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REPORT OF INVESTIGATION No. 14

THE Cu, Pb, Zn, Mn, Mo and Sb CONTENT  
OF STREAM AND SPRING SEDIMENTS,  
YORK COUNTY, NEW BRUNSWICK

by

V. B. AUSTRIA, JR.

MINERAL RESOURCES BRANCH  
DEPARTMENT OF NATURAL RESOURCES  
PROVINCE OF NEW BRUNSWICK  
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## INTRODUCTION

A reconnaissance sampling of drainage sediments was carried out in the southern part of York County, New Brunswick during the summer of 1970. This was a continuation of the regional sampling program initiated by the Mineral Resources Branch in 1966 (Wolfe, Mason, and Mazerolle 1967), carried on to 1967 (Wolfe and Szabo, 1968) and to 1968-1969 (Austria, 1970).

The geochemical survey is designed to obtain the regional distribution patterns of trace elements and establish criteria for their interpretation in relation to bedrock composition and secondary environment. This report includes the distribution of Cu, Pb, Zn, Mo, Mn, and Sb in stream and spring sediments.

In addition to regional sampling, a detailed stream sediment and soil sampling program was made near the Lake George antimony deposits to gather information which may prove useful in the search for the metal elsewhere. Preliminary results of the study is included here, and a more comprehensive report on the behavior and distribution of antimony in the secondary environment will be published in the near future.

## REGIONAL GEOLOGY

The area has been mapped on a regional scale by H.A. Lee (1956), W.M. Tupper (1956), J.M. Patterson (1957), R.K. Clark (1961), C.S. Clark (1961), and by J.C. Smith (1966). A compilation of the work published by these workers is shown on Map 1.

Dated rocks in the area ranges in age from Silurian to Pennsylvanian. Silurian strata include: greywacke, quartzite, argillite, slate and limestone that have been locally metamorphosed to hornfels, schists and gneisses near intrusive contacts. The intrusive rocks of Devonian age are mainly granite and quartz-monzonite. Red and grey conglomerate sandstone and shale of Mississippian to Pennsylvanian age overlie older units.

### SILURIAN

Silurian stratigraphy comprises two belts that border the granite batholith on the east and west. Compositional variations and association in the west belt are more diversified than those of the east belt, but despite these dissimilarities, units of west and east belts are correlative in age on the basis of fossils.

Stratigraphy of the west belt includes metasedimentary and metamorphic rocks with associated extrusive and intrusive rocks. Quartz-mica schist, gneiss and hornfels (1) are found mainly near granitic contacts or as inclusions in the granitic mass. These rocks are probably the metamorphic equivalents of dark grey and green argillite and slate (2) and of black limestone and argillaceous limestone (2a) (Patterson, 1957). Minor pebble conglomerate and greywacke (2b) are associated with argillite and slate.

In contrast, the strata of the east belt are made mainly of greywacke and quartzite with associated slate and argillite (3). These rocks grade locally to hornfels near granite contact (Patterson, 1956; R.K. Clark, 1961).

Extrusive rocks composed of andesite and porphyritic amphibolitic lavas (4), and intrusive rocks composed of porphyritic rhyolite and quartz porphyry (4a) have been mapped within metasedimentary rocks of the west belt (Tupper, 1956; Patterson, 1956). No equivalents of these rock units have been found in the east belt.

## DEVONIAN

The Devonian batholith which underlies more than half of the map-area is composed mainly of granite and quartz-monzonite (Patterson, 1956; Smith, 1966). Grano-diorite and aplite constitute a minor part of the granitic mass.

The granitic rocks intrude and metamorphose older units. Metamorphic effect of intrusion is generally more intense and more widespread in the west than in the east (Ruthledge, 1956).

## MISSISSIPPIAN

The Mississippian strata includes closely related volcanic and sedimentary units. Rhyolite and porphyritic rhyolite with interbedded tuff and breccia (6) comprise the volcanic sequence. Sedimentary rocks include: red conglomerate and sandstone with interbedded siltstone and minor tuff (7).

A major northeast fault separates Mississippian units from older Silurian units on the west. They are overlain by younger Mississippian and Pennsylvanian strata on the east.

## MISSISSIPPIAN AND PENNSYLVANIAN

Red conglomerate and sandstone with interbedded grey conglomerate and sandstone and minor carbonaceous sandstone (8) predominate within the strata of Mississippian and Pennsylvanian age (R.K. Clark, 1961). They are exposed mainly along a narrow northeast belt where the overlying Pennsylvanian strata have been eroded.

The sedimentary beds dip moderately to the east, but in general, they are relatively undeformed.

## PENNSYLVANIAN

Flat-lying sedimentary strata of Pennsylvanian age underlie most of the southeastern part of the area. Here, pebble conglomerate and grey sandstone grade locally into red conglomerate, sandstone and shale (9). Manganiferous and carbonaceous beds are commonly associated with the grey beds (C.S. Clark, 1961).

Erosional remnants of quartz-pebble conglomerate have been mapped north of Lake George (Patterson, 1957). They unconformably overlie older Silurian strata.

