THE GEOCHEMISTRY OF MOLYBDENUM IN THE BATHURST DISTRICT, NEW BRUNSWICK

A THESIS
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by
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ABSTRACT

In an attempt to establish the abundance and the general behaviour of molybdenum in various earth materials of the Bathurst district, rocks, ores, gossans, and soils were sampled and analyzed for molybdenum. A modification of the thiocyanate-stannous chloride method of analysis was used.

The molybdenum content of all types of igneous, sedimentary, and metamorphic rocks analyzed ranges from 0.3 to 3.0 p.p.m. with the higher values occurring in the Nigadoo quartz-feldspar porphyry and black schist of the Tetagouche Group. High molybdenum values are attributed to the presence of disseminated sulphides and a high carbon and manganese content.

While there is only a small variation in the molybdenum content of the rocks, substantial differences were encountered between ores of the four sulphide deposits investigated. The values range from 1.0 to as high as 112 p.p.m. This range is also reflected in the gossan zones developed over the ore bodies.

Normal podzolic soils of the district contained from less than 0.2 to 4.0 p.p.m. molybdenum with an average value of 1.2 p.p.m. In most cases the highest concentrations of molybdenum in the soil profiles were found in the B and C horizons, with the B horizons having the greatest frequency of high values. Soil pH and the abundance of sesquioxides and clay minerals govern the relative amounts of molybdenum in the different horizons.

From a geochemical prospecting viewpoint this study indicates that a random geochemical sampling of granites can be effectively used in deciding whether the granites are molybdenum-bearing or not. Similarly, the results of soil and stream sediment sampling may indicate anomalous areas that mark abnormal concentrations of molybdenum in the underlying rock formations.

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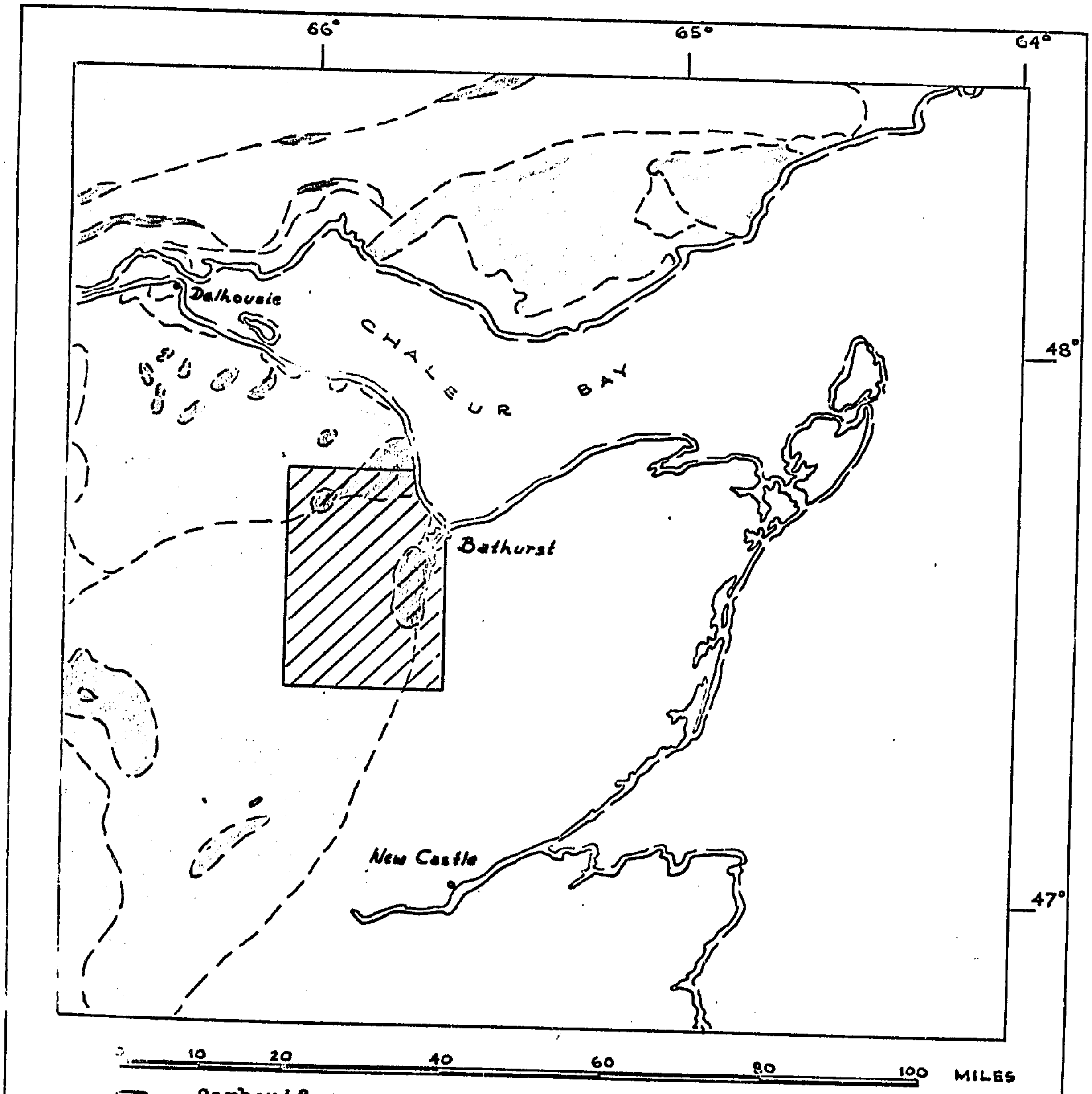
CHAPTER I

INTRODUCTION

An extensive study of the geochemistry, mineralogy, petrology, and areal geology of the Bathurst - Newcastle Mineral Belt by the Geological Survey of Canada has been in progress since 1958. The purpose of this project is to give a complete picture of the distribution of major and trace elements in various earth materials of the district. This, combined with other geological evidence available, it is hoped will give an accurate idea of the origin of the various polymetallic sulphide deposits present in the area.

The present study of the geochemistry of molybdenum in the Bathurst district is only a small fraction of the overall geologic investigation. The aims of the study were (1) to select the best and most practical analytical method for the determination of small quantities of molybdenum in a variety of earth materials; (2) to establish the general distribution of the element in soils, rocks, sulphides, and to offer a logical explanations for any abnormalities found; and (3) to investigate the applicability of pedogeochemical techniques, and stream-sediment sampling utilizing molybdenum as an indicator in searching for molybdenum mineralization and other base metal deposits.



Source: Geological Map of the Maritime Provinces, F. J. Alcock, 1949.

FIGURE 1. Index - Regional Geological Map.

To achieve these aims samples were collected from soil profiles representative of the whole district, from the common rock units, and from the different materials constituting mineralized zones. Two stream systems draining known mineralized areas were also sampled in considerable detail.

All samples were analyzed for molybdenum by the writer using the thiocyanate method both in the field laboratories and in the geochemical laboratory of the Geological Survey of Canada in Ottawa. J. J. Lynch and G. Mihailov analyzed some of the samples for Cu, Pb, Zn, As, and Sb using methods as described in GSC Papers 59-3, 63-8, and 63-29.

Previous geochemical studies in the area include those by Davies (1960)[1], Presant (1963), and Mitchell (1960).

A number of studies bearing on the geochemistry of molybdenum have been published. A discussion of these is presented in Appendix I.

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[1] See Bibliography

ACKNOWLEDGEMENTS

The writer would like to extend his sincere gratitude to Dr. R.W. Boyle of the Geological Survey of Canada for suggesting the thesis problem and supervising the course of research. His helpful suggestions and criticisms are most valuable during the writing of the manuscript.

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The Canadian Government financial assistance, in the form of Colombo Plan scholarship, is greatly acknowledged, without which this study would not have been possible.

CHAPTER II

1. GEOMORPHOLOGY

The area investigated (figure 1) is typical of an uplifted glaciated peneplain. It is an irregularly rolling land surface sloping gently to the east. The highest elevation of about 900 feet above sea level is found in the southwestern corner of the area.

With the exception of the river systems north of the Tetagouche River, there is no apparent relation between the drainage pattern and the underlying geological structure. All of the systems have a general flow perpendicular to the coast line. Evidence of valley rejuvenation, due to post glacial uplift, is clearly indicated by most of the major river in the district in the form of steep canyons, narrow gorges, falls and rapids.

The past existence of extensive glaciation is shown by thick glacial drift covering most of the area. Glacial striae on a few of the outcrops indicate an east to northeasterly direction of ice movements. The irregularities on the otherwise flat topography are mainly due to the presence of drumlins, kames, eskers and other glacial or glacio-fluvial deposits.

2. GENERAL GEOLOGY

The lack of outcrop combined with the highly deformed nature of the rock formations creates difficulties in constructing the sequence of geological events in the district. For this reason disagreement among several investigators working in different sections of the district is readily understandable.

Early geological reports of the area are by Young (1911) and Alcock (1935, 1951). More recent investigations, prior to as well as after the mining boom of 1953, include works by: Skinner and McAlary (1952); Skinner (1953, 1955, 1956); Holyk (1956); Smith (1957), and Skinner (1958); Davies (1960); and Boyle and Davies (1964).

Information for the following brief geological descriptions were taken mainly from Smith and Skinner (1958).

Smith and Skinner recognized three regional geological units in the Bathurst area as follows: the Ordovician folded belt; the Silurian folded belt, and the Pennsylvanian cover. The Ordovician folded belt is more highly deformed than the Silurian folded belt. They are separated by a regional fault system known locally as the Rocky Brook-Millstream "Break".

Middle Ordovician

The oldest rocks exposed in the Bathurst area comprise the Middle Ordovician Tetagouche Group which consists of highly deformed metamorphic rocks of sedimentary and volcanic origin.

Table 1

Table of Formation

ERA	PERIOD	ROCK UNIT	LITHOLOGY
CENOZOIC	Pleistocene	--	stratified gravels, glacial drift
		unconformity	
PALAEOZOIC	Pennsylvanian	Clifton Fm.	grey - sandstone, shale conglomerate, grit
		Bathurst Fm.	red - sandstone, shale conglomerate, grit
		unconformity	
	Devonian	Basic intrusives	diabase, diabasic gabbro, gabbro, diorite, serpentinite
		Acid intrusives	biotite granite, granite porphyry, aplite, gneissic granite
		intrusive contact	
	Silurian	Chaleur Bay Group	- calcareous slate, subgreywacke, limestone, minor basalt - basalt, trachyte
		unconformity	
	Ordovician	Tetagouche Group	- argillaceous meta-sedimentary rocks - basic meta-volcanic rocks - quartz-feldspar "porphyry" - acid volcanic rocks - siliceous sedimentary rocks

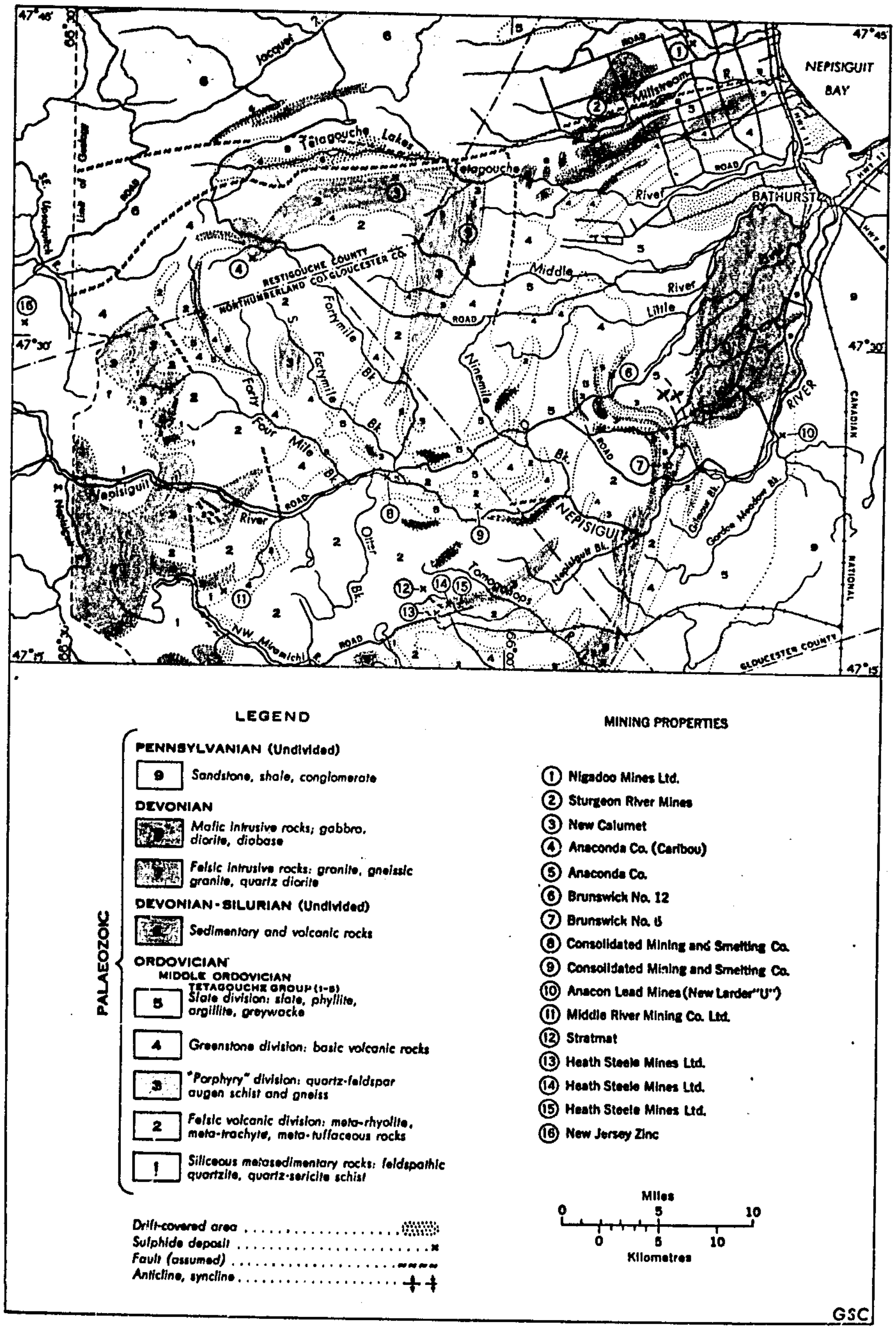

Figure 2. Geology and principal base metal deposits, Bathurst-Newcastle area, New Brunswick (After Smith, 1957)

