ni observed in the uranium ore in the Beaverlodge area by earlier investigators are also found in stream sediments. However, analyses of rocks from the area show that the U, Ra, and some of the Pb are not found in the same rock minerals as Zn, Cu, and Ni. The latter are concentrated in hornblende and biotite.

Linear multiple regression analysis shows that one quarter to one half of the data variability of trace element content of sediments is accounted for by organic matter, Fe, and Mn in the sediments.

As a result of weathering of rocks and mineral occurrences and adsorption by organic matter in sediments uranium is found in much higher concentrations in the -60 mesh stream sediments than in surface bedrock.

The marked degree of disequilibrium between uranium and radium observed in stream sediments and surface bedrock suggests that chemical weathering in the Beaverlodge area is severe and may affect other trace elements in a similar way.

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PART B

A COMPARISON OF GEOCHEMICAL EXPLORATION METHODS IN THE
BEAVERLODGE AREA, SASKATCHEWAN; LAKE VERSUS STREAM SAMPLING

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PART B
A COMPARISON OF GEOCHEMICAL EXPLORATION METHODS IN THE BEAVERLODGE AREA, SASKATCHEWAN; LAKE VERSUS STREAM SAMPLING

ABSTRACT

To determine the relationship of trace elements in lakes and streams, water and sediment samples were collected from a 30-square-mile area just east of Eldorado, Saskatchewan at a sampling density of 4 samples per square mile. A number of site variables were recorded in the field and the samples analyzed for a number of trace and minor elements.

Correlations within, and contour maps of the raw data show that lake samples give essentially the same geochemical information as stream samples. Removal of environmental and minor element influences using multiple regression analysis does not alter this lake-stream relationship, but does correct for false anomalies produced by these independent variables.

In densely forested wilderness such as that encountered in the Beaverlodge area, lake sampling is an attractive alternative for geochemical surveys as it costs about one-half as much as stream sampling.

RÉSUMÉ

Pour établir des relations entre des éléments à l'état de trace dans des lacs et cours d'eau, on a recueilli dans une zone de 30 milles carrés située juste à l'est d'Eldorado, Saskatchewan, des échantillons d'eau et de sédiments à raison de quatre au mille carré. On a enregistré un certain nombre de variables sur le terrain et les échantillons ont été analysés en fonction d'un certain nombre d'éléments à l'état de trace et d'éléments mineurs.

Les corrélations et les cartes en courbes des premières données démontrent que les échantillons de lac et ceux de cours d'eau fournissent essentiellement les mêmes renseignements. L'élimination des influences du milieu des éléments mineurs par l'analyse de régression multiple ne change rien à cette relation lac-cours d'eau mais corrige les fausses anomalies engendrées par ces variables indépendantes.

Dans les forêts denses comme celles qu'on retrouve dans la région de Beaverlodge, les échantillons de lac peuvent avantageusement remplacer, dans les recherches géochimiques, l'échantillonnage de cours d'eau qui nécessite des coûts environ deux fois plus élèves.

Les sédiments de cours d'eau et les roches de cette région constituent un cas extrême de déséquilibre radioactif. Alors que les sédiments de cours d'eau contiennent au-delà de deux fois plus d'uranium décelé par fluorimétrie que par radiométrie, on découvre dans les roches presque quatre fois plus d'uranium par radiométrie que par fluorimétrie.

INTRODUCTION

One of the most difficult and time consuming tasks during the comparison study of regional uranium prospecting methods (Dyck et al., 1971) was accessing the sample sites. The reason for this was the persistent cover of spruce over the whole area, mingled with birch and willow along streams, making helicopter landings beside streams practically impossible. Sampling crews, therefore, had to land on lakes, taxi to shore, and walk to the streams, often over rugged outcrops or through swamp and muskeg. Even taxiing to shore with the helicopter was hazardous because of frequent steep outcrops or spruce at lake edges. The abundance of small lakes in the area, therefore, made them an attractive alternative for geochemical surveys, provided the information obtainable from the lakes would reflect the dispersion of trace elements as well as streams were known

to do. That this was so for radon in waters was already evident from the regional survey (Dyck et al., 1971). The question remained – was this true for other elements, and not only in waters but also in sediments? Arnold (1970) and Allan (1971) have since shown that copper in lake sediments and waters outline copper-rich areas. However, at the time no other published data were available, even though personal communications indicated that a number of companies use lake sediments in their search for ore deposits.

After the completion of the regional sampling for the comparison of uranium exploration methods, a comparative study was undertaken by resampling an area in the Beaverlodge area. Both stream and lake water and sediments were sampled and analyzed for a number of trace elements. The results were then compared statistically and graphically.