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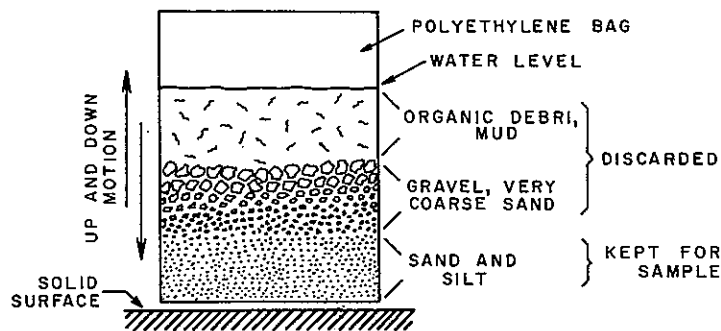
## GEOCHEMICAL INVESTIGATIONS

### FIELD AND ANALYTICAL PROCEDURES

#### SAMPLING TECHNIQUE

Samples of fine sand and silt were collected from active stream channels, rivulets, and springs. A uniform density of sampling was not accomplished because of the irregular drainage pattern and the limited access to some parts of the area, and also, as a result of maintaining uniformity of sample type. Swamps and boggy places were avoided but rivulets and springs that feed into these areas were sampled.

Preliminary sizing of sampled materials was done at sample sites. This was accomplished by jiggging the sediments in polyethylene bags and using stream water as the separating medium. See sketch below:



Sufficient amount of fine sand and silt can be obtained from gravelly stream beds by repeating the above process several times.

The process also washes away much of the suspended solids which may contain varying amounts of metals. Table 1 shows the relative variations in the metal content between the "unwashed" and "washed" samples from several localities. Variations may depend on the amount and nature of suspended solids.

Bulk samples of granitic rocks and of the different units representing Silurian stratigraphy were collected at random. Table 2 shows the range and average Cu, Pb, Zn, Mo, and Mn content of bedrock types.

#### ANALYTICAL METHODS

The sediment samples were dried and sieved, and estimates of metal content were made on the minus 80 - mesh fractions. Analysis for Cu, Pb, Zn, Mo, Mn and Sb were done by the Research and Productivity Council in Fredericton.

TABLE 1

Comparative Estimates of Metals in "Unwashed"  
and "Washed" samples

Sample Number	Cu		Pb		Zn		Mo		Mn	
70 1284	5	2	21	12	97	93	3	1	1570	990
70 1287	20	15	25	26	130	118	2	1	3270	1630
70 1269	13	8	33	11	140	126	1	2	3030	1540
70 1291	11	9	95	76	95	114	1	1	900	595
70 1293	14	8	56	26	111	95	1	1	1810	1480
70 1295	11	8	38	35	118	100	3	2	1750	1390
70 1299	14	9	40	44	147	118	8	9	3820	5160
70 1302	8	5	26	30	83	79	1	1	1140	960
70 1305	21	13	21	19	85	71	1	1	1040	765
70 1323	19	13	24	22	89	71	3	2	1850	1610
70 1325	9	6	32	21	136	112	9	8	8070	5850
70 1329	22	20	35	40	80	64	2	1	3410	535
70 1334	19	11	26	19	122	92	6	2	1310	1130
70 1337	7	7	55	69	69	67	4	4	6420	8820
70 1345	33	18	33	29	82	75	3	2	1100	550
70 1346	21	12	13	20	44	52	1	1	1040	1290
70 1347	21	20	25	18	98	68	1	1	1960	1470
70 1348	36	30	52	43	135	110	2	2	2390	1470

left column - unwashed or non-homogenized  
right column - washed or homogenized

TABLE 2

Estimates of Abundance of Metal in Bedrock

Rock type	n	Cu	Pb	Zn	Mo	Mn
Dev. granite, quartz monzonite	20	6-47* 17**	1-36 10	17-77 30	1-3 1	130-830 280
Sil. Greywacke	11	9-180 70	16-54 31	17-96 55	1-17 5	255-1500 775
Sil. schist, gneiss	13	10-124 47	4-69 25	26-112 73	1-6 5	190-1100 520
Sil. limestone	2	24-54	14-25	54-87	3-4	920-3500