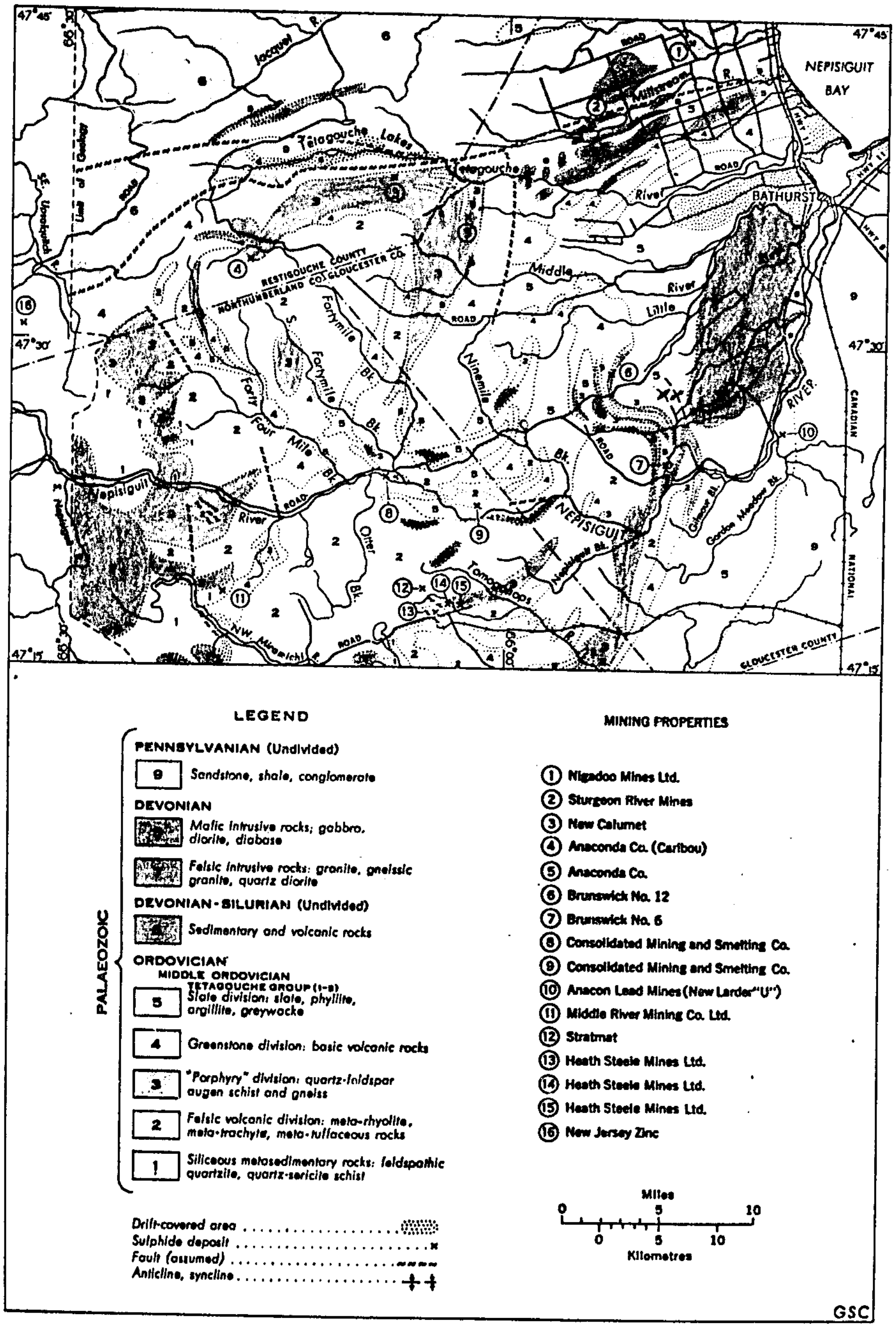

Figure 2. Geology and principal base metal deposits, Bathurst-Newcastle area, New Brunswick (After Smith, 1957)

The group is divided into five lithologic units, though their stratigraphic order is not well established. The most widely accepted succession from oldest to youngest is as follows: siliceous metasedimentary rocks, acid volcanics, quartz-feldspar augen schist, basic volcanics and argillaceous metasedimentary rocks.

Siliceous metasedimentary rocks are abundant in the western and southern part of the district. They consist mainly of feldspathic quartzite, quartz-sericite schist, and interbedded slate.

As shown in Figure 2, the acid volcanic division of this group clearly represents "part of the core" of the folded belt. This metamorphic unit is represented by quartz-sericite schist, quartz-chlorite schist, meta-porphyries, meta-rhyolite, meta-tuff, and locally meta-agglomerate and breccias.

The quartz-feldspar augen schist is characterized by large porphyroblasts of glassy quartz and pink alkali feldspar up to half an inch long. Minor layers of meta-rhyolite and chlorite schist are also included in this division.

The basic meta-volcanic rocks of the Tetagouche Group are mainly schistose, fine grained spilitic meta-basalts, with amygdaloidal structure in places, rarely pillowed. The association of jasper and magnetite-bearing cherts with the unit is common.

Argillaceous metasedimentary rocks predominant in the eastern part of the district. They consist of varicoloured slates, schistose siliceous argillites, phyllites, grey quartzite and greywacke. Thin graphitic layers usually with disseminated sulphides are also common in this division.

Middle Silurian

The Silurian rocks comprise the Chaleur Bay Group and can be divided into two members: (1) Fossiliferous sedimentary rocks, which consist mainly of argillite, calcareous slate, fine grained greywacke, limestone and minor conglomerate; and (2) a volcanic member consisting of basaltic and trachytic rock types.

Devonian (?) Intrusives

Both the Tetagouche and Chaleur Bay Groups are cut by acid and basic intrusives, presumably of Devonian age.

The acid intrusives are mainly coarse granular to semiporphyritic granite, gneissic granite and quartz-feldspar porphyry dykes and stocks. Smith and Skinner (1958) report contact aureoles, some over a mile wide, which can be observed around the large granitic bodies. From available reports and recent observations, a close relation between molybdenite occurrences and the existing granite bodies (Bathurst and Nicholas Dénys granites, see Map 1) is indicated.

Diabasic dykes and sills with ophitic to semiophitic texture are abundant in the northern part of the district. These are associated with diorites and serpentinites in places.

Pennsylvanian

Lying unconformably over most of the older formation are flat lying Pennsylvanian rocks. These are found almost exclusively east of Nepisiguit River. Erosional remnants are also found near Beresford and further inland near Tetagouche Lakes. It is therefore reasonable to assume that at one time these rocks covered the entire area.

The lower part of the Pennsylvanian group of rocks is represented by the Bathurst formation which consists mainly of red sandstone, shale, and fine conglomerate. The upper part is known as the Clifton formation. Although lithologically similar to the Bathurst formation, it can be distinguished by its predominantly grey color and the presence of plant remains.

Pleistocene

Two types of unconsolidated sediments are known in the area: (1) stratified marine clays, sands, and gravels with shells and plant remains distributed in small areas bordering Bathurst harbor, (2) glacial deposits which cover the greater part of the district and which are recognized in the field as tills, stratified sands and gravels, as well as loose angular boulders having diameters up to 10 to 20 feet.

CHAPTER III

MINERAL DEPOSITS

General Statement

Deposits of various types occur in the district. These include massive lead-zinc-copper-silver sulphide deposits mainly in Ordovician rocks; lead-zinc-copper-silver sulphide vein deposits principally in Silurian rocks; magnetite-hematite iron deposits, and a manganese deposit near Tetagouche Falls. Only the sulphide deposits are exploited at the present time.

Sulphide Deposits

McAllister (1954, 1959) divided the sulphide deposits of the Bathurst area into two different structural types: those occurring in north-south striking structures and those in east-west and northwest structures. The first are fine grained, low grade replacement bodies, whereas the second are fissure fillings or small replacement bodies, with coarser grained and higher grade ores.

Two types of mineralizations are recognized in the first structural group:

a) Massive pyrite with galena, sphalerite, minor chalcopyrite, and appreciable values in silver.

b) Pyrrhotite-chalcopyrite type with minor zinc, lead, and silver values.

The two types sometimes occur together as at the Brunswick No. 6 and Brunswick No. 12 deposits, with indications that type (b) is a younger phase of mineralization.

In the second group, a sequence of high to low temperature mineralization is recognized by MacKenzie (1952) as follows:

a) Quartz-arsenopyrite
b) Pyrite-arsenopyrite-sphalerite-galena-chalcopyrite-tetrahedrite
c) Quartz-chalcopyrite
d) Chalcopyrite-pyrrhotite
e) Sphalerite-chalcopyrite-pyrrhotite-galena with values in silver
f) Galena-sphalerite-calcite with high contents of silver

In connection with the present study, of notable interest is the occurrence of molybdenite associated with the Bathurst batholith, as well as in a number of other new occurrences recently discovered in the Nicholas Dénys area. In the Bathurst granite, molybdenite is found as flakes and fine crystals disseminated throughout the host rock and rarely also along minor joints. The mineral appears to favour aplitic phase of the granite. Along the Rocky Brook - Millstream "Break" several small sulphide deposits with minor molybdenite are reported to occur. In 1963 drilling by one of the companies working in the area, revealed molybdenite-bearing garnet-diopside skarn with minor scheelite.

The presence of the mineral in parts of the Nicholas Denys granite has also been proven by drilling in 1964.

Iron Formation

Banded iron formation consisting mainly of alternating layers of magnetite, hematite, chert, and chlorite occurs at numerous points in the area. It is particularly abundant in the Brunswick No. 6 deposit where it is traceable southward to the Austin Brook Iron deposit. Boyle and Davies (1964) recognized three facies within the formation as follows: a magnetite-rich oxide facies; a hematite-rich oxide facies; and a chlorite facies.

In the vacinity of the Rocky Brook - Millstream "Break" there are magnetite deposits which have been described by Young (1911) and Skinner (1953). These are long, narrow contact metamorphic lenticular bodies consisting of banded magnetite and skarn minerals.

Manganese

According to Skinner (1953, p. 4) "Manganese occurs as narrow seams and plates of manganite in quartz veins and as veinlets in red slate at Tetagouche Falls, and a deposit of bog manganese of unknown dimensions occurs on Middle River, about 5 miles west of the granite batholith".

CHAPTER IV

SAMPLING PROCEDURE

General Statement

Samples of different materials were collected for the following purposes:

1. To establish the general distribution of molybdenum in soil profiles, and the different rock types of the district.
2. To make a detailed study of the behaviour of molybdenum in the polymetallic sulphide deposits.
3. To investigate the possibility of using stream sediments in prospecting for molybdenum as an indicator.

The preparation of soils and stream sediments were done in the field. Rocks and other consolidated materials were prepared in the sample preparation room of the Geological Survey of Canada in Ottawa. All precautions were taken against external contamination during the course of the sample preparations.

Megascopic description of each sample is given elsewhere in the thesis. For the extremely fine grained materials, mineralogical determinations were done by means of X-ray diffraction.

The distribution of samples and groups of samples collected is shown on Map 1 (in pocket).

Soils

Ninety-two soil profiles were collected from relatively scattered localities over the district. In addition to this, twelve profiles were obtained from a collection made by Presant (1963). Sixty-four of these represent the normal soil of the district, and the other forty were collected from known mineralized areas.