SAMPLING AND ANALYTICAL METHODS

The choice of a 30-square-mile area for this comparison study was based on the radon results from the regional survey and the ease of access from the base camp situated at Eldorado. By moving three miles upstream from the mining camp it was expected that contamination would not be a serious factor. The UTM coordinates of the corners of the nearly square sampling area are: 647900E, 6610000N, 655600E, 6612150N, 650000E, 6601000N, 657650E, 6603000N (Zone 12). The sampling was carried out as follows: when the helicopter had landed near the mouth or head of a stream, one man was let out at the shore as close as possible to the mouth of the stream to take two stream water and sediment samples, 200 to 400 feet apart and with the first one 20 to 100 feet from the lake. Another man moved

with the helicopter close enough to the mouth or head of the stream (usually 15 to 20 feet from the shore) so that he was able to take a lake sediment sample with a five-foot-long tube and a water sample while kneeling on the helicopter float (see Fig. 1). A second lake site, usually from an inactive bay in the same lake, i.e. a bay which did not have an active stream associated with it, was sampled in the same manner. The sampling team then moved to another set of related sites. In this manner 125 lake and 126 stream samples from 50 different lakes were obtained. The sample site locations are shown in Figure 2. The samples comprise 63 sets, each set consisting of two stream samples and one lake sample. Forty-nine of these sets are at streams flowing into lakes and 14 at streams flowing out of lakes. The sediment samples consist of the active layer at the bottom of the lake and as a rule are very fine textured and rich in organic matter, almost like gyttja.

Ideally the sample site pattern for each lake should have been as shown in Figure 3. Because there were more inflowing streams than outflowing ones, the sampling biases the inflow sites. In order to maintain a reasonably uniform sampling density over the whole of the target area not all lakes were sampled at all three locations. Therefore, the lake-stream comparison is completely valid only if one assumes that, on the average, the general environment of the sampled lakes and streams is comparable. In order to minimize the effect of aberrant samples all comparisons were made with log-transformed data.

The waters were analyzed in the field laboratory for radon, pH, and alkalinity. The sediments were dried and screened and the minus 60-mesh fraction analyzed in Ottawa for Ra, U, Zn, Cu, Pb, Ni, Fe, and Mn. The analytical data for Zn, Cu, Pb, Ni, Fe and Mn were obtained by atomic absorption spectrophotometry after a dilute nitric acid leach of the samples. Radium determinations were made by extracting the radon from the leach liquor which had been kept in a tightly sealed bottle for a known length of time, and counting the radon activity in a radon counter. Studies with several radioactive standards suggest that the radium results may be ~25% high. Uranium was determined fluorimetrically on the nitric acid leach solution.

It had become evident in the field that the samples contained large and varying amounts of organic matter. This was even more apparent in the laboratory working with dried and

Figure 1.

In forested regions of the Canadian Shield lake sampling is an economic alternative to stream sampling for geochemical mineral exploration.

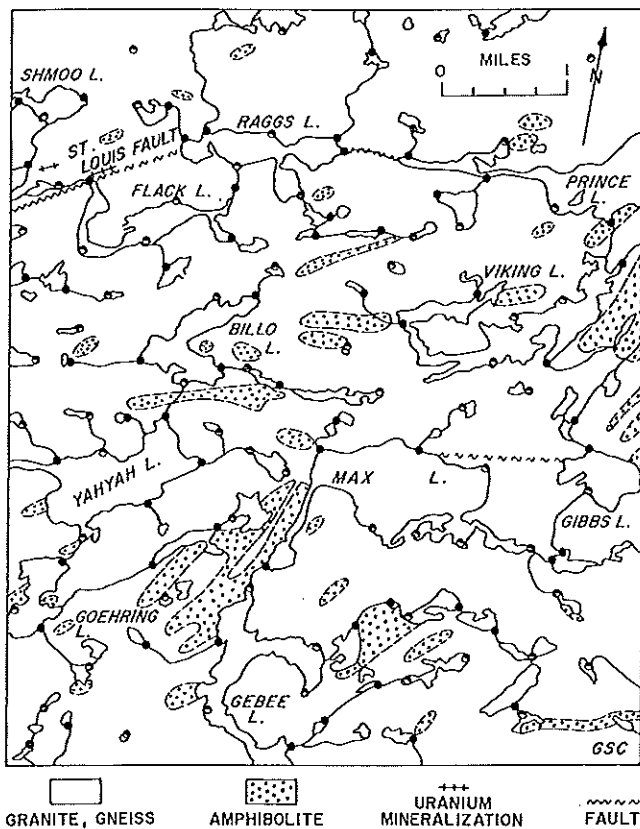GRANITE, GNEISS   AMPHIBOLITE   URANIUM MINERALIZATION   FAULT

Figure 2. Sample site locations. (Solid points are sample site sets comprising one lake and two stream sites. Half solid points are lake sites only).