\* range

\*\* average

Mn
30-830
280
55-1500
775
30-1100
520
30-3500

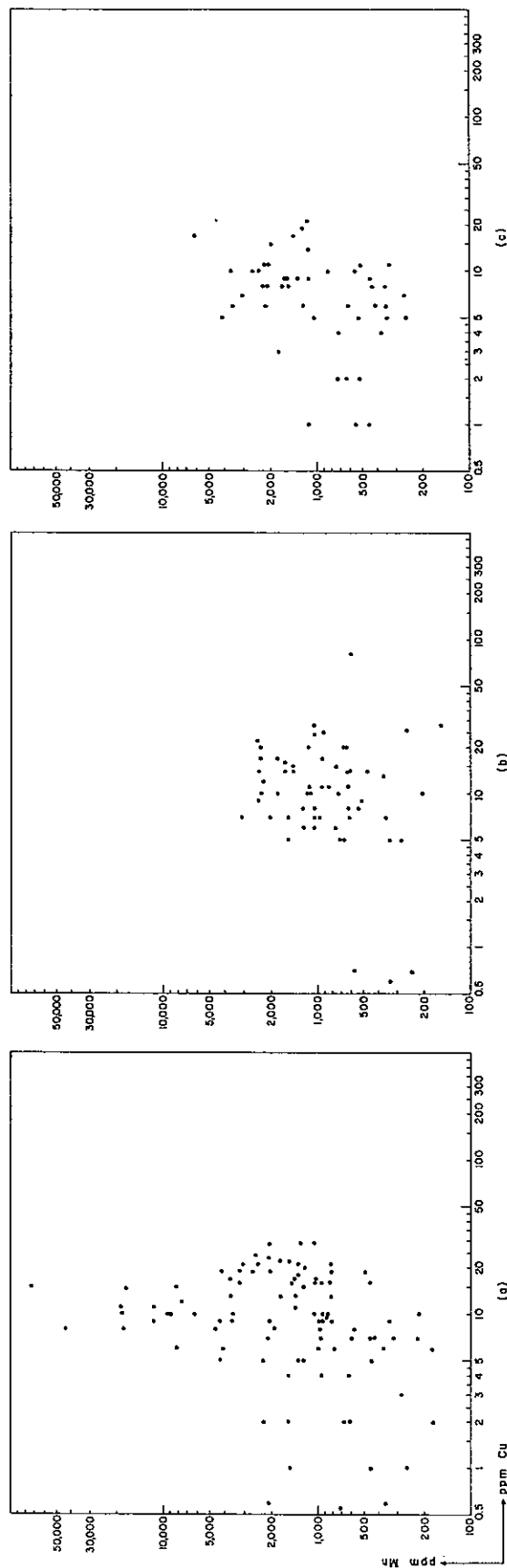


FIGURE 1 : Copper-manganese ratio in relation to bedrock type : (a) granite, (b) Silurian sedimentary rocks, (c) Carboniferous sedimentary rocks

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Higher than average concentrations and anomalous concentrations of copper are distributed mostly in areas underlain by granitic rocks and by Silurian sedimentary and metamorphic rocks. Average and below average concentrations are spread mainly in the areas underlain by Mississippian and Pennsylvanian sedimentary rocks.

Sediment-bedrock relationships may explain some anomalies related to Silurian units but not those related to granitic rocks. The average copper content of Silurian units is significantly higher than that of granitic rocks (Table 2), but this is not reflected in the gross regional distribution of the metal in the sediments. The sediment-bedrock relationship in granitic terrain could have been offset by the secondary environment.

Accumulation of copper in mud or organic-rich sediments is suggested by higher copper values obtained from "unwashed" samples relative to those of "washed" samples (Table 1). Significant fluctuation of metal values can therefore be expected in places where separation of mud and organic sediments from fine sand and silt is not feasible.

Samples from springs and spring-fed rivulets generally contain higher concentrations of copper than those taken from larger streams. High pH and Eh conditions in most spring environments favor the precipitation of most metals, including copper, from underground water with relatively low pH and Eh. More important here is probably the adsorbing and coprecipitating effect of manganese and iron oxides (Hawkes and Webb, 1962).

No data are available on the iron content of stream and spring sediments, but elsewhere, it has been found that about 50 percent of the total copper in sediments from background areas is fixed by iron oxides (Rose, Dahlberg and Keith, 1970).

The effect of manganese on the fixation of copper is not significant as suggested by the poor correlation between the two metals (Fig. 1). This is clearly demonstrated in scatter diagram for granitic terrain showing extremely high manganese to copper ratios (Fig. 1a).

#### DISPERSION OF LEAD

The lead content of stream and spring sediments ranges from 2 ppm to 210 ppm with an average of about 23 ppm. Map 3 shows the regional dispersion patterns and the statistical distribution of lead.

The frequency distribution plot indicates that lead distribution is not normal but positively skewed. The broken line shown in the cumulative percentage graph indicates that the distribution is not homogeneous and the two segments of the broken line may represent two log-normally distributed populations.

Higher than average concentrations of lead are found in many parts of the area but anomalous concentrations are most conspicuous in granitic terrain. Average and below average concentrations of the metal are distributed mostly in areas underlain by Carboniferous sedimentary rocks.

The lead content of granitic rocks is low compared to that of Silurian sedimentary and metamorphic units (Table 2), but this relative abundance of the metal in