Profiles were channel sampled from holes of about two to three square feet in area and ten to forty inches deep, specifically dug for the purpose. Incomplete soil profiles were obtained from some areas because difficulties were encountered due to water seepages or large boulders. Approximately one half pound of each soil horizon was collected in a waterproof paper envelope. A small portion was used for pH measurement immediately after sampling, following the method described by Atkinson *et. al.* (1958). Samples were then dried in the sun or in a drying oven, followed by sieving through an 80 mesh screen. The -80 mesh fractions were retained for analyses, and the coarser fractions, after determining their rock composition, were discarded.

All samples were analyzed for their molybdenum content, using the method described in Chapter V.

Rocks

Because of the large area covered by this investigation only the common rocks could be sampled and these only sporadically since outcrops are sparse. However, the samples taken are deemed to be representative of the specific rock types. Thirty-six samples were taken to represent the various rocks in the formations and minor intrusives in the area. These include 20 samples from the Tetagouche Group, of which 4 are graphitic schist, 5 from the Chaleur Bay group, and 2 from the Pennsylvanian rocks. Basic dykes and sills are represented by 9 samples. Because of their close association with molybdenite occurrences special emphasis was given to the granitic rocks of the district. With this consideration in mind, 79 specimens representing the different facies of the granitic bodies were collected. Of these, 44 are from the Bathurst batholith, 13 from the Nicholas Dénys granite, and 22 are of quartz-feldspar porphyry from the Nigadoo stock.

After being crushed and sieved, the -150 mesh fractions of the samples were analyzed for molybdenum. Most of the granitic rocks were also analyzed for Cu, Pb, Zn, As and Sb. Four graphitic schists of the Tetagouche group were analyzed for sulphur and total carbon.

Ores and Gossans

Twenty samples of sulphide ores were collected from the Brunswick No. 6, New Larder "U", Sturgeon River, and Nigadoo deposits. Although most of the samples were relatively fresh, there were several which have been highly oxidized. With the exception of the Nigadoo ore, the massive, finely crystalline nature of the sulphides prevented separation of the different mineral phases.

Samples of gossan material and recent iron hydroxide precipitates were collected from a number of sulphide deposits including the New Larder "U", Sturgeon River, and the Brunswick No. 6 deposits. Detailed sampling of the various phases of the gossan were done on the latter deposit. In this gossan a profile (Figure 5) generally consists, from top to bottom of hard cap, leached till, residual gossan, and altered sulphides. A detailed study of the nature and origin of the Brunswick No. 6 gossan has been described by Rajah (1963) and Boyle and Davies (1964).

Other than gossans and sulphides, three samples of iron formation and two of manganites from the Tetagouche Falls were also collected.

Some of the samples, aside from analyses of their molybdenum content, were also subjected to qualitative X-ray spectrochemical analysis with confirmation by wet chemical methods.

Stream Sediments

Work on stream sediments of the Millstream system, in the northern part of the district, was initiated by A.Y. Smith, then of the Geological Survey of Canada (see G.S.C. Paper 63-1, pp. 52-53), in an attempt to study the methods of sampling and sample treatment in a known environment where a number of deposits occur. The fact that the Millstream River system drains an area containing several small deposits representing concentrations of Cu, Pb, Zn, Ag, As, Sb, Au, and probably also Mo, offers an ideal situation to conduct a pilot study on the applicability of stream sediments for mineral exploration. The writer undertook the project, mainly in the interest of studying molybdenum distribution in relation to polymetallic sulphide deposits (Tauchid, 1964).

The presence of boulders with molybdenite in the area underlain by the Bathurst granite presents a good case for the study of the use of stream sediments in molybdenum prospecting. This area was sampled, therefore, at 24 selected sites.

Stream sediment sampling sites were chosen on the basis of their accessibility to roads and trails, and whenever possible at the junction of two intersecting streams.

After being dried and sieved, the -80 mesh fractions of the stream sediments were retained for analysis. All samples were analyzed for their Mo, Zn, Pb, and Cu contents.

CHAPTER V

LABORATORY PROCEDURE

General Statement

The different earth materials collected were prepared according to their nature and composition as described below. The -80 mesh fraction of soils and stream sediments were used in the analysis, and the rocks, sulphides, and gossans were ground to -150 to -200 mesh prior to analysis.

Several analytical methods for the determination of small quantities of molybdenum are known. Sandell (1959) describes and reviews several of these in considerable detail. Among those available, modifications of the thiocyanate-stannous chloride and the dithiol methods are commonly used in geochemical work. The potassium ethyl xanthate method, according to Perry (1960), has advantages for samples with high values, but is relatively less suitable for samples with molybdenum concentrations less than 5 p.p.m.

The thiocyanate-stannous chloride method is based on the reaction between quinquevalent molybdenum and thiocyanate in an acidic reducing solution. Amber-colored molybdenum thyocyanate is produced, possibly $Mo(CNS)_5$ (Sandell, 1959). The immiscible organic solvent for extraction of the amber-colored compound most commonly employed is isoamyl alcohol or isopropyl ether.

Dithiol (toluene -3, 4- dithiol), in a dilute mineral acid medium yields a slightly soluble dark green product with hexavalent molybdenum which is extractable with butyl acetate.

In this particular study, the thiocyanate-stannous chloride method was chosen because of its high sensitivity, selectivity, and practicality. A detailed discussion on a comparative study of the analytical procedures tried is presented later in this Chapter.

Experimental

Geological materials of different types, including soils, stream sediments, rocks, sulphides, and some iron and manganese hydroxides and oxides were collected and analyzed for molybdenum as well as for other elements. Analysis for elements other than molybdenum were done by Mr. J.J. Lynch and his staff of the Geochemical Section, Geological Survey of Canada. Hence the following discussion is limited to the determination of molybdenum only.

The thiocyanate-stannous chloride method used in geochemical analysis for molybdenum was originally described by Ward (1951a). To obtain more reliable results and to improve the sensitivity required for the present study, the following modifications were adopted.

1. A large sample weight was used. This increased the sensitivity of the method, especially in samples where only a low content of molybdenum is present.
2. Different sample decomposition methods were tried. This ensured the liberation of all molybdenum in the samples.

3. A new standard color series for low contents of molybdenum were prepared.
4. Larger amounts of isopropyl ether were employed as extractant for the molybdenum thiocyanate. This permitted easier reading of the colored organic layers. In the analysis 0.6 ml. of isopropyl ether was used instead of 0.3 ml. as originally suggested by Ward (1951a).
5. Iron in the form of ferrous ammonium sulphate was added to the standard and blank solutions. This procedure gives standards and blanks similar to the composition of the sample extracts which usually contain much iron. It also tends to intensify the color of the molybdenum thiocyanate as suggested by Sandell (1959).

Although these modifications give rise to a number of problems, especially in the fusions of the samples, the greater sensitivity achieved outweighs the disadvantages.

Analytical Procedure

Briefly the method can be described as follows. After the sample is fused and leached, molybdenum in the solution is reacted with potassium thiocyanate in an acidic solution in the presence of a reducing reagent. Iron, commonly present in all samples, reacts with $(CNS)^-$ in the ferric state to form deep red $Fe(CNS)_3$. This color inhibits the reading of the less prominent amber colored $Mo(CNS)_5$. Addition of stannous chloride reduces the iron to ferrous thiocyanate which is colorless and soluble. The amber colored molybdenum thiocyanate is then extracted into isopropyl ether. Interference by tungsten, which commonly exists in close association with molybdenum in nature, is prevented by addition of solid sodium tartrate to the solution. According to Ward (1951a), moderate amounts of fluoride and phospate do not interfere with the method. This is also true for small amounts of gold, selenium and tellurium. Large amounts of rhenium interfere with the method but since this element occurs in nature in very low concentrations the interference is negligible.

Sample Decomposition

To select the best decomposition method for the materials collected, the following were tried:

I. Fusion with equal weights of Na_2CO_3 and KNO_3.
II. Fusion with a mixture of Na_2CO_3, NaCl, and KNO_3.
III. Digestion by H_2SO_4.
IV. Digestion by a mixture of HNO_3 and HCl.
V. Fusion with potassium pyrosulphate.

Procedure:

I. Fusion with Na_2CO_3 and KNO_3

In this procedure the flux consists of equal weights of finely ground (-80 mesh) KNO_3 and Na_2CO_3. 0.1 g of each sample was ground together with 0.5 g flux in a mullite mortar and transfered to a clean pyrex test tube (16 x 150 mm). The test tube was then heated over a gas burner until fusion was complete;

each fusion usually required 4 to 5 minutes. After cooling, 4 ml of metal free water was added to the test tube, and the tube was placed in a hot water bath for about 5 minutes. The test tube was then removed from the water bath and placed in a rack. One milliliter of the clear supernatant solution was used for analysis. This decomposition method was successfully used by Ward (1951a).

II. Fusion with a mixture of Na_2CO_3, NaCl, and KNO_3

This fusion method is fully described by Stanton and Gilbert (1956).

A mixture of Na_2CO_3, NaCl, and KNO_3 in the ratio 5:4:1 comprised the fusion mixture. 0.25 g of finely sieved sample was mixed together with 1.25 g of flux, and this mixture was fused in a nickel crucible until frothing had ceased. After cooling, 2 ml of metal free water was added, and the slurry allowed to stand overnight. The aqueous solution was transferred into a clean test tube and adjusted to 10 ml (a modification) with metal free water. The solution was brought to a boil over a gas flame and was then allowed to cool and settle. 8 ml of the clear supernatant solution was used for analysis.

III. Digestion by H_2SO_4

This test tube method was formulated and used at the Geology Department, Carleton University, Ottawa[1]. One gram of

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[1] Malcolm Clegg - personal communication.

the finely sieved sample was digested with 2 ml, 9N H_2SO_4 solution in a hot water bath for about one hour. After cooling, the volume was adjusted to 10 ml with metal free water. A 2 ml aliquot was then used for the molybdenum determination.

IV. Digestion by a mixture of HNO_3 and HCl

An acid digestion by means of a mixture of HCl and HNO_3 is described by Ginburg (1960, pp. 267 - 269). This decomposition method is intended for the extraction of available Pb, Cu, Zn, W, Mo, and Ag in rocks.

For this method, a 0.5 g of sample was placed in a 100 ml beaker and moistened with 10 ml of metal free water. Ten milliliters of 1:1 HCl and 5 ml of 1:1 HNO_3 solutions were added and the mixture was evaporated nearly to dryness. About 4 ml of 1:1 HNO_3 and 10 ml of metal free water were added to the beaker. After boiling the mixture, it was filtered through a filter paper into a 50 ml volumetric flask. The residue was then washed 5 or 7 times with hot metal free water. This solution contained the available Pb, Cu, Zn, Mo, and Ag. Ten milliliter aliquots were used for the molybdenum determinations.

V. Fusion with $K_2S_2O_7$

The use of potassium pyrosulphate was suggested by A.Y. Smith, formerly of the Geological Survey of Canada. This fusion is thought to be particularly effective for secondary materials, as well as for sulphides.

0.5 g of the finely sieved sample was mixed well with 2.5 g of potassium pyrosulphate in a clean pyrex test tube

(18 x 150 mm). The sample was then fused over a gas flame until frothing ceased. Five or six minutes were usually required for a single fusion. After the melt was allowed to cool, it was leached with 4 ml of 2N HCl and heated on a low gas flame or hot sand tray until all of the melt had disintegrated. The volume was then adjusted to 10 ml with metal free water and allowed to settle until a clear solution was obtained. A 4 ml aliquot was used for the analysis.

Result of Decomposition Experiments

Three soil and leached till samples were used for the experiments employing methods I, II, III, and IV. Another set of eight leached tills were also subjected to decomposition methods II, III, and V. Aliquots obtained from the above decompositions were then analyzed for their molybdenum content using the thiocyanate-stannous chloride method. The results of the analysis are tabulated in Table 2.

Discussion:

Method I

Experiments using this method were unsuccessful. Cooling and adherence of the melt around the inside bottom walls of the test tubes caused cracks in the lower part of all test tubes used for these fusions. When metal free water was added to the cool melt, leaks commonly occurred. This caused inaccuracies in the analytical results. Several attempts to refuse the samples gave similar results.

Table 2

Correlative Results on Sample Extractions

METHOD	I*	II	III	IV	V
SAMPLE NUMBER	Mo concentration in p.p.m.				
BH-5004 c	Dis-continued.	11.	4.0	Dis-continued.	9.0
BH-5004 d		17.	8.0		14.
BH-5005 a		23.	11.		16.
BH-5005 b		12.	6.5		10.
BH-5005 c		21.	5.5		27.
BH-5006 b		10.	11.		11.
BH-5006 c		7.5	5.5		5.0
BH-5006 d		9.5	9.0		10.
BH-5007 b		12.	7.5		-
BH-5011 d		8.5	2.5		-
BH-5011 e		19.	13.		-

* I. Fusion with a mixture of sodium carbonate and potassium nitrate.