screened samples. To get a more accurate relative measure of the organic content of the samples than was obtained visually at the sites, the volume of a 250 mg sample was measured using a tapered and graduated centrifuge tube. A sample rich in organic matter occupies a larger volume per unit weight, i.e., its denisty is lower. A minus 60-mesh air dry sample of sand has a density of approximately 1.4 g/cm^3. For the samples from the detailed study area a mean density of 0.36 for stream samples and 0.52 for lake samples was obtained. Hence, it was thought that the variable volume would give a fairly good and quick measure of the relative content of organic matter in sediments. This was confirmed by ashing 12 lake and 12 stream sediment samples and comparing the loss of weight on ignition to the volume of the air-dried sample (this report, Pt. A).

All field and laboratory observations were entered on computer cards for computation, grouping and sorting. The variables with abbreviations and dimensions are listed in Table 1. Not all the listed variables lent themselves to computer calculations or made obvious contributions to the study. For example, the fractions of sand, silt, and clay as judged by eye by the sampler at the site did not correlate meaningfully with trace element content, even though it is known that certain clays adsorb trace elements strongly. It appears, therefore,

that the visual estimate of clay content is insufficiently accurate in these particular samples and other means will have to be found to make an estimate of this variable.

RESULTS AND DISCUSSION

The geometric means of variables determined in this study, grouped by sample type, are listed in Tables 2 and 3. Cumulative chi square values indicated that the distributions of the trace elements lean towards lognormal; hence, only log-transformed data are used in this report.

It is interesting and at first somewhat perplexing to note (see Tables 2 and 3) that most trace element concentrations in sediments are somewhat higher at the head of streams (outflow), i.e., streams flowing out of a lake, compared to the mouth of streams (inflow), or inactive lake sites. Using the dispersion concept, the order of decreasing element content should be as follows: inflow stream, inflow bay, outflow bay, outflow stream, inactive bay. In actual fact we often see this pattern broken. Two related variables, size of lake and organic matter content of the sediment best explain these observations. The proportion of organic matter was greater in sediments from the outflow bays, and since most trace elements were strongly adsorbed by organic matter in lake sediments one can conclude that it had an appreciable influence on the distribution of trace elements in the drainage systems. The trace element dependence on organic matter is also observed in streams except that, with higher contents of organic matter, the concentrations are somewhat higher. Radium is not adsorbed by organic matter, hence it and radon show the expected element distribution pattern in a drainage system.

Because of the apparent dependence of the trace element content on the content of Fe, Mn, organic matter, and to a lesser extent on other environmental variables, the comparison of lake and stream samples could be misleading. One could argue that the positive correlation between related stream and lake sample variables was due to these "independent" variables. Hence a measure of, and correction for, the effect independent variables have on the trace element content was obtained by multiple regression analysis using a computer program published by Krumbein et al. (1964) and modified for use in Ottawa by Garrett and Hobbs (pers. comm., 1971). Recent applications of multiple regression analysis techniques to stream sediment geochemistry have been reported by Rose and Suhr (1971) and Chatupa and Fletcher (1972). For this work the first eight variables shown in Tables 2 and 3 were in turn made the dependent variables and the remaining variables the independent ones. Essentially the program uses the degree of interdependence or correlation between all the data for certain variables to calculate the expected trace element content of a specific sample assuming a linear dependence of trace element content on the chosen independent variables. These predicted values

Table 1.

Variables determined in this study.