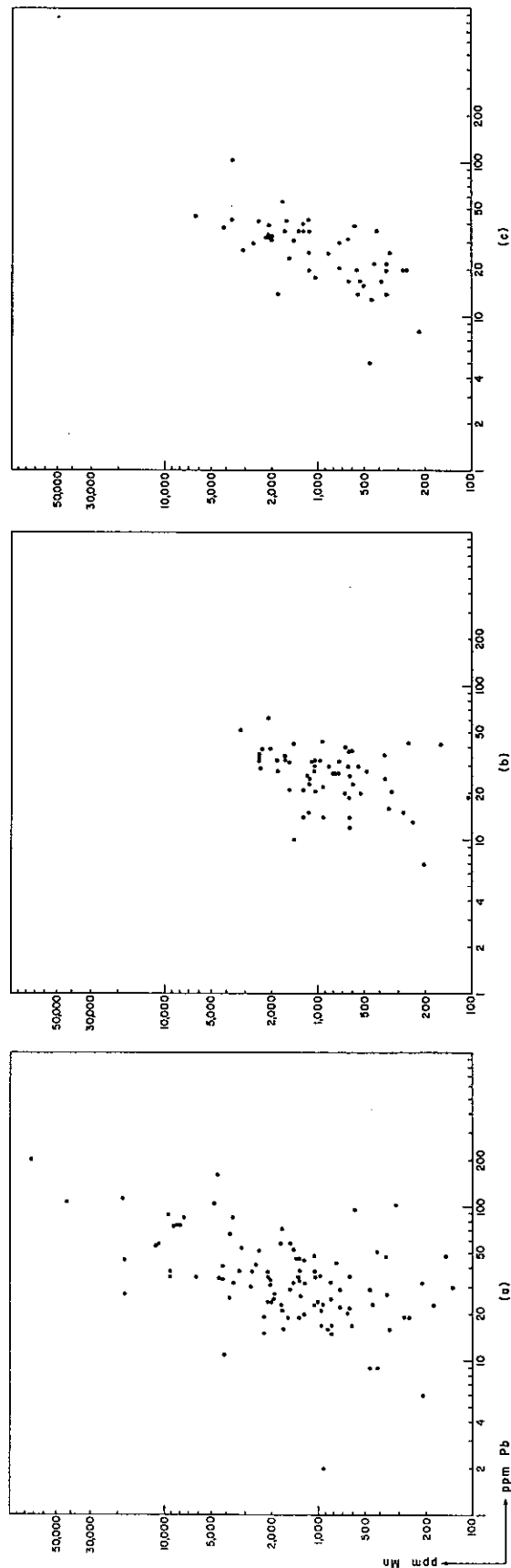


FIGURE 2 : Lead-manganese ratio in relation to bedrock type : (a) granite, (b) Silurian sedimentary rocks, (c) Carboniferous sedimentary rocks

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bedrock is not reflected in the sediments. Concentration of lead in sediments seems to be more related to secondary factors rather than to primary (bedrock) concentration.

High lead values are generally correlative with extremely high concentrations of manganese. The scatter diagrams for manganese and lead ratios (Figure 2) suggest positive correlations between the two metals in all three of the bedrock environments specified. The relationship can be expressed roughly by a power function of formula  $y = ax^b$ : where  $y$  = concentration of manganese;  $x$  = concentration of lead; and  $a$  and  $b$  are constants.

Strong absorptive capacity of manganese oxides may explain the significant enrichment of lead in manganiferous sediments. It is not unlikely that the higher abundance of lead in granitic terrain could have been effected by high abundance of manganese in sediments derived from granitic rocks.

Lead, like copper, shows enrichment in sediments with high mud or organic content. Higher concentration of the metal in "unwashed" samples relative to the corresponding "washed" samples is indicated in Table 2. Enrichment factor for lead is nevertheless, lower than that for copper.

#### DISPERSION OF ZINC

The zinc content of stream and spring sediments ranges from 3 ppm to 366 ppm with an average of about 70 ppm. Map 4 shows the dispersion patterns and statistical distributions of zinc.

The frequency distribution plots indicate that zinc distribution is more log-normal than normal. The broken line shown in the cumulative percentage graph indicates that the distribution is not homogeneous and it may be possibly a combination of two or more populations.

The regional dispersion patterns of zinc is very similar to that of lead, that is, high abundance is related to the distribution of granitic rocks and average abundance to the distribution of Carboniferous sedimentary rocks. Similarly, the relative abundance of zinc in drainage sediments may not be related to the abundance in the bedrock. This reverse trend may be due to the effect of factors associated with the secondary environment.

Zinc is generally more mobile than lead under most conditions normally found on the surface but its mobility can be greatly reduced by adsorption or co-precipitation with manganese and iron oxides. Like lead, high values of zinc are correlative with high concentrations of manganese, indicating enrichment of both metals in manganiferous sediments. Parallel behavior of zinc and lead in relation of manganese is indicated further by the similarities between the scatter diagrams shown on figures 2 and 3.

Comparative data on the zinc content between "unwashed" and "washed" samples (Table 1) show no significant enrichment of the metal in sediments with high mud or organic content.