II. Fusion with a mixture of sodium carbonate, sodium chloride, and potassium nitrate.

III. Sulphuric acid digestion.

IV. Digestion with a mixture of hydrochloric and nitric acid.

V. Fusion with potassium pyrosulphate.

Method II

Fusion with a mixture of Na_2CO_3, NaCl, and KNO_3 is considered the most satisfactory of all the methods tried. As shown in Table 2, the results of analysis of samples decomposed by this technique gave the highest range of values and thus the most complete extraction of the available molybdenum. The only disadvantage of this method is the time consumed, especially if a large number of samples are to be analyzed. A white silicious residue which sometimes formed around the interface of the aqueous solution and the organic phase could conceivably result in erroneous readings.

Method III

Of all the methods, this was the simplest to manage and although an intense color of $Fe(CNS)_3$ was observed, addition of $SnCl_2$ solution was not required. In Table 2, the relatively low range of values obtained as compared to the other methods is apparent. However, they are all in the right proportion. Attempts to improve the method, by increasing the concentration and amount of H_2SO_4 solution, did not produce significant changes.

Method IV

Acid leaching using a mixture of 1:1 HCl and 1:1 HNO_3 solution, followed by the thiocyanate-stannous chloride method of determination is described as successful by Ginzburg (1960). This could be true for materials with negligible amounts of iron. But in materials such as were used in this investigation the abundance of iron in the samples required an impractical amount of $SnCl_2$ solution (over 7 ml) for the reduction of Fe^{+3} to Fe^{+2} . The use of an oxidizing acid, HNO_3, in the final step of the decomposition method accentuates the problem. The long involved steps only add to the impracticality of this method for a large number of determinations, especially when the samples are high in iron.

Method V

Pyrosulphate fusions have been successfully used for sample attack where Pb, Cu, Zn, Ni, and Co are to be determined. For materials where molybdenum is present in hydroxides, oxides, sulphides, and in an absorbed or interstitial form, this type of sample attack was found to be effective.

Difficulties were encountered when the sample contained a high amounts of organic matter. After several attempts, it was decided that samples high in organic materials should be ashed first before fusing.

Method Employed

As mentioned earlier, the thiocyanate-stannous chloride method was used to determine the molybdenum content of the samples investigated in this project. Experiments on the decomposition of samples, combined with a knowledge of the nature and approximate chemical composition of the materials to be analyzed, led to the selection of the following technique.

1. Fusion with $K_2S_2O_7$ for soils, stream sediments, gossans, oxides, hydroxides, and sulphides.

2. Fusion with a mixture of Na_2CO_3, NaCl, and KNO_3 in 5:4:1 ratio for rocks with silicates as their major constituents.

To ensure the reliability of some analysis, about 25 per cent of the samples were subjected to both fusion methods. One large advantage in using potassium pyrosulphate as flux is that the resulting solution can also be used in the determination of Pb, Cu, Zn, Ni, and Co.

The tabulation of the complete analytical data for molybdenum and other elements, is presented in a separate section of the thesis, as Appendix II.

SAMPLE PREPARATION

A. Unconsolidated Materials

Equipment Required :

- Kraft paper sample envelopes made with water resistant glue, approximately 6 x 3 inches.
- Oven for drying samples.
- Porcelain mortar and pestle 3 1/2 inches in diameter.
- Non containinating sieves with 20 and 80 mesh screen (these can be made from two plastic sandwich boxes and bolting cloth).
- Stiff brush, for cleaning sieves.
- Plastic vials, 10 g capacity.

Procedure :

1. Dry samples in air or in an oven at about 100° C in their original envelopes.

2. Break soil lumps using the porcelain mortar and pestle.
3. Sieve the loose material first through the 20 mesh screen and then through the 80 mesh screen. Retain the -80 mesh fraction and place in a numbered vial.
4. Clean all equipment with brush after each sample.

B. Consolidated Materials

Additional Equipment Required :

- Chipmunk jaw crusher.
- Braun pulverizer fitted with ceramic plates.
- Small ceramic ball-mill which can be attached to a paint shaker.
- Stainless steel sieves.

Procedure :

1. Break a 2 or 3 pound sample into pieces about 2 inches in diameter.
2. Pass the pieces through the Chipmunk jaw crusher to produce pieces about 1/4 inch in diameter.
3. Pass the sample through a ceramic disc pulverizer. This yields a powder of about -60 mesh.
4. Place the samples on a large sheet of paper. Roll and mix thoroughly.
5. Place a scooped sample of about 10 g in a ceramic ball-mill attached to a paint shaker for about 1/2 hour.
6. Transfer sample to a vial and mix thoroughly by shaking.

7. Clean crusher, grinder, and ball-mill with stiff brush and finally remove any small particles by directing a stream of compressed air at the jaws, plates, etc.

ANALYTICAL PROCEDURE

Equipment Required :

- Torsion balance, 500 mg capacity,sensitive to 1 mg.
- Reagent balance, 1 kg capacity.
- Fluorescent titration illuminator.
- Water still and mixed resin demineralizing unit.
- Electric hot plate, 10" x 12" equipped with a sand tray with a 1/2 to 1 inch layer of sand and racks to support 50 test tubes (18 x 150 mm) on the tray.
- Electric furnace, for ashing.
- 4 Bunsen burners, equipped with rings and triangles.
- 2 racks to hold 10 test tubes (16 x 150 mm).
- Lucite spoons, 1 g, 0.5 g, and 0.2 g capacity.
- 2 aspirator bottles, polyethylene, 5 gal. capacity.
- 2 reagent bottles, polyethylene, 500 ml.
- 4 reagent bottles, polyethylene, 125 ml.
- 2 wash bottles, polyethylene, 500 ml.
- 2 reagent bottles, pyrex, 500 ml.
- 6 reagent bottles, pyrex, 250 ml.
- 100 test-tubes, pyrex, rimless, 18 x 150 mm.
- 200 test-tubes, pyrex, rimless, 16 x 150 mm.
- 1 graduated cylinder, pyrex, 500 ml.

- 1 graduated cylinder, pyrex, 100 ml.
- 1 graduated cylinder, pyrex, stoppered, 100 ml.
- 1 graduated cylinder, pyrex, 25 ml.
- 2 automatic pipettes, graduated, 5 ml
- 2 automatic pipettes, graduated, 2 ml.
- 2 pipettes, graduated, serological, pyrex, 10 x 0.1 ml.
- 2 pipettes, graduated, serological, pyrex, 5 x 0.1 ml.
- 2 pipettes, graduated, serological, pyrex, 2 x 0.1 ml.
- 1 flask, volumetric, pyrex, 500 ml.
- 2 beakers, pyrex, 600 ml.
- 4 dropping bottles, 30 ml capacity.
- 50 nickel crucibles, 20 ml capacity.
- 20 combustion boats, porcelain, 60 x 10 mm.
- 2 spatulas, stainless steel, length 7 inches.
- 2 spatulas, stainless steel, 4 inch blade.
- Miscellaneous items such as : glass writing diamond, wax pencils, magic marker, labels, tripods, wire gauze, tongs, clamps, safety lighters, corks (# 5), porcelain pipette supports, pyrex glass rods, test tube brushes, tygon tubing, stop-clocks, pair of scissors, absorbent tissues, pH paper, etc.

Preparation of Equipment and Reagents

1. Number 50 test tubes, 18 x 150 mm, and calibrate at 10 ml.
2. Calibrate 70 test tubes, 16 x 150 mm, at 10 ml.
3. Mark the tops of 13 corks (# 5) 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, and 5.0.

4. Prepare a 10% stannous chloride solution by dissolving 10 g of $SnCl_2.2H_2O$ in 100 ml of 2N HCl. Add tin metal (mossy) to aid in dissolution. Prepare fresh solution at weekly intervals.

5. Prepare a 5% potassium thiocyante solution by dissolving 10 g of KCNS in 200 ml of water[1].

6. Prepare a 1% ferrous ammonium sulphate solution by dissolving 1 g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in 100 ml 0.2N sulphuric acid.

7. Prepare a 0.01% standard molybdenum solution by dissolving 0.075 g of pure MoO_3 in 20 ml 1N NaOH. Make the solution just acid with 1N HCl and dilute to 500 ml with water. This solution containes 100 micrograms of Mo per ml.

8. Prepare a 0.0001% standard molybdenum solution by diluting 1 ml of the 0.01% Mo standard solution to 100 ml with water. Prepare a fresh solution daily, at least one hour before using.

9. Prepare a 1% phenolphthalein solution by dissolving 1 g of phenolphthalein in 100 ml ethyl alcohol (absolute).

10. Prepare a 1N NaOH solution by dissolving 2 g of NaOH pellets with 50 ml water.

11. Prepare 2N HCl solution by diluting 17 ml of concentrated HCl (sp.gr. 1.19) to 100 ml with water.

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1 - water = metal free water. In all references hereafter "water" means - metal free water.

12. Prepare 0.2N H_2SO_4 solution by adding 0.6 ml of concentrated H_2SO_4 (sp.gr. 1.835) to 50 ml water and diluting to 100 ml with water.
13. Prepare a fusion mixture by mixing thoroughly 200 g of Na_2CO_3, 160 g of NaCl, and 40 g of KNO_3 and sieve through a 20 mesh screen.

Procedure

Ashing :

Samples from the A_0 and A_{00} horizons of soil profiles, because of their high organic content, are difficult to deal with if fused with potassium pyrosulphate. They require larger amounts of flux and take a long time to fuse. For this reason, ashing previous to fusion is recommended.

Procedure :

1. Weigh 0.5 g of the finely ground sample and place in a combustion boat.
2. Place the combustion boat in a furnace preheated to 450 C. for about an hour.
3. Transfer the ashed sample to a fusion test tube (18 x 150 mm).
4. Follow steps for fusion with potassium pyrosulphate.

Sample Extraction :

A. Fusion with potassium pyrosulphate

1. Fuse 0.5 g of the finely sieved sample with 2.5 g of potassium pyrosulphate in a pyrex test tube (18 x 150 mm). Complete fusion usually requires 5 to 6 minutes.

2. Allow the tube to cool and leach with 4 ml of 2N HCl solution.
3. Heat the tube until all the melt is broken up (on heated sand tray).
4. Make the volume up to the 10 ml mark, mix, and let it settle.
5. Proceed with the molybdenum determination as below.

B. Fusion with a mixture of sodium carbonate, sodium chloride, and potassium nitrate in a 5:4:1 ratio.

1. In a nickel crucible thoroughly mix 0.5 g of sieved sample with 2.5 g flux.
2. Fuse on gas burner until frothing has ceased.
3. Allow the melt to cool and add about 4 ml of water.
4. Allow to stand overnight.
5. Transfer the contents of the crucible into a clean test tube. Use glass rod to facilitate pouring into the tube.
6. Adjust the volume to the 10 ml mark with the water washings from the crucible.
7. Bring to a boil over low heat, allow to cool and settle.
8. Proceed with molybdenum determination as below.

Molybdenum Determination :

1. Pipette (use automatic pipette) 4 ml of the clear solution into a clean test tube (16 x 150 mm).
2. Add one drop of 1% phenolphthalein indicator.

3 a. For samples fused with potassium pyrosulphate. Add concentrated NH_4OH drop by drop until violet-red color starts to appear.

3 b. For samples fused with a mixture of sodium carbonate, sodium chloride, and potassium nitrate. Add 2N HCl drop by drop until the red color starts to disappear.

4. Add about 10 mg sodium tartrate powder (use scoop) and dilute the sample solution to 10 ml with water.

5. Add 1 ml concentrated HCl and shake until a clear solution is obtained.

6. Add 0.6 ml of 5% KCNS solution and shake.

7. Add 1 ml of 10% $SnCl_2$ solution and shake until all the ferric ion (red or yellow color) is reduced (colorless).

8. Allow to stand for at least one minute.

9. Add 0.6 ml isopropyl-ether and shake for 90 seconds.

10. Compare the colored isopropyl-ether layer to that of the standard.

Preparation of Standards :

1. Into 13 clean calibrated test tubes (16 x 150 mm) pipette 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0 and 5.0 ml of 0.0001% standard molybdenum solution.

2. Add to each test tube 2 drops of 1% ferrous ammonium sulphate solution.

3. Follow steps 4 to 9 of the procedure for the molybdenum determination.

4. Prepare a new set of standards each day.

Estimation of Molybdenum Content

The molybdenum content of the sample can be calculated from the following equation:

Mo in p.p.m. =

$$\underbrace{\frac{\text{final volume (ml)}}{\text{weight of sample(g)} \times \text{aliquot used(ml)}}}_{A} \times \underbrace{\mu\text{g of matching standard}}_{B}$$

Since the final volume, weight of sample, and aliquot are always the same, A is a constant for this particular case. Hence B is the only variable.

Following the previously described analytical procedure

$$A = \frac{10}{0.5 \times 4} = 5$$

Hence the original equation can be written :

$$\text{Mo in p.p.m.} = 5 \times \mu\text{g of matching standard}$$

If a high value is expected, however, the weight of the sample and/or the amount of the aliquot can be adjusted accordingly. The original equation should then be applied for purpose of calculation.