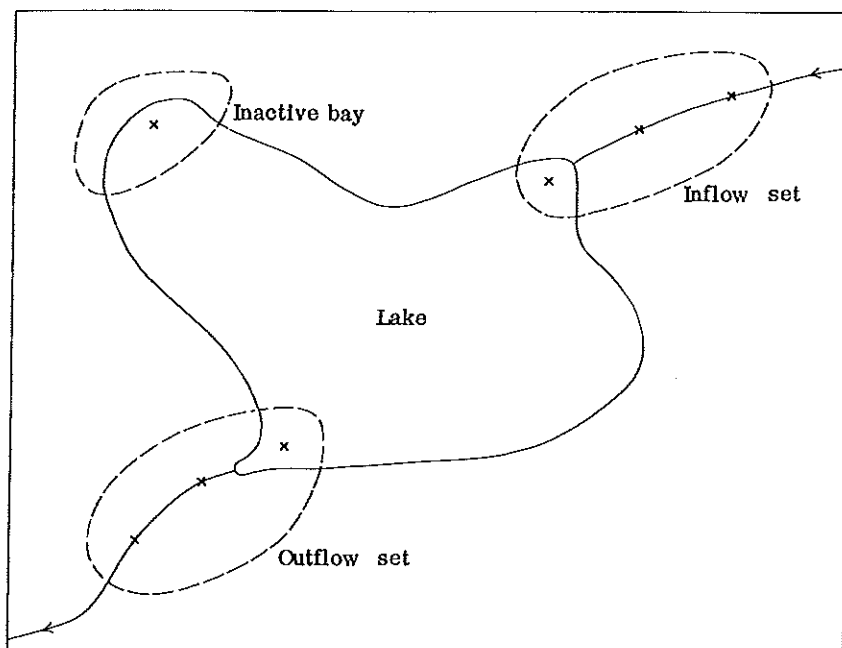| Variables	Dimensions or relative scale	Abbreviations of:		Detect. limit
		Variable	Dimension	
1. – determined at sample site:				
Depth of lake or stream at site	Feet	Depth	ft	0.5
Width of stream at site	Feet	Width	ft	1.0
Temperature of water	Degrees Centigrade	Temp.	°C	0.5
Colour of water	1=clear; 2=yellow;	Colour	–	–
Turbulence of water	0=still; 1=slight; 2=moderate; 3=strong;	Turb.	–	–
Level of water	1=dry; 2=low; 3=normal; 4=high;	Level	–	–
Flow rate	0=stagnant; 1=slow; 2=moderate; 3=fast;	Flow	–	–
Composition of sediment:	gravel, sand, silt, clay, organic matter.	–	–	–
	Relative scale: 0 to 9.	–	–	–
Boulder fraction in stream bed	Relative scale: 0 to 9.	Bold	–	–
2. – determined in field laboratory:				
Radon in water	Picocuries per litre	Rn	pc/1	1.0
Alkalinity of water as $CaCO_3$	Parts per million	Alka.	ppm	0.5
Acidity of water	–	pH	–	0.05
Coordinates of sample site	UTM grid; 1:50,000 scale	–	–	–
Elevation of sample site	Feet	Elev.	ft	20.0
Area of sampled lake	Square kilometres	Area	km^2	0.1
3. – determined in Ottawa laboratory:				
Uranium in water	Parts per billion	U(H_2O)	ppb	0.5
Uranium in sediment	Parts per million	U(Sed.)	ppm	1.0
Copper in sediment	Parts per million	Cu	ppm	3.0
Lead in sediment	Parts per million	Pb	ppm	3.0
Zinc in sediment	Parts per million	Zn	ppm	3.0
Nickel in sediment	Parts per million	Ni	ppm	3.0
Iron in sediment	Per cent	Fe	%	0.05
Manganese in sediment	Parts per million	Mn	ppm	10.0
Radium in sediment	Picocuries per gram	Ra	pc/g	0.5
Volume of 250 mg of dry (–60 mesh) sediment	Millilitres	Vol.	ml	0.1

Figure 3. Explanation of sample site locations.

are akin to unique background values for each element at each site. One way of ascertaining the efficacy of regression analysis is to calculate the per cent reduction in variance of the trace element content due to the regression. These percentages are shown in Table 4. It is at once evident that organic matter (Vol.), Fe, and Mn exert a much stronger influence on the variation in the trace element content in sediments than the other variables. Zn and Ni in stream sediments are an exception with zero per cent reduction in variance due to organic matter. However, the alkalinity and flow of the streams seem to be responsible for a somewhat greater reduction in variance for these two elements.

Plotting normalized residuals is perhaps the most useful way in which multiple regression analysis can be applied to geochemical exploration. The concentration ratios (antilogs of residuals of log-transformed data), are an indication by what factor the measured values deviate from the predicted, or background values of the samples. Ratios much greater than one may indicate mineralization.

To demonstrate graphically the effect regression analysis can have, contour maps of raw U, Rn, and Ra data are compared to concentration ratio maps in Figures 4 and 5. The base for these maps was prepared from topographic maps and geological reports by Christie (1953) and Blake (1955). To conserve space Rn in waters and Ra in sediments are combined in one map: as are U in waters and U in sediments. The contour levels for these maps are given in Table 5. To reduce crowding only two contour levels for each element were used. Unfortunately, this resulted in more spotty and weaker looking coincidences of anomalies. For example, the individual radon highs of lake results around Yahyah Lake (point 1, maps 5A and 5C) become one large high if

the $\overline{X}+\frac{1}{2}S$ contour is left in.