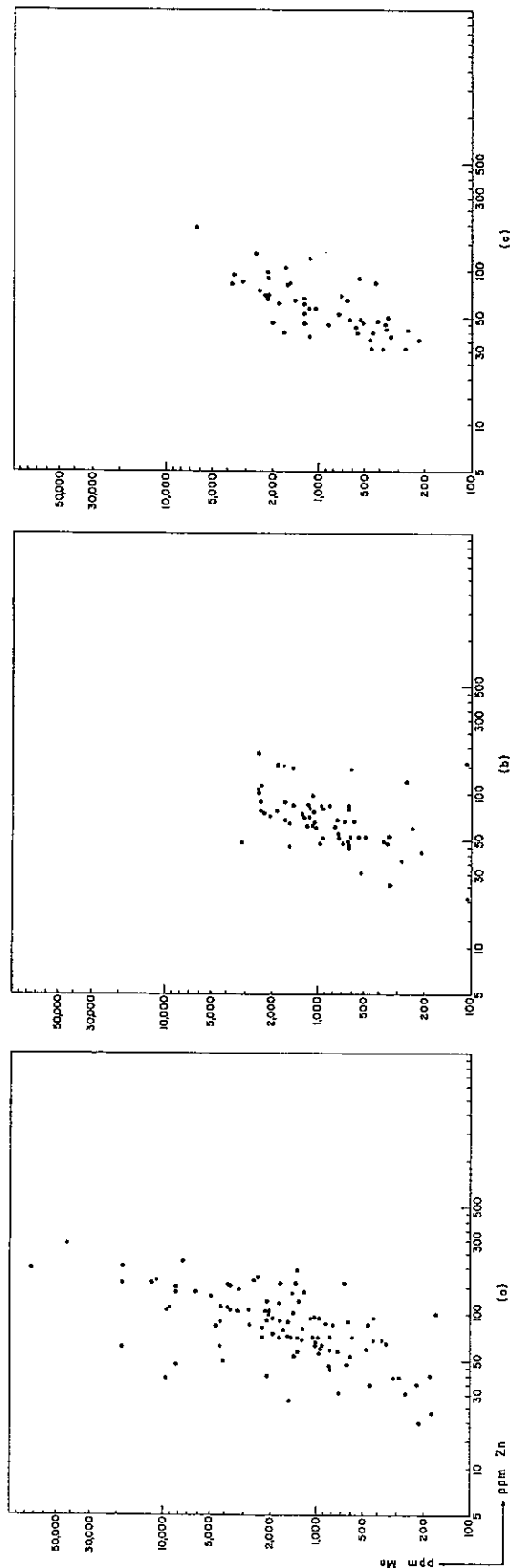


FIGURE 3 : Zinc-manganese ratio in relation to bedrock type: (a) granite, (b) Silurian sedimentary rocks, (c) carboniferous sedimentary rocks

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## DISPERSION OF MOLYBDENUM

The molybdenum content of stream and spring sediments ranges from less than 1 ppm to 70 ppm with an average of 2 ppm (Map 5).

The histogram of molybdenum indicates extreme deviation of the distribution from normally (extreme positive skewness). The cumulative percentage distribution graph showing a broken line indicates that the distribution is non-homogeneous and may be composed of more than two populations.

The areal distribution of higher than average and anomalous concentrations of molybdenum is closely related to the regional distribution of granitic rocks, notably in the western and southwestern parts of the area. Average and below average concentrations are related mostly to Carboniferous rocks and, to some extent, to Silurian units.

Estimate of abundance of molybdenum in bedrocks surprisingly showed lower average for granitic rocks than for Silurian sedimentary and metamorphic rocks (Table 2). Some Silurian strata contain unusual high values which may not constitute economic concentrations of molybdenum. The bedrock data nevertheless do not substantiate sediment-bedrock correlation.

Extreme values of molybdenum are generally correlative with extreme values of manganese, though the scatter diagrams (Figure 4) show vague correlation between the two metals, particularly in non-granitic terrain. Positive correlation is indicated only in the upper range of manganese concentration, or above 5,000 ppm (Figure 4a), and these order of concentration is found mostly in granitic terrain.

Molybdenum, like copper, shows enrichment in spring sediments, possibly, due to precipitation of secondary minerals of the metal or as a result of absorption by freshly precipitated manganese and iron oxides.

No significant accumulation of molybdenum in muddy or organic-rich sediments is indicated by the similar values obtained from both "unwashed" and "washed" samples (Table 1).

## DISPERSION OF MANGANESE

The manganese content of stream and spring sediments ranges from 20 ppm to 73,000 ppm with an average of about 1140 ppm. Map 6 shows the dispersion patterns and the statistical distribution of manganese.

The histogram of manganese indicates that the distribution is not normal. Possible log-normal but otherwise heterogeneous distribution is suggested by the broken line shown in the cumulative percentage plot.

Highly anomalous concentrations of manganese are distributed mostly in areas underlain by granitic rocks, but these distributions seem not related to any appreciable concentration in bedrock (Table 2). Non-granitic terrains are characterized by low or average abundance of the metal. Some extremely high values found here are most probably related to manganiferous beds associated with Silurian or Carboniferous strata.