Productivity

If samples are fused in batches of 25 (in nickel crucibles) or 50 (in test tubes), 25 to 50 determinations per man day (8 hours) can be performed. Organic matter in the samples may reduce the speed of the fusions in test tubes if potassium pyrosulphate is used for flux.

Precision

To ensure the precision of the analyses, several groups of samples were analyzed more than once using the same method of extraction (potassium pyrosulphate fusion) and molybdenum determination (thiocyanate-stannous chloride method). Some of the results are listed below.

Sample number	Date of analysis	Mo in p.p.m.	Date of analysis	Mo in p.p.m.
BH-5502	12-06-'63	2.0	6-11-'63	1.8
BH-5503	"	1.2	"	1.4
BH-5511	"	0.5	"	0.5
BH-5512	"	0.4	"	0.5
BH-5513	"	1.0	"	0.7
BH-5516	"	1.7	"	1.4
BH-5517	"	1.2	"	0.7
BH-5518	"	0.5	"	0.5
BH-5520	"	0.5	"	0.5
BH-5528	"	0.7	"	0.9
BH-5529	"	2.0	"	2.8
BH-5530	"	1.5	"	1.8
BH-5531	"	1.2	"	1.2
BH-5532	"	1.5	"	1.6
BH-5535	"	0.5	"	0.5
BH-5537	"	1.0	"	1.2
BH-5662	14-11-'63	40.	20-11-'63	36.
BH-5669	19-11-'63	9.5	"	7.5

It is generally observed that low values have higher reproducibility as compared to the high ones. The differences in the results is probably due to the inhomogeneity of the samples and to some extent were operative errors.

Reagents Required for 1,000 Determinations

All chemicals listed below should be of highest purity (ACS reagent grade where possible).

- 500	ml	Ammonium hydroxide, concentrated.
- 200	ml	Ethyl-alcohol (absolute).
- 20	g	Ferrous ammonium sulphate.
- 4,000	ml	Hudrochloric acid, concentrated.
- 4,000	ml	Isopropyl-ether, peroxide-free.
- 5	g	Molybdic anhydride.
- 5	g	Phenolphthalein.
- 200	g	Potassium nitrate, fine granular.
- 1,000	g	Potassium pyrosulphate, fused, powder.
- 100	g	Potassium thiocyanate.
- 500	g	Sodium carbonate, anhydrous, powder.
- 400	g	Sodium chloride.
- 10	g	Sodium hydroxide, pellet.
- 500	g	Sodium tartrate.
- 100	g	Stannous chloride.
- 10	ml	Sulphuric acid, concentrated.
- 20	g	Tin, mossy.

CHAPTER VI

2. THE GEOCHEMISTRY OF MOLYBDENUM IN THE ROCKS

General Statement

Work by Kuroda and Sandell (1954) provides some fundamental data on the distribution of molybdenum in various types of rocks. Additional data, mainly for igneous rocks, are found in the works of Vinogradov, et. al. (1958); Rabinovich, et. al. (1958); and Tauson and Studenikova (1959). These data, together with other scattered data for igneous as well as for sedimentary and metamorphic rocks, are compiled in Appendix I (see Geochemistry of Molybdenum - in Igneous and Igneous-type rocks, in Sedimentary rocks, and in Metamorphic rocks, pp.I-13 - I-19). The latest estimate of the crustal abundance of molybdenum as given by Kuroda and Sandell (1958) and Vinogradov, et. al.(1958) is 1.0 ± 0.5 p.p. m.

The molybdenum content of all types of igneous, sedimentary, and metamorphic rocks within the area covered by this investigation is given in the Tables and Figures that follow. The Tetagouche Group rocks are discussed first, followed by the Chaleur Bay Group, the various acid and basic intrusives, and the Pennsylvanian rocks. Values for some miscellaneous rocks and minerals such as iron formation and manganese nodules and ores are also included.

The Mode of Occurrences of Molybdenum in Rocks

In igneous rocks, between 50 to 85% of the bulk of the molybdenum content is reported to occur in feldspar. The remainder is found in biotite, hornblende, accessory minerals (sphene, ilmenite, magnetite, and zircon), pyroxenes, olivines, and minor amounts in quartz (see Table 14, Appendix I). Although it is known that certain accessory minerals have high concentrations of this element, the total amount in all of accessory minerals of a rock may only constitute 1% of the molybdenum content of the rock. The presence of molybdenum in the minerals of igneous rocks is generally explained by the replaceability of Ti^{+4}, Fe^{+3}, Al^{+3}, and probably also Mg^{+2} and Si^{+4} by Mo^{+4}. Because of its chalcophilic character, the molybdenum in igneous rocks may also be present as the sulphide, molybdenite, or as a minor constituent of other sulphide minerals.

The manner in which molybdenum occurs in sedimentary rocks has not been clearly established. Initially, the element may have been deposited as 1) an adsorbed constituent of clay minerals and manganese and iron hydroxide colloids; 2) a component of organic compunds, 3) a co-precipitate with iron sulphide, or 4) as a constituent of certain resistant molybdenum bearing minerals. The environment of deposition and the manner in which the molybdenum reached the site of deposition decide which of these would predominate. Abnormal conditions may prevail in some cases, giving rise to higher than average enrichments, or vice versa very low amounts in some facies of sedimentary rocks.

The mode of occurrence of molybdenum in metamorphic rocks depends on the origin of the rocks. Mobilization and reconstitution during metamorphism may affect the state in which molybdenum is present in these rocks. The absence of studies on the distribution of molybdenum in the different minerals and facies of metamorphic rocks makes it difficult for one to trace the history of the element during metamorphism.

Result of Analysis and Discussion

General

Table 3 summarizes data on the molybdenum content of the various rock units in the Bathurst district. Data on individual rock samples are presented in Appendix II, pp. II-2 - II-7. A glance through these data indicates little variation in the molybdenum contents. Values higher than 3.0 p.p.m. are found mainly in the Nigadoo quartz-feldspar porphyry and black schists of the Tetagouche Group.

Tetagouche Group

Twenty rock samples of the 5 principal rock types were collected and analyzed for their molybdenum content. Despite the variations in rock types, the analysis exhibit little difference from one rock type to another.

The volcanics of the group are represented by : acid volcanics with rhyolitic composition, basic volcanics, and quartz-feldspar augen schists. The molybdenum content in these rocks is 4.0, 0.5, and 0.7 p.p.m. respectively. The acid volcanic rock, which shows rusty weathered surfaces, had the

Table 3

Molybdenum Content in Rocks of the Bathurst District

	Number of analysis	Mo in p.p.m.	
		Range	Average
Tetagouche Group			
- Acid volcanics, rusty weathering	1	-	4.0
- Quartz-feldspar augen schists	3	0.7 - 3.0	1.5
- Basic volcanics, basaltic	1	-	0.5
- Metasedimentary rocks: argillite, phyllite, and quartzite	11	0.3 - 3.0	1.2
- Metasedimentary rocks: black schist	4	1.5 - 15.0	6.5
Chaleur Bay Group			
- Argillite, greywacke, and slate	4	0.5 - 1.5	1.1
- Mineralized argillite near vein	1	-	7.0
Acid Intrusives			
- Bathurst porphyritic granite	44	0.2 - 29.0	1.7
- Bathurst porphyritic granite less 4 higher than average samples	40	0.2 - 2.5	0.7
- Nicholas Dénys granite	12	0.3 - 28.0	2.9
- Nicholas Dénys granite less 1 higher than average sample	11	0.3 - 2.5	0.7
- Nigadoo quartz-feldspar porphyry	22	1.2 - 8.0	4.1
Basic Intrusives			
- Diabase and gabbro	9	0.2 - 1.7	1.0
Pennsylvanian Rocks			
- Red sandstone and conglomerate	2	0.3 - 0.7	0.5

highest molybdenum content. This is probably due to the presence of finely disseminated sulphides in the rock. It is of interest to note, that several rhyolites from Texas, Montana, and Minnesota also contain from 3.2 to 4.3 p.p.m. molybdenum (Kuroda and Sandell, 1954).

The occurrence of molybdenum in volcanic rocks is the same as that of intrusive rocks, that is, if it is not present in sulphides, it occurs principally in feldspar or in small amounts in the accessory minerals, biotite, hornblende, and pyroxenes.

The quartz-feldspar augen schists or "porphyries" of the Tetagouche Group are represented by three samples of which one is distinctly pyro-clastic, and hence was included under the volcanics in the earlier discussion. The two remaining samples are quartz-feldspar augen schist and phyllite with disseminated sulphides. Their molybdenum values are 0.8, and 3.0 p.p.m. respectively. It is reasonable then to assume that the high value in the phyllite is attributed to the presence of sulphide minerals. Without knowing the origin of these rocks, explanations on the molybdenum occurrences in these rocks will not be attempted.

Metasediments of the Tetagouche Group are represented by eleven samples of varicolored argillites and slates, phyllites, quartz-chlorite schists, and grey quartzites. The molybdenum content of these rocks ranges from 0.3 to 3.0 p.p.m., with an average value of 1.2 p.p.m. (see Table 3). Three of these samples contain disseminated sulphides and one contains some manganite veinlets. It is of particular interest that these four rocks have molybdenum contents that are higher than average.

The molybdenum in the metasediments of the Tetagouche Group was probably deposited as a sorbed constituent on the original clay minerals. In the red argillites and slates, it may also have been coprecipitated by iron hydroxides. The association of high molybdenum contents with sulphide-and manganite-bearing rocks suggests that this element is concentrated in these minerals. This is partly supported by the fact that an analysis of a crystalline manganite from the same locality gave 13 p.p.m. molybdenum (see Table 5).

The enrichment of molybdenum and several other elements in black shales and their derivatives is common. A prime example is the Kupferschiefer of central Europe. Four black schists of the Tetagouche Group have an average molybdenum content of 6.5 p.p.m., the highest for any rock type in the district. The results of sulphur and total carbon analysis on the same samples indicate a close sympathetic relation between the three elements (see Table 4). The presence of disseminated sulphides, combined with the fact that the molybdenum and sulphur contents of these rocks are proportional, suggests, that molybdenum is concentrated in the sulphides, possibly as a sorbed constituent. The results of experiments by Korolev (1956) and Sugawara, <u>et. al</u>. (1961) on coprecipitation of molybdenum with iron sulphide support this speculation. However, the relation of molybdenum with carbon in the rocks

Table 4

Mo, S, and C Content in Black Schists

SAMPLE #	DESCRIPTION	Mo in p.p.m	S in %	C in %
BH-5524-62	Black schist with quartz stringers, near Sturgeon River deposit.	15.0	1.37	1.14
BH-5666-63	Black schist disseminated with sulphides, near New Larder "U" deposit.	2.0	0.48	0.15
BH-5667-63	Black schist disseminated with sulphides, near New Larder "U" deposit.	1.5	0.60	0.65
BH-5668-63	Black schist disseminated with sulphides, near New Larder "U" deposit.	7.5	1.64	1.69

suggests that molybdenum also have been enriched by biogenic process. Experiments by Krauskopf (1956) failed to find a conclusive answeer as to how molybdenum is concentrated in marine sediments. He favors, however, the idea that biologic processes play an important role. Wedepohl (1964), in discussing elemental concentrations in the Kupferschiefer, observed a relation between molybdenum and carbon content, but less so between molybdenum and sulphur. High concentrations of molybdenum together with vanadium and uranium have also been reported by Almassy (1956) in coal measures. He is of the opinion that these elements were originally contained in the sapropel. Boyle (personal communication 1964) also found as high as 110 p.p.m. molybdenum in Pennsylvanian coal from Cape Breton Island, N.S. These observations point to an important connection between molybdenum and biogenic carbon, bearing in mind, however, that most coals contain some sulphur (sulphides) with which some of the molybdenum may be associated. The writer is of the opinion that certain organisms, in marine as well as continental environments, are capable of concentrating molybdenum from their surroundings. Once the element is concentrated, it may be sedimented directly in the bodies of the dead organisms, or it may be released into the surrounding aqueous media. In a reducing environment chemical precipitation as sulphide and/or adsorption and coprecipitation by iron sulphides may then follow. Such mechanisms seem to account for the relatively high contents of molybdenum in the black schists of the Tetagouche Group.

Chaleur Bay Group

This Group is represented by 5 speciments of dark grey argillite, greywacke, metaconglomerate, grey slate, and cherty argillite. From Table 3 it is seen that the molybdenum content of these rocks varies from 0.5 to 1.5 p.p.m., with one value of 7.0 p.p.m. This high value was obtained from a dense dark grey sulphide-bearing argillite which constitutes the wall rock of the Nigadoo sulphide deposit. Discounting this mineralized specimen, the average molybdenum content of the Chaleur Bay Group is 1.1 p.p.m.