It is apparent that the ratio maps are quite similar to the raw data maps. Both sets of maps outline several areas where U and its decay products, Ra and Rn, occur in greater abundance. Allowing for map-edge effects produced by the computer contouring program and the frequency with which the element highs occur in all 8 maps, the three most prominent areas, in order of apparent significance, are located as follows: (1) around Yahyah Lake (point 1), (2) south of Schmoo Lake (point 2), (3) north of Gibbs Lake (point 3). In addition there are a number of coincident single point highs witnessing to the fact that there are numerous U showings in the area. Examining the maps in detail one does find differences between the raw and the regressed maps, particularly in the case of Rn in streams. For example, the Rn anomaly in the northwest corner of the raw stream data map (point 2, map 5B) is slightly enhanced in the ratio map, probably because of the higher than normal water temperature and the below average iron and manganese content in the sediment at that site. Iron and manganese, particularly manganese, correlate positively with Ra, the immediate parent of Rn. The below average manganese content also affects an increase in Ra in the ratio map at this stream site. The Rn-temperature correlation is negative for two reasons. One is strictly a solubility factor and the other stems from the fact that the coldest waters are at or near springs. The spring water has been sealed underground and hence the Rn has not been able to escape to the atmosphere as it does in surface waters. Two other stream Rn anomalies are strongly reduced in the ratio map; the one in the northwest corner of map 5B (point 4) because of low temperatures (6 and 3°C) and the one near the middle of map 5B (point 5) due to an unusually high Fe content (3%) in the sediment. Similarly a small Ra anomaly at the east end of Flack Lake (point 6, map 5B) disappears due to an unusually high Mn content (31,100 ppm) in the sediment.

There are fewer differences between the raw data maps and the regression data maps produced from lake sample variables. Mainly because the independent variables differ less from lake to lake than they do from stream to stream. Compare the standard deviations in Table 2. They are appreciably smaller for the lake variables. The cause of the increase in the highs of the Rn concentration ratios around Yahyah Lake (point 1, map 5C) is not apparent from a check of the independent variables. Nonetheless, the increase fits in well with the high stream Rn levels and the high lake U levels of this area. It should be noted though, that Yahyah Lake had the highest average pH and alkalinity values of the 10 largest lakes in the area. Since U forms carbonate and bicarbonate complexes in aqueous solutions the water highs could be in part due to the high alkalinity.

Table 2.
Geometric means and standard deviations of lake samples (numbers in brackets are number of samples).

Variable	All (125)		Inflow (57)		Outflow (35)		Inactive (33)	
	X	Log S	X	Log S	X	Log S	X	Log S
Rn, pc/1	2.2	.593	2.6	.724	2.2	.497	1.2	.818
U(H$_2$O), ppb	1.0	.306	1.1	.298	0.9	.443	1.0	.293
Ra, pc/g	0.9	.304	1.0	.308	0.9	.447	0.9	.268
U(Sed.), ppm	17.1	.596	19.3	.533	20.2	.473	11.7	.658
Zn, ppm	36.2	.350	31.8	.240	47.6	.276	33.9	.377
Cu, ppm	11.0	.518	9.1	.737	14.1	.352	9.4	.693
Pb, ppm	2.0	.743	1.6	1.231	2.5	1.013	2.4	1.043
Ni, ppm	9.0	.284	8.3	.288	11.0	.224	8.3	.318
Mn, ppm	168.4	.287	189.5	.283	180.4	.253	127.3	.294
Fe, %	0.77	.279	0.84	.284	0.77	.240	0.69	.303
Vol., ml*	0.44	.193	0.42	.185	0.47	.189	0.44	.212
pH	7.66	.024	7.70	.018	7.67	.025	7.59	.030
Alka., ppm	26.9	.210	27.7	.166	29.2	.197	23.6	.201
Area, km^2	0.17	.766	0.30	.680	0.06	.590	0.20	.849
Depth, ft	3.1	.193	2.9	.214	3.1	.193	3.6	.140
Temp., ^{o}C	19.3	.031	19.6	.030	19.2	.033	18.5	.044
Elev., ft	1255	.036	1226	.030	1275	.031	1284	.046

*Volume of 250 mg of dry (-60 mesh) sediment.

Table 3.
Geometric means and standard deviations of stream samples (numbers in brackets are numbers of samples).

Variable	All (126)		Inflow (98)		Outflow (28)	
	X	Log S	X	Log S	X	Log S
Rn, pc/1	35.1	1.012	48.1	.980	11.6	.993
U(H$_2$O), ppb	1.0	.291	1.0	.292	0.8	.270
Ra, pc/g	1.2	.482	1.3	.452	1.0	.578
U(Sed.), ppm	23.1	.589	22.5	.613	25.3	.508
Zn, ppm	28.0	.345	25.5	.335	39.0	.351
Cu, ppm	18.3	.347	17.3	.359	22.4	.293
Pb, ppm	8.3	.588	7.3	.638	13.1	.280
Ni, ppm	10.1	.361	9.3	.344	13.6	.398
Mn, ppm	334.5	.627	330.4	.618	349.6	.670
Fe, %	0.94	.383	1.02	.362	0.72	.439
Vol., ml*	0.63	.205	0.60	.205	0.77	.183
pH	7.02	.028	7.01	.027	7.04	.030
Alka., ppm	36.7	.214	38.5	.206	31.2	.228
Width, ft	4.0	.447	3.7	.424	5.1	.513
Depth, ft	1.5	.290	1.4	.303	1.8	.227
Temp., ^{o}C	12.7	.185	12.0	.196	14.8	.117
Elev., ft	1245	.031	1233	.031	1286	.032
Flow	0.5	.823	0.5	.835	0.7	.779

*Volume of 250 mg grams of dry (-60 mesh) sediment.