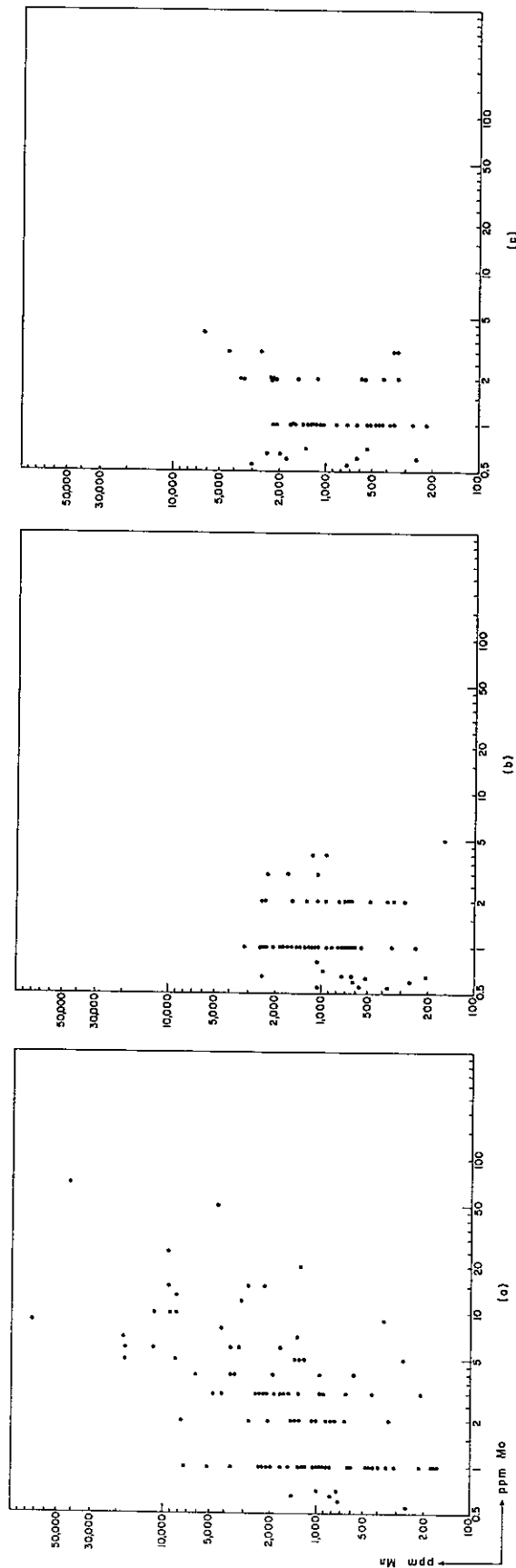


FIGURE 4: Molybdenum-manganese ratio in relation to bedrock type: (a) granite, (b) Silurian sedimentary rocks, (c) Carboniferous sedimentary rocks

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Precipitation of manganese in surficial environment is largely a function of pH and Eh, i.e. it is favored where condition is basic and highly oxidizing. Drainage environments are normally neutral to basic and oxidizing; so that, accumulation of manganese in drainage sediments is most favored where the adjacent soil environment is acidic and reducing (Horsnail, Nichol, Webb, 1969).

Estimate of abundance of manganese over granitic terrain in southern New Brunswick indicated relative impoverishment in soil and enrichment in drainage sediments based on the primary metal content of bedrock (Austria, in preparation). Soil derived from granite is acidic (pH = 4.5) whereas stream water is basic (pH 7.5), but both environments are oxidizing; so that, the mobility of manganese here may be largely a function of pH. The observed accumulation of manganese related to granitic rocks in southern New Brunswick or in the present area may be explained by the above behavior of the metal.

Greater abundance of manganese in non-granitic bedrock is not reflected in the distribution in drainage sediments. This may be due to less acidic nature of the soil which may not inhibit precipitation of the metal, thus limiting the amount of dissolved metal available to surface and underground waters.

Manganese hydroxides and hydrous oxides are effective scavengers of minor elements. Previous discussions have shown possible significant accumulations of Pb, Zn, and Mo in manganiferous sediments, and such accumulations may constitute anomalies unrelated to economic concentrations of metals in bedrock.

#### DISPERSION OF ANTIMONY IN DRAINAGE SEDIMENTS

Antimony content of stream and spring sediments is generally low. More than 95 per cent of the samples failed to yield traces of the metal or below the detection limit of 1 ppm. Map 7 shows the regional distribution of antimony.

Uniform background distribution of antimony in the area is indicative of relative stability of the metal in drainage environment. Unlike Cu, Pb, Zn, or Mo, antimony shows no fluctuations with physical or compositional variations of samples, and observed fluctuations may be entirely related to primary content in bedrock.

Highly anomalous dispersion trains found north of Lake George can be directly related to known deposit of antimony in that area. Traces of the metal have been picked up elsewhere, and these areas may warrant further investigations.

The inset map of Map 7 shows in a more detailed scale the results of the resampling of streams near known deposits. The applicability of drainage sediment method in prospecting for antimony is demonstrated here. Drainage surveys would have delineated a general target area for more detailed study (bank and soil sampling) to get closer to the source of dispersed metal in drainage sediments.

Known mineralized structures in the area trend E-W (Prout and Hibbard veins) and NNE (Lawrence vein) (Shaw, 1940). No orebody has been found anywhere near Waterloo Lake so that it is highly probable that the anomalous dispersion train on the east fork of the stream that feeds to Waterloo Lake is related to an unknown source. The area between Lake George Road and the stream confluence warrants more detailed follow-up work.

Accumulation of anomalous concentrations of antimony in lake sediments is indicated by the significant drop in metal values on the downstream side of Waterloo Lake. Further downstream, the anomalous concentration dissipates, more likely, as a result of dilution from Jocelyn Brook.

#### DISPERSION OF ANTIMONY IN SOIL

Preliminary results of profile and traverse soil sampling over and adjacent to the known orebodies indicated the presence of mineralization.

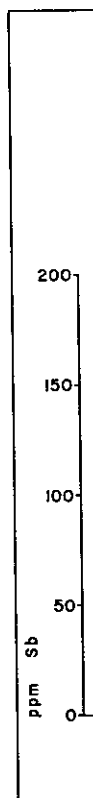
The unconsolidated overburden consists mainly of glacial drifts. The vertical profile includes a layer of undecomposed organic litter ( $A_0$ ) overlying 3 to 6 feet of gravel and clay deposit. Soil development is inhibited because of poor drainage condition, but in less waterlogged places soil differentiation can be discerned. This includes a black layer composed of finely divided decomposed organic matter ( $A_1$ ), a layer of light-grey soil ( $A_2$ ), and a layer of brown soil (B). In the absence of  $A_2$  and B soil, a thin layer of grey-brown soil (also designated as B) separates the organic layer from the glacial deposit. The gravel and clay deposit (designated here as C) rests directly on large blocks of local bedrock.