As in the Tetagouche Group, the molybdenum in these sediments is probably bound on the clay minerals as a sorbed constituent, or it may also be in original unweathered primary mineral constituents. The only high value encountered in the Group is that from the sulphide-bearing rock, and hence most of the element probably occurs as a minor constituent of the sulphides.

A small replacement and fracture filling molybdenite deposit was recently discovered (end of 1963) by one of the companies working in the Nicholas Dénys area. This occurs in a thin band of contact metamorphic garnet-diopside skarn of the Chaleur Bay Group. The fact that molybdenite crystals also occur in the granite immediately north of this deposit, suggests, that the intrusive may have been the source of the molybdenum in the skarn.

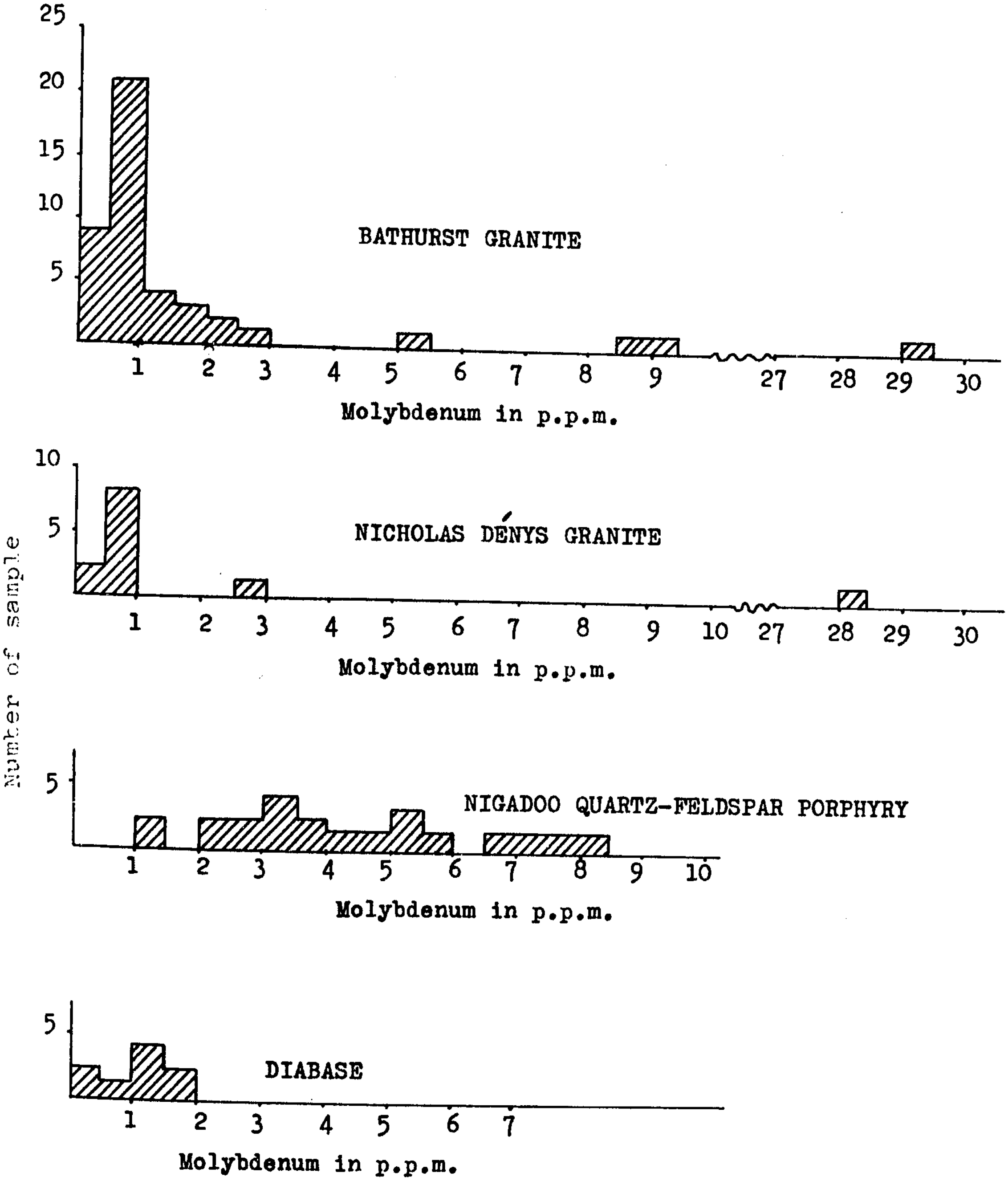


FIGURE 3. Frequency distribution of molybdenum in diabase and granitic rocks.

Acid Intrusives

Bathurst Granite

Table 3 gives the range and average values of the 44 samples of granite analyzed (see Appendix II, pp. II-3 - II-4). Of these, only 4 (9%) have values equal to or higher than 5.0 p.p.m. molybdenum; the remaining 91% of the samples contain from 0.2 to 2.5 p.p.m. molybdenum, with an average value of 0.7 p.p.m. The average for all 44 samples is 1.7 p.p.m. molybdenum. The average derived from the 40 analysis (0.7 p.p.m.), excluding the 4 high values, is probably a close approximation of the average molybdenum content of the granites.

The frequency distribution of molybdenum for the Bathurst granite is presented in Figure 3. From this diagram it is evident that there are probably two modes of occurrence of molybdenum. First, there is a group with molybdenum values lower than 3.0 p.p.m. and second, there is a grouping around 5.0 p.p.m. Mo. In the first group, the bulk of molybdenum presumably occurs mainly in the feldspars and in biotite and hornblende in that order. Very samll amounts may also be present in the accessory minerals and quartz. For the second group the fact that molybdenite is found in over 6 different localities in the area leads to the conclusion that the bulk of the molybdenum probably occurs as disseminated molybdenite or in other sulphide minerals in the rocks.

The majority of the Bathurst granite samples were also analyzed for Zn, Cu, Pb, As, and Sb (see Appendix II, pp. II-3 - II-4). There is no apparent relation between molybdenum and these elements in this granite. In one sample (BH-5599-62) for example, where the Zn, Cu, Pb, and Sb content is normal, the highest Mo (29 p.p.m.) and As (26 p.p.m.) values are present.

Nicholas Dénys Granite:

The trace element distribution of Cu, Pb, Zn, As, Sb, and Mo in the Nicholas Dénys granite does not vary much from that in the Bathurst batholith. A comparison of the frequency distribution for molybdenum between the two intrusives, despite a much smaller number of analysis from the Nicholas Dénys granite, indicates a close similarity (Figure 3). From 12 analysis, only one sample yields 28.0 p.p.m. molybdenum, and the remainder contain from 0.3 to 2.5 p.p.m. molybdenum (see Table 3). The form in which molybdenum is present in this rock, based on the previously mentioned data, is presumably the same as it is in the Bathurst granite.

Up to the time when the writer completed his field work (summer 1963), there had not been any report with respect to the occurrence of molybdenite in the Nicholas Dénys granite, although J.L. Davies (personal communication, 1963) had observed two molybdenite showings north and south of the body. The results of the molybdenum analysis, a similar frequency distribution pattern to that of the Bathurst granite, and the results of a stream sediment survey in the area (Tauchid, 1964), suggested that molybdenite should be associated with this granite body. This speculation was verified by the recent discovery of minor amounts of molybdenite and other sulphide minerals in some of the diamond drill cores obtained from the granite (A.B. Baldwin, personal communication, 1964). To ascertain the economic possibilities of the granite as a molybdenite source, the company involved is carrying out further detailed surveys.

Nigadoo Quartz-Feldspar Porphyry:

Among all acid igenous rocks of the Bathurst district, the Nigadoo quartz-feldspar porphyry (Figure 20) is unique in that it is greatly enriched in disseminated sulphides (Martin, 1963). Analysis of this rock also reveal abnormally high Mo, Zn, Cu, Pb, As, and Sb contents (see Appendix II, pp II-5 - II-6). The range and average values of these elements are as follows:

Element	No. of Analysis	Range	Average
		in p.p.m.	
Mo	22	1.2 - 8.0	4.1
Zn	19	40 - 5200	1232
Cu	19	65 - 400	161
Pb	19	25 - 4000	905
As	19	25 - 4200	522
Sb	19	2.5 - 23	7.8

As shown in Figure 3, the frequency distribution for molybdenum in the Nigadoo porphyry is entirely different from that of the Bathurst and Nicholas Dénys granites. This is probably due to the different manner of occurrence of molybdenum in these various granitic bodies. The abnormal molybdenum concentration in the Nigadoo porphyry is probably the result of an enrichment process which was active during the emplacement of the Nigadoo sulphide deposit. Hence the bulk of the molybdenum is probably present as a minor constituent of the disseminated sulphides.

Basic Intrusives

The basic intrusives of the district are represented by dense, fine to coarsely crystalline diabase, generally with ophitic or semiophitic texture. In the Nicholas Dénys area, there is a tendency for these rocks to be serpentinized as one proceeds westward. Some of the samples analyzed contain minor amounts of sulphides. The molybdenum content of the diabase ranges from 0.2 to 1.7 p.p.m.; the average value from 9 analysis is 1.0 p.p.m. In contrast to the granites, the individual analysis of the diabase show a rather uniform trend (Appendix II, p. II-7). Furthermore, in Figure 3, it is noticed that the frequency distribution for molybdenum in the diabase of the district, is different from that for granite. This is contrary to the results reported by Kuroda and Sandell (1954) who found the distributions to be the same in both basic and acidic rocks. A slightly different mode of occurrence of this element in the two rock types is thought to be the most plausible reason. Other than feldspars, magnetite presumably plays an important role as the mineral carrier for molybdenum in the basic intrusives. The remainder may be in pyroxenes, olivine, and sulphide minerals.

Pennsylvanian Cover

Only two composite samples of greenish yellow sandstone and red conglomerate and sandstone from this formation were analyzed for molybdenum. The molybdenum contents of these rocks are, 0.7 and 0.3 p.p.m. respectively. The higher of the two was obtained from greenish yellow sandstone with some plant remains. Molybdenum in these rocks was probably adsorbed and coprecipitated with iron oxide and in less amounts with the clay constituent of the rocks. The plant remains may also have had an influence on concentrating molybdenum by reduction from its soluble salts.

Miscellaneous

Iron Formation:

The iron formation of the Tetagouche Group is represented by banded hematite, magnetite, jasper, and chlorite. Adjacent to the sulphide bodies, these are generally partly replaced or contain disseminated sulphides. Analysis of 3 samples from the Brunswick No. 6 and the Austin Brook Iron deposits gave an average value of 1.4 p.p.m. molybdenum (see Table 5). This is relatively low when compared to most known values reported for iron ores. The general belief is, that molybdenum was precipitated together with iron oxides. The writer is of the opinion, that the amounts of molybdenum coprecipitated in an iron rich environment is dependant on the availability of the element.

Manganese Ore:

Manganese oxide concretions and manganite crystals in the red argillites of the Tetagouche Group contain, 11.5 and 13.0 p.p.m. molybdenum (see Table 5). Hydroxide of manganese is a well known scavenger for a number of metals, among which is molybdenum. Hence it is thought that molybdenum was enriched through adsorption and coprecipitation by the manganese hydroxide colloid, and later partly remobilized together with the oxide.

Table 5

Mo Content in Manganese and Iron Ores

SAMPLE Number	LOCATION	DESCRIPTION	Mo in p.p.m.
BH-5533a-62	Tetagouche Falls	Non crystalline manganese oxides; spherical balls in red argillite	11.5
BH-5533c-62	Tetagouche Falls	Fine to medium crystalline manganite; veinlets in red argillite	13.0
BH-5538-62	Brunswick No. 6	Finely banded hematite and magnetite	1.0
BH-5539-62	Brunswick No. 6	Cherty iron ore with disseminated sulphides	2.2
BH-5545-62	Austin Brook	Banded magnetite and hematite with disseminated sulphides	1.0

2. THE GEOCHEMISTRY OF MOLYBDENUM IN THE POLYMETALLIC SULPHIDE DEPOSITS

General Statement

Molybdenum is one of the chalcophilic elements commonly concentrated in sulphides. Previous work, mainly by the Noddacks (1931), Grip (1951), Fleischer (1955), and Michalek (1958) provide us with data on the distribution of molybdenum in various sulphide minerals. A summary of these is presented in Appendix I, pp. I-12 - I-13. It is generally thought that molybdenum is particularly enriched in chalcopyrite and copper-rich pyrite. However, the results of the investigation by Michalek do not seem to support this view.

The occurrence of molybdenum in sulphide minerals is probably due to isomorphous substitution and adsorption. The first is probably the most significant in high temperature sulphides, where Mo^{+4} (0.70 Å) probably replaces Fe^{+3} (0.64 Å), Fe^{+2} (0.74 Å), Cu^{+2} (0.72 Å), and also Ni^{+2} (0.69 Å). The second is more important in low temperature processes.