Table 4.
Percentage of the variance of dependent variables accounted for by individual independent variables.

Independent Variables	Rn SS*	Rn LS*	(H₂O) SS	(H₂O) LS	Ra SS	Ra LS	U(Sed.) SS	U(Sed.) LS	Zn SS	Zn LS	Cu SS	Cu LS	Pb SS	Pb LS	Ni SS	Ni LS
Width or Area	8	0	2	1	2	0	1	7	4	22	1	15	1	11	1	7
Depth	2	6	1	0	2	0	0	5	0	1	3	0	3	0	0	1
Flow	0	--	2	--	2	--	5	--	6	--	8	--	9	--	5	--
Temp.	29	1	0	3	1	0	4	3	6	4	2	2	0	3	1	0
Elev.	3	10	5	13	4	3	6	3	0	8	1	1	0	5	1	0
Alka.	11	11	3	9	3	4	9	16	8	1	3	4	0	0	6	0
Mn	2	1	1	0	35	9	0	12	27	27	2	13	14	14	15	26
Fe	2	0	1	0	13	3	3	1	27	22	0	7	7	7	22	23
Vol.**	0	2	0	2	0	6	28	30	0	38	15	53	14	43	0	27
pH	14	1	3	4	0	0	0	2	3	6	2	0	0	2	1	2

*SS = stream samples.   LS = lake samples.   **Volume of 250 mg of dry (-60) mesh sediment.

Table 5.
Contour levels of trace element plots shown in Figures 4 and 5.
(Lower contour = $\overline{X}$ + S; Higher contour = $\overline{X}$ + 1.5S)

Variable	Concentration contours Lakes		Concentration contours Streams		Concentration ratio contours Lakes		Concentration ratio contours Streams	
Rn	8.7	18.7	312.0	967.0	2.9	5.1	4.0	8.2
U(H₂O)	2.3	3.4	1.9	2.6	1.9	2.6	1.9	2.7
Ra	1.9	2.6	3.7	6.4	1.9	2.5	2.1	3.1
U(Sed.)	65	129	89.0	175.0	2.2	3.3	2.5	4.0

However, the fact that calcite is found in the gangue of U ore of existing mines may in fact be more significant for the observed U-pH-Alka. coincidence in this area. But regression analysis cannot differentiate between two different causes which produce identical results. In such cases the investigator has to rely on geological knowledge and field experience. Anomaly 7 (map 4C) demonstrates clearly the effect of pH and alkalinity on the U residuals of lake waters. In this case, the unusually low pH and alkalinity of 6.6 and 4.2 respectively, were sufficient to put an anomaly on the ratio map. The reader must keep in mind though that this anomaly, as well as several others, appears larger also because of the manner in which the computer program projects trends near the edge of maps. The effect of a lack of organic matter is demonstrated by anomaly 8 appearing in the northeast corner of ratio map 4C. The raw data map 4A does not have an anomaly at this point because the sediment sample contained only 8 ppm U compared to a mean of 17 ppm.

However, a check showed that this sample contained virtually no organic matter. Hence 8 ppm U in the clastic sediment became significant when compared to the average organic-rich sediment sample in the area. The final test of the usefulness of regression analysis must come from follow-up work in the field. The over-all results of this comparison indicate that the method gives additional information helpful in interpreting field situations.