The results of profile sampling (Figure 5) showed that underlying bedrock mineralization can be detected with the use of materials of B or C layers, but for economic considerations, the B soil was selected and was used in the subsequent traverse soil sampling.

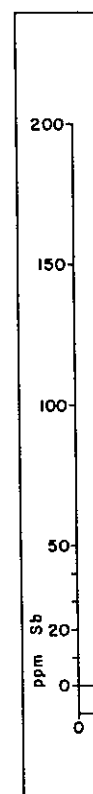
Aside from orientation purposes as described above, profile sampling can be effective in locating the bedrock source of metals dispersed in the overburden. This is well demonstrated in Pit No. 3 which is nearest to the known vein (Hibbard Vein) and where the vertical distribution of antimony increases at depth.

In the traversed soil sampling that followed, samples were taken at variable depths to include only the materials of the designated B horizon. Samples were collected at 50 feet center from four 4,000 feet long traverses, 500 feet apart and laid out almost at right angles to the Prout and Hibbard veins. Figure 6 shows the distribution of antimony in soil based on partial results obtained from two soil traverses. It indicates the location of the anomalous soil zone in relation to underlying mineralized veins, thus demonstrating the applicability of soil geochemistry in locating and delineating much smaller target area for trenching and other more detailed investigation to locate the bedrock source of metal.

Lateral migration of antimony is not extensive as shown by width of the anomalous zone which is about 3 times the distance between the two veins. It is also noted that values south of the anomalous zone fluctuates at a higher level than the values to the north. These may suggest that lateral movement of antimony is mainly by clastic dispersion. The anomalous dispersion halo tend to be displaced to the south, conforming to the general trend of glaciation. Redistribution of antimony in surficial materials by clastic or hydro-morphic processes is one of the topics in the current research on the metal.



Figure



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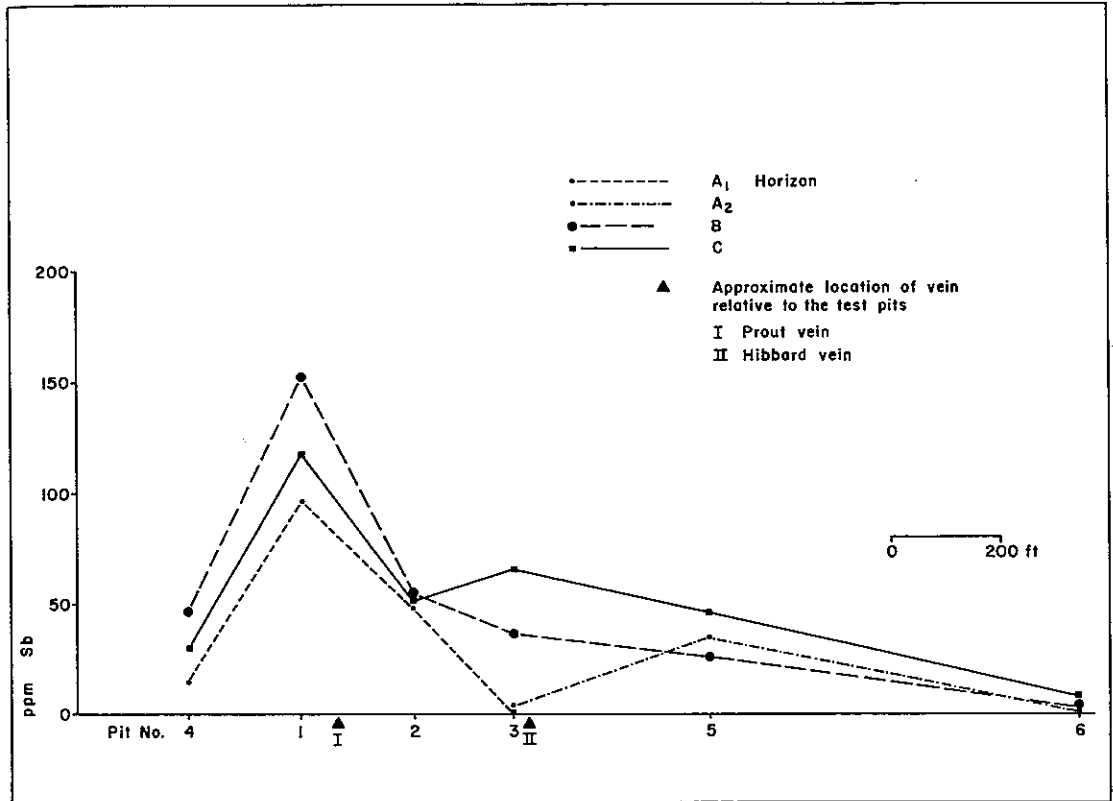