Where molybdenum is present in the supergene zone it is oxidized to Mo^{+6} which forms readily soluble complexes with oxygen and sulphate ions. In these forms the molybdenum migrates in ground and surface waters and is ultimately adsorbed by various hydrates, precipitated as secondary molybdate (if it is plentiful in the environment), or coprecipitated as a minor constituent of a number of secondary basic salts.

Result of Analysis and Discussion

Sulphides

The results of molybdenum analysis on the sulphide ores of the Brunswick No. 6, New Larder "U", Sturgeon River, and Nigadoo deposits are presented in Table 6. These data indicate apparent differences in the molybdenum content of the various deposits. These differences may be due to the varied mineralogical composition of the various ores, but the major governing factor leading to the observed distribution was probably the result of a difference in the availability of the element in the mineralizing solutions.

The ore of the Brunswick No. 6 deposit consists mainly of pyrite (± 75%), sphalerite, galena, and smaller amounts of chalcopyrite and pyrrhotite. Arsenopyrite, bornite, tetrahedrite, stannite, boulangerite, cassiterite, and domeykite are also reported (Boyle and Davies, 1964). Of the 5 samples analyzed, 4 were collected from just below the gossan zone. These were highly weathered, loose sandy sulphides and yielded from 8.0 to 26.0 p.p.m. Mo with an average value of 16.5 p.p.m. The molybdenum content of one fresh massive sulphide sample was 5.0 p.p.m. These results seem to indicate a slight near surface enrichment of molybdenum in the ore body.

The New Larder "U" deposit is represented by 5 samples taken from a number of diamond drill cores and one (BH-5521-62) collected from the mine dump. Mineralogically, the deposit consists of pyrite, sphalerite, galena, chalcopyrite, pyrrhotite, and minor arsenopyrite. The results of the molybdenum

Table 6

Molybdenum Content in Sulphides

SAMPLE Number	DESCRIPTION (main constituents)	Mo in p.p.m.
	Brunswick No. 6	
BH-5005d-62	Mainly pyrite, soft altered	16.0
BH-5007f-62	Mainly pyrite, soft altered	16.0
BH-5008d-62	Mainly pyrite, soft altered	26.0
BH-5009f-62	Mainly pyrite, soft altered	8.0
BH-5550-62	Mainly pyrite, dense crystalline	5.0
	Average	12.2
	New Larder "U"	
BH-5521-62	Pyrite, arsenopyrite, chalcopyrite	3.5
BH-5660-63	Mainly pyrite and chalcopyrite	12.0
BH-5661-63	Mainly galena, sphalerite, and pyrite	52.0
BH-5662-63	Pyrrhotite, chalcopyrite, and galena	36.0
BH-5663-63	Pyrrhotite, pyrite, and galena	14.0
BH-5664-63	Pyrrhotite, pyrite, galena, and chalcopyrite	112.0
	Average	38.2
	Sturgeon River	
BH-5506-62	Mainly pyrite and galena, altered	2.0
	Nigadoo	
BH-5501-62	Arsenopyrite, sphalerite, and galena, altered	5.0
BH-5504-62	Pyrite, arsenopyrite, and sphalerite	2.0
BH-5654-63	Galena	1.0
BH-5655-63	Sphalerite	1.2
BH-5656-63	Pyrrhotite	1.4
BH-5657-63	Arsenopyrite	3.8
BH-5658-63	Chalcopyrite	4.3
BH-5659-63	Chalcopyrite	2.8
	Average	2.8

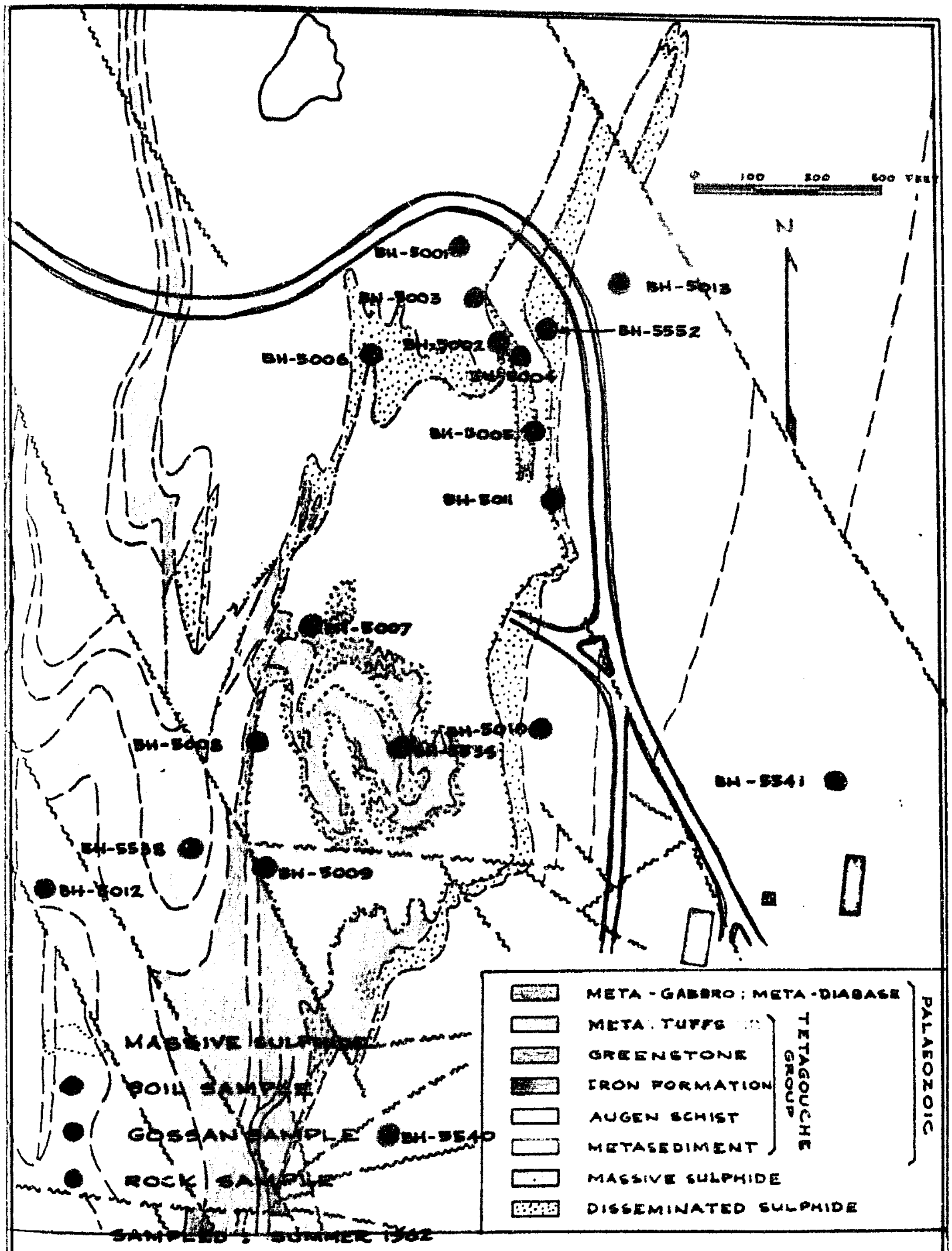


FIGURE 4. GEOLOGY MAP OF BRUNSWICK No. 6 DEPOSIT, after Boyle and Davies (1964).

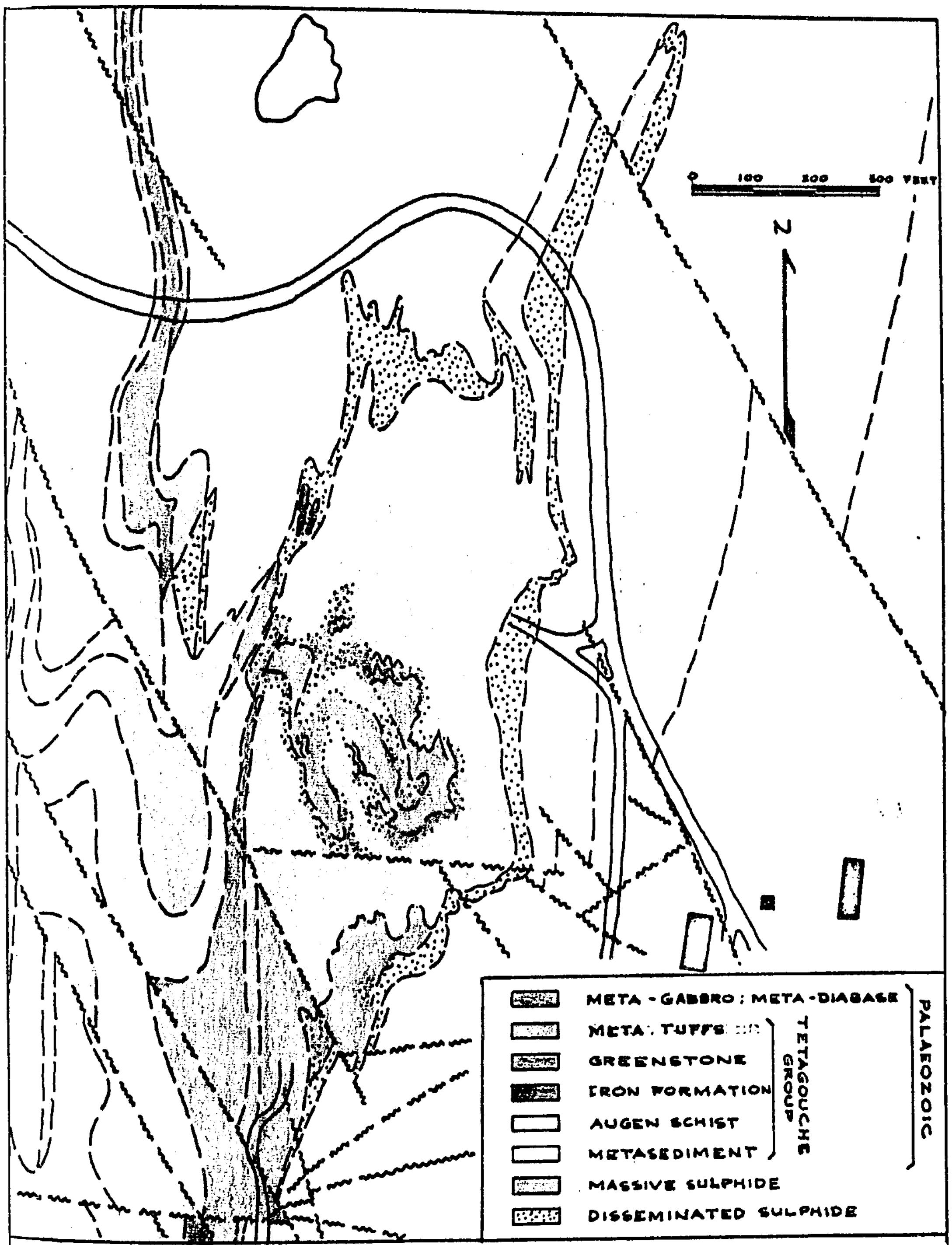


FIGURE 4. GEOLOGY MAP OF BRUNSWICK No. 6 DEPOSIT, after Boyle and Davies (1964).

analysis on the 6 samples show a range of 3.5 to 112.0 p.p.m. with an average value of 38.2 p.p.m. Of these only one sample contains less than 10.0 p.p.m. Mo. As shown in Table 6, the New Larder "U" sulphides have the highest range and average molybdenum values of the four sulphide bodies investigated.

Only one composite sample was collected from the dump of the Sturgeon River Mine. It consisted mainly of fine-grained pyrite and galena. The molybdenum content of this sample is 2.0 p.p.m.

The coarse crystalline nature of the Nigadoo sulphides enabled separation of the different mineral phases present. The deposit consists of pyrrhotite, pyrite, sphalerite, galena, chalcopyrite, arsenopyrite, and stannite in a multi-generation calcite gangue (Kalliokoski, 1961). The average molybdenum content of 6 individual and 2 composite samples of sulphides, is 2.8 p.p.m. As shown in Table 6, chalcopyrite had the highest content of the sulphides analyzed. It is of interest to note that the average molybdenum content of the quartz-feldspar porphyry at the Nigadoo mine is higher than the molybdenum content of the ore (compare Tables 3 and 6).