The similarity between lake maps and stream maps for the three elements U, Ra, and Rn shown in Figures 4 and 5 is also unmistakable, although the maps are by no means identical. Ra gives the weakest anomalies. No doubt its extremely low mobility is responsible for this. The mobility of Rn is somewhat greater than that of Ra, at least in streams, and hence it gives somewhat more coherent anomalies. As was noted earlier, the spotty appearance of the anomalies is partly due to the fact that only two contours were used for each element.
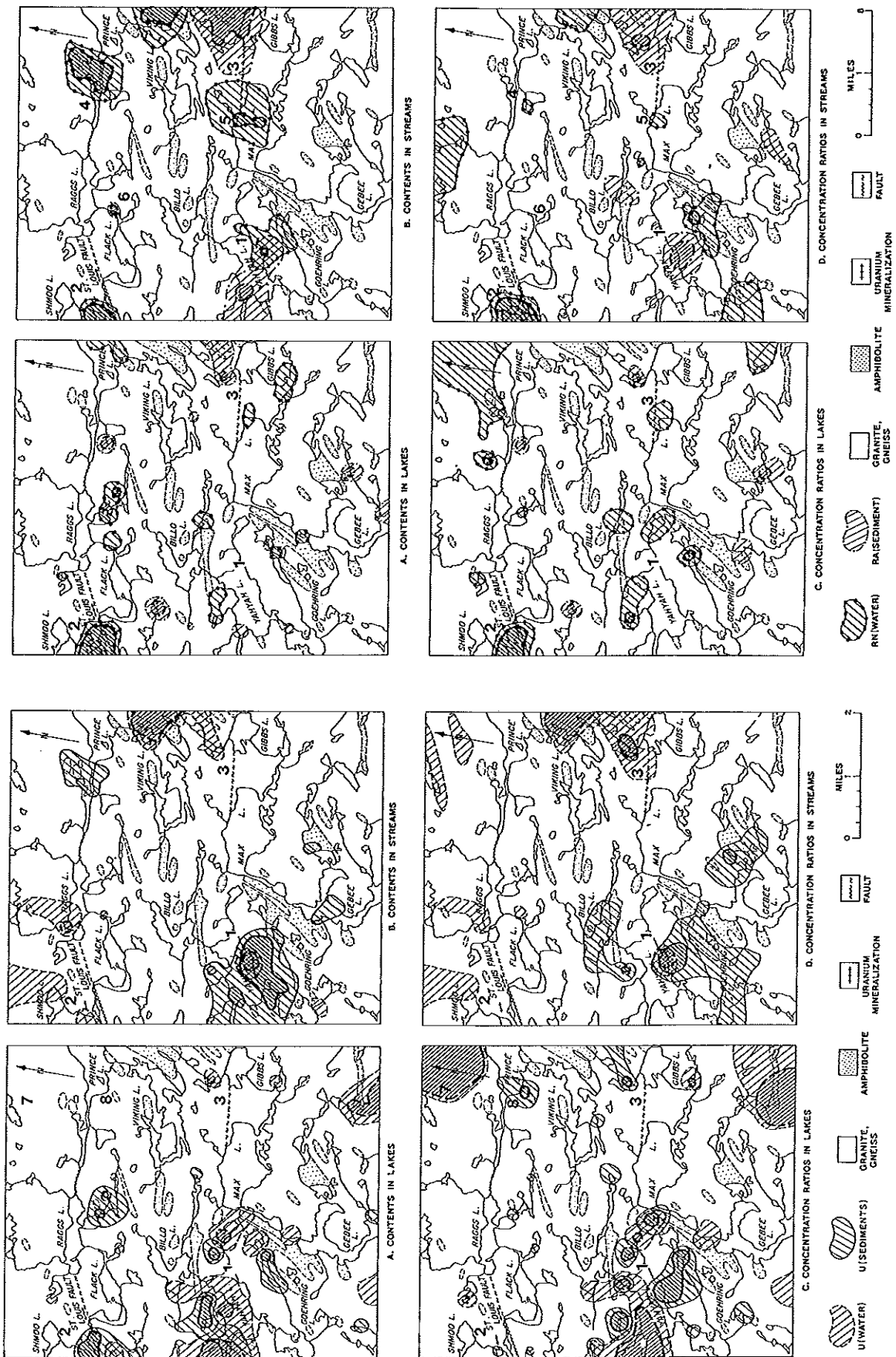
Figure 4. Comparison of uranium maps.

Figure 5. Comparison of radium and radon maps.

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Table 6.
Comparison of correlation coefficients of trace element concentrations of samples from 63 related sites.
$(r_{.95} = .24; r_{.99} = .34)$

Related Site pairs	Variable							
	Rn	U(H$_2$O)	Ra	U(Sed.)	Zn	Cu	Pb	Ni
	Before regression analysis							
Lake-Stream	+.08	+.15	+.34	+.53	+.39	+.41	+.24	+.47
Stream-Stream	+.61	+.27	+.39	+.70	+.59	+.65	+.91	+.63
	After regression analysis							
Lake-Stream	+.28	+.12	+.27	+.35	+.09	+.36	+.23	+.26
Stream-Stream	+.44	+.15	+.14	+.46	+.27	+.31	+.56	+.43

Adding the $\bar{X}+\frac{1}{2}S$ contour to the maps joins a number of the point anomalies to form fewer larger ones.