Figure 5: Profile distribution of antimony in test pits

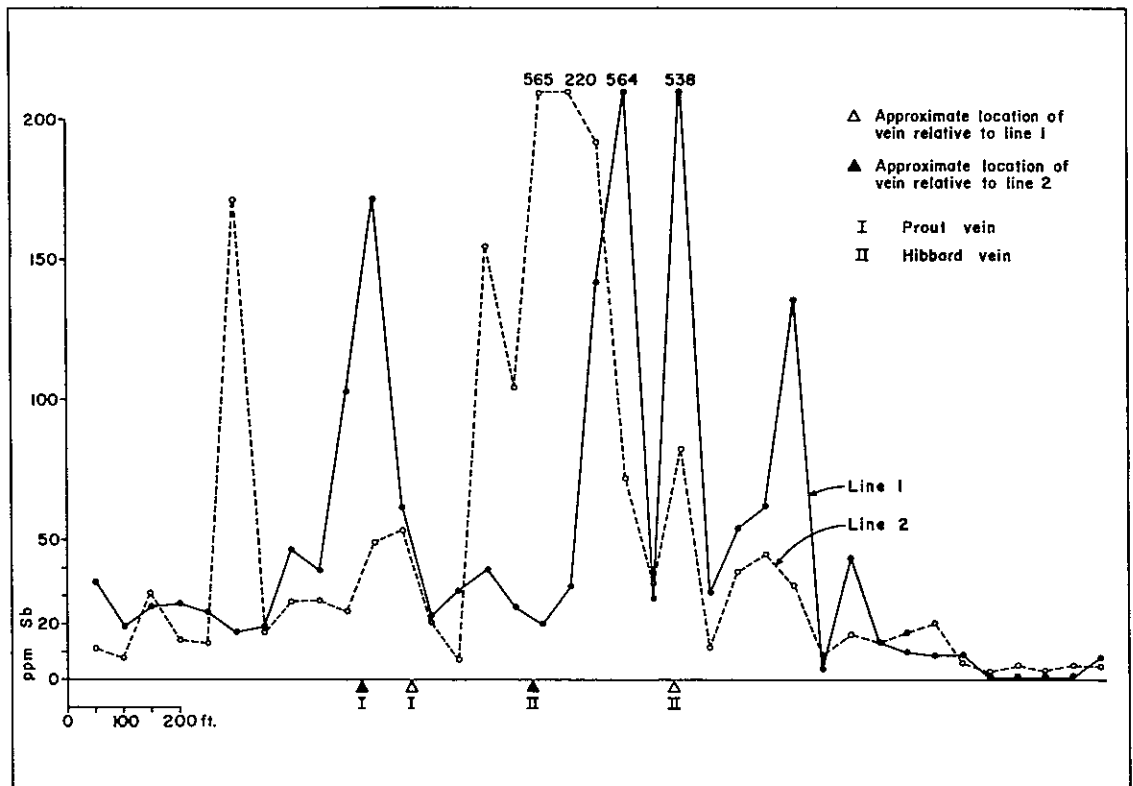


FIGURE 6: Distribution of antimony in soil below the "A" horizon

### CONCLUSION AND SUGGESTIONS

Dispersion of Cu, Pb, Zn, Mo, Mn, and Sb in stream and spring sediments indicated regional or local variations which may be due to bedrock composition, secondary environment or both. Variations shown by antimony are essentially local and these may be related primarily to bedrock composition.

High regional abundance of Cu, Pb, Zn, Mo and Mn in drainage sediments is related to granitic rocks, and to some extent, to Silurian sedimentary and metamorphic rocks. Normal and below normal abundance of these metals is associated with Mississippian and Pennsylvanian strata.

Influence of bedrock composition on the gross regional variations of metal in drainage sediments is poorly defined. Estimated abundances of Cu, Pb, Zn, Mo, and Mn in granitic rocks and Silurian units are not correlative with their regional abundance of granitic sediments do not correspond to the low metal content of granitic rocks.

Secondary factors associated with granitic environment seem favorable for the concentration of metals in drainage sediments. Unusual accumulation of manganese in granitic sediments may be due to contrasting pH and Eh between soil and drainage environments where the low pH and Eh of soil permits migration of manganese which is later precipitated in the drainage environment in response to increase of pH and Eh. Minor metals may or may not strictly follow the course taken by manganese and iron in response to changes in pH and Eh but their mobility in the drainage environment may be restricted as a result of adsorption by manganese and iron oxides, clay minerals, and organic gel.

Significant accumulation of Pb, Zn, and Mo in manganiferous sediments may produce anomalies entirely unrelated to mineralization. Similarly, non-significant accumulation of Cu may be related only to the organic, clay or iron-content of sediments. These factors should be considered in assessing the significance of high metal concentrations, particularly those associated with granitic environment.

Spring environment may have to be assessed separately from stream environment, and this may require adjustment of background concentration in some places. High concentration of metals found in most springs may be largely due to precipitation of secondary minerals from underground waters or to the scavenging effect of freshly precipitated manganese and iron oxides.

Preliminary data on the distribution of antimony in stream sediments and soil indicated that near-surface antimony deposits underlain by glacial drifts can be detected by conventional geochemical methods. Additional information on the nature of migration and fixation of antimony in the secondary environment may provide useful criteria in the interpretation of dispersion patterns under diverse sets of chemical and physical condition, or otherwise, provide the basis for modification of field techniques to suit local conditions.

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