Gossans

The general profile of the gossan overlying the Brunswick No. 6 deposit is illustrated in Figure 5. It consists of well cemented, brecciated, and laminated hardcap at the top, underlain in turn by unconsolidated clayey leached till and porous residual gossan. Directly beneath this profile the sulphides

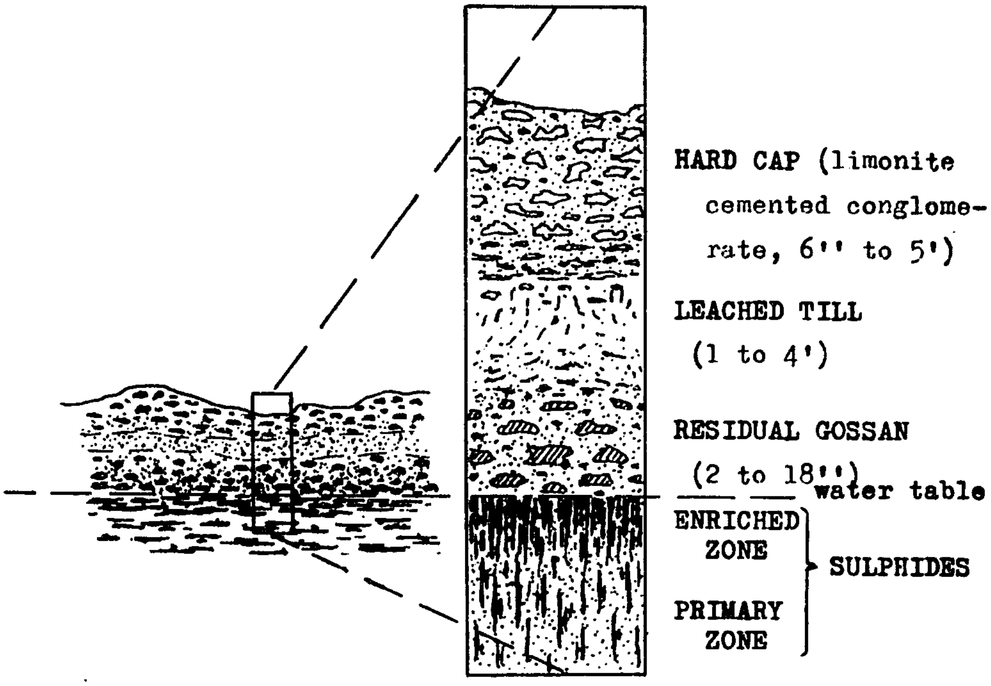


FIGURE 5. Idealized gossan zones of Brunswick No. 6 deposit.

have been weathered to soft, unconsolidated, sandy to silty material. The profiles differ from one location to the other in their mineralogical compositions. A general idea of the mineralogy of the various zones in the profile is given in Figure 6.

The gossan of the Brunswick No. 6 deposit is enriched in molybdenum (see Tables 7, 8, and Appendix II, pp. II-7 - II-8). In Table 7, the results of molybdenum analysis on 5 gossan profiles (Figure 4) is summarized. Two of these profiles, BH-5007 and BH-5008, show a similar pattern of molybdenum distribution in the different zones of the gossan. In general, molybdenum is depleted in the hardcap, increases downward, and reaches a maximum in the residual gossan. In both profiles, the altered sulphides contain less molybdenum than the overlying residual gossan. Rajah (1963) reported a similar pattern for the distribution of lead and silver. The reverse is true for iron.

The small amounts of molybdenum in the gossan zones discount the possibility that it is present as a secondary molybdenum mineral. The inverse relationship of molybdenum content with iron distribution in the gossan profiles also suggests that the amount of the element fixed by iron hydroxide and oxide are not too significant. It is probable, therefore, that molybdenum as MoO_4^{-2} replaces AsO_4^{-3} in beudantite and/or SO_4^{-2} in anglesite and jarosite. The high values in some of the leached tills (pH= 2.8) are probably due to the adsorption of molybdenum by clay minerals and sesquioxides, an effect which

Table 7

Molybdenum Distribution in the Gossan of the Brunswick No. 6 Deposit.

Description	Mo content in p.p.m.						
	Profile Number					RANGE	AVERAGE
	BH 5004	BH 5006	BH 5007	BH 5008	BH 5009		
Hardcap	12.0	10.0	1.6	1.0	4.0	1.0-12.0	5.7
Leached Till	17.8	9.0	9.0	28.0	19.0	9.0-28.0	16.6
Residual Gossan	16.2	11.2	18.7	33.0	4.0	4.0-33.0	16.6
Enriched Zone (altered sulphides)	16.0	-	16.0	26.0	8.0	8.0-26.0	16.5

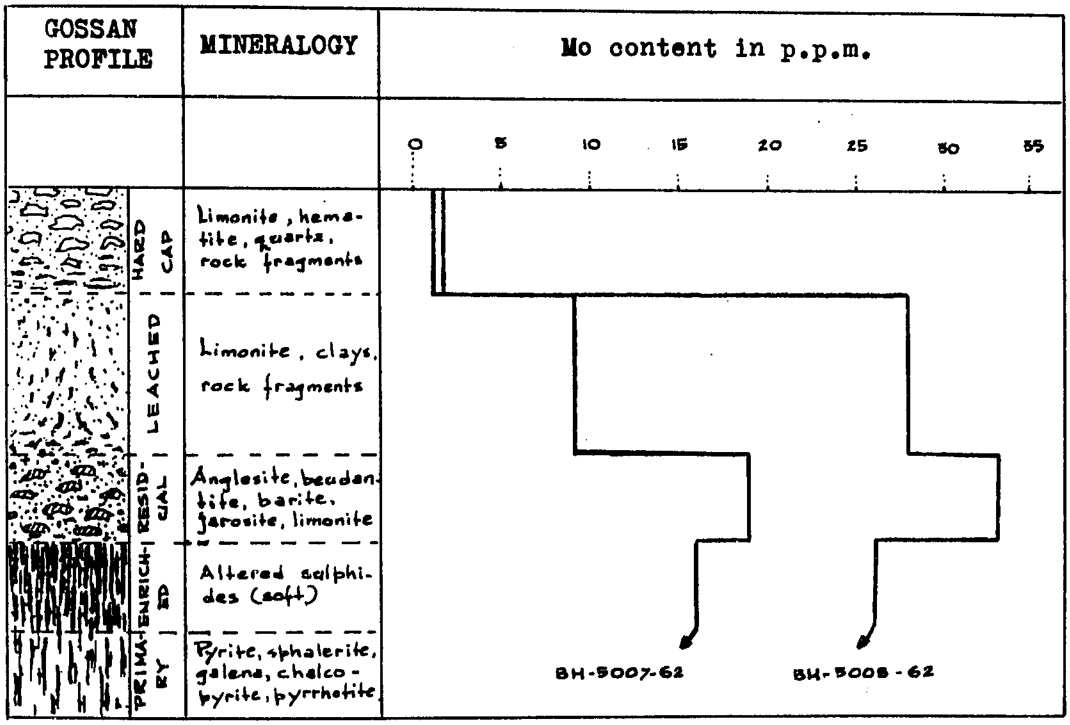


FIGURE 6. Molybdenum distribution in idealized gossan profiles of Brunswick No. 6 deposit.

Table 8

Molybdenum Contents of Gossan

SAMPLE Number	LOCATION	DESCRIPTION	Mo in p.p.m.
BH-5552-62	Brunswick No. 6	Yellow to green brecciated gossan (transported)	30.
BH-5522-62	New Larder "U"	Bright yellow gossan on sulphide disseminated quartzite	10.
BH-5508-62	Sturgeon River	Yellow, red, dark - brown gossan	9.0
BH-5509-62	Sturgeon River	Yellowish red to dark brown gossan, with unaltered sulphides	2.0

is enhanced in an acid environment (see also page 78).

For comparison, analysis of individual gossan samples from the Sturgeon River and New Larder "U" deposits are presented in Table 8. In general these two gossans are not as highly enriched in molybdenum as those at the Brunswick No. 6 deposit.

Iron Hydroxide Precipitates

Recent iron hydroxide precipitates at the orifices of springs and diamond drill holes in the vicinity of the sulphide deposits, were sampled and analyzed for Mo, Zn, Cu, Pb, As, and Sb. The results of the colorimetric and X-ray analysis are presented in Table 9. Of particular interest are three samples collected from the Brunswick No. 6 area. These were sampled two feet, ten feet, and fifteen feet away from the orifice of a diamond drill hole. As shown in Table 9, the three samples show a decrease in their molybdenum content as the distance from the spring increases.

The nature of molybdenum in these materials is probably as a sorbed constituent on iron hydroxide, and/or, as suggested earlier, the element as MoO_4^{-2} may replace AsO_4^{-3} and SO_4^{-2} in some of the secondary salts. The phenomena of decrease with distance from the orifice of the drill hole may, therefore, be due to the rapid coprecipitation of the molybdenum with iron hydroxides near the orifice. Any molybdenum remaining in solution is then taken up either by iron hydroxides or by the basic sulphate - arsenate of lead and ferric iron which form some distance from the drill hole.

Three other iron hydroxide precipitates from the New Larder "U" and Austin Brook Iron deposits were also investigated (see Table 9). Despite the high molybdenum content in the sulphides of the New Larder "U" deposit, the two iron hydroxides from the area contain only 1.5 and 2.0 p.p.m. molybdenum.

Table 9

Molybdenum Content in Iron Hydroxide Precipitates

SAMPLE Number	LOCATION	Mo	Zn	Cu	Pb	As	Sb	Other constituents
		in p.p.m.						
BH-5167-63	Brunswick No. 6 2 feet from orifice of drill hole	16.0	560	140	3000	4600	270	Fe - M* Y,Zr - Tr
BH-5168-63	Brunswick No. 6 10 feet from orifice of drill hole	14.0	480	80	3200	5700	340	Fe - M Y,Zr - Tr
BH-5169-63	Brunswick No. 6 15 feet from orifice of drill hole	13.0	520	110	7200	1200	160	Fe - M Zr - Tr
BH-5170-63	Austin Brook	1.6	-	-	-	-	-	Fe - M Zr,Ti - Tr
BH-5171-63	New Larder "U"	1.5	-	-	-	Tr	-	Fe,Mn - M Ti,Zr, Sr,Y - Tr
BH-5172-63	New Larder "U"	2.0	-	-	-	-	-	-

* M - Major = 10%

Tr - Trace = 0.1%

\- not determined

3. THE GEOCHEMISTRY OF MOLYBDENUM IN THE SOILS

General Statement

The soils of the Bathurst district are of the podzolic type, developed under a heavy forest cover in the cool humid climate, typical of the Maritime provinces. The process of soil development in this environment leads to a general acid condition which is due to the leaching action of meteoric water, a feature that removes all bases from the soil surface layers. The pH of the normal soils of the district ranges from 4.2 to 6.8, whereas in mineralized areas it varies from 3.9 to 7.6. In normal profiles the pH generally increases downward, the A_2 horizons being the most acidic.

A general soil profile for the district has the following horizons (Figure 7, and also Plate 1):

A_{00}	Loose, undecomposed organic remains (mainly plants), light to dark brown in color.
A_0	Dark brown to black humified organic materials.
A_2	Zone of maximum leaching, whitish to pinkish grey in color. Usually irregular in thickness.
B_1	Zone of accumulation, mainly of iron and aluminum compounds, from the leached horizon as well as from the layer underneath. Reddish brown to yellowish red in color.
B_2	Reddish yellow to yellowish brown transition zone.
C	Unconsolidated parent material, generally till, gravel or sand. Color variable. Till is generally yellowish to dark brown.

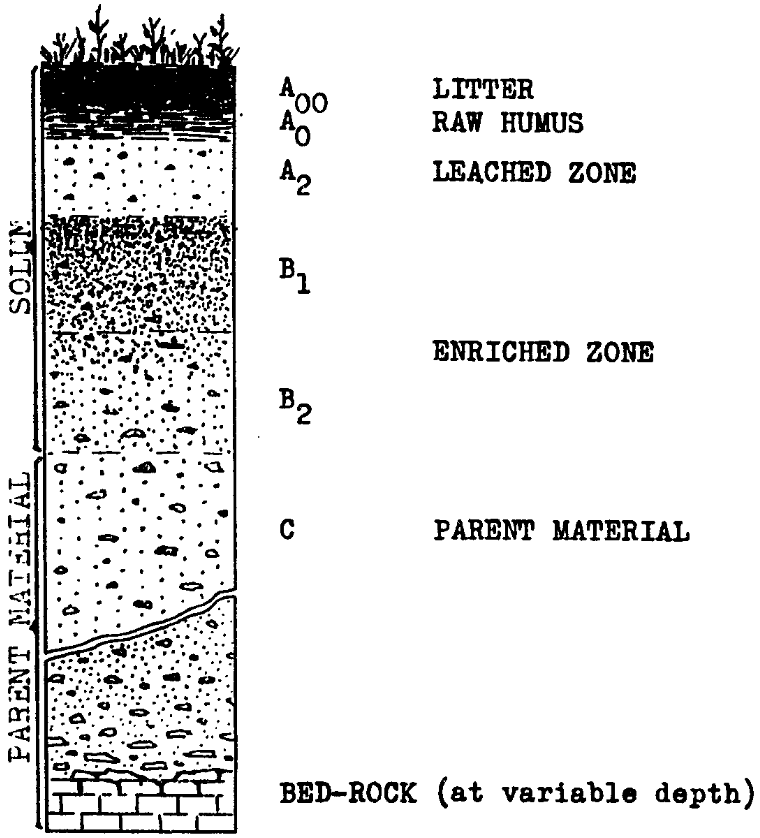