No maps were produced for Zn, Cu, Pb, and Ni. However, their close stream-lake association is evident from the correlation coefficients shown in Table 6. For this comparison the data for the lake-stream sets (using the stream sample closest to the lake) and the pairs of stream sediment samples from each set were used for the calculations. It would be disturbing indeed if the stream sediment pairs would not correlate positively. The fact that the variables from the related lake and stream sites also correlate positively is evidence that lake samples are giving the same geochemical information as stream samples. Radon and uranium in the water of the merged lake-stream sites, however, correlate only weakly. The dilution of the lake water by the bulk of the water is probably responsible for this feature. In order that there be no doubt as to the validity of these lake-stream correlations, the correlation coefficients after regression analysis were also obtained and included in Table 6. After all, one could argue that since the trace element content was so dependent on the organic matter and iron and manganese, the correlation might be due to these rather than to a common source. In fact, a somewhat weaker correlation is obtained generally using regression data. The shift in the observed correlation coefficients can be explained in two ways: First, assume that multiple regression analysis has removed all external influences, except those due to an anomalous source. Then a positive correlation after regression analysis must be due to this source. If no significant source exists the correlation should drop to zero after application of regression analysis. Only if there is a marked difference in the independent variables between related sites can one expect improvement in correlation after regression analysis provided there is a trace element source of significance upstream. On the basis of this argument the observed correlations between identical trace elements from the related sites could be due in part to the similarity of independent variables of the sites and in part due to a common source. The radon correlation could be said to improve because of the large difference in the independent variables, temperature and

depth of water in going from the stream to the lake; Zn on the other hand, loses most of the correlation because it has no significant point source.

Secondly, and probably more importantly, the fact that the residuals generally show a drop in correlation implies that the predicted values contain significant systematic interrelationships suggesting that the chosen 10 independent variables were not really independent of each other. For example, the variables width, depth, level and flow should really be entered as one compound variable denoting the volume flow rate of a stream. Similarly, alkalinity and pH are so closely related that only one need be used. Elevation appears several times as an independent variable of importance in the regression. Since size of stream or lake and temperature diminish with increasing elevation these variables are not really independent of each other, and hence only one or two of these would be required in the regression equation. Iron presents a somewhat different problem. Its common mode of occurrence as a constituent of many mineral deposits of economic importance makes iron particularly difficult to apply wisely in regression analysis. One would really have to know first what fraction of the iron in a sample was due to leached iron from nonmineralized rock and what due to iron in the mineral occurrences of interest to the prospector. It should be noted that the variance of the dependent variables did not change appreciably with an increase in the number of independent variables beyond 5. However, a problem arises in making the proper choice. There is little doubt about organic matter and manganese but the remaining independent variables are interrelated and should be screened carefully. The clay-size fraction presents a problem similar to that of iron. Clays have an appreciable and variable capacity to adsorb trace elements but the fraction could also contain other mineral particles of clay size. Ideally one should also allow for rock type. In a geochemical survey over large areas encompassing several distinct rock types, independent variables allowing for rock type could be used, by including major and/or minor elements for each rock type in the region.

The results of this study and the above discussion indicate some of the complexities and potentials of multiple regression analysis in geochemical exploration. The small number of samples collected for this study do not warrant further manipulation of the data. More samples with stricter control on site location and painstaking search for truly independent variables will make regression analysis a powerful tool in the search for ore deposits.

COST COMPARISON

As outlined in the introduction, the stream and lake samples were collected at the same time. During the time that one man collected two stream samples from the same stream about 200 to 400 feet apart, another man, staying with the helicopter, collected two lake samples from two different sites. In this manner an average of three lakes and three streams were sampled per hour. The 20 minutes per site included the time it took to fly from field camp to sampling area, taxiing to shore to let off the person sampling the stream, collecting three water samples from three different depths in the lake, collecting a sediment sample from the lake bottom, flying to another lake site, sampling it in the same manner, and returning to pick up the man with the stream samples before repeating the sampling cycle. Of this 20 minutes about one quarter was spent in moving the stream sampling man and one quarter in collecting the three lake water samples, leaving an average of 10 minutes per lake sediment sample, or about six lake samples per hour. Since helicopter time is by far the most expensive single item in a geochemical sampling program, it can be calculated that to collect such a sample costs approximately $28 using a small helicopter such as the Bell 47G2. By comparison the 550 stream sites sampled during the regional survey just prior to the detailed study, took 193 helicopter hours, or just over twenty minutes per sample. The greatest delay was caused by the fact that the helicopter was unable to land at the stream sampling site, but had to land instead on the lake at the mouth of the stream then taxi to shore to let the sampler off. Since many streams were swampy the sampler had to walk sometimes as much as one-half mile to the stream site. Thus, for the regional survey the average cost per stream sample, including helicopter time, labor, travel, and field camp expenditures amounted to $53.

It is thus apparent that a lake sampling program in densely forested areas is much more economical provided the information obtained from the lake samples is of equal value to that obtained from stream samples. That this is so in terrane like that encountered in the Beaverlodge area has been demonstrated in this report.

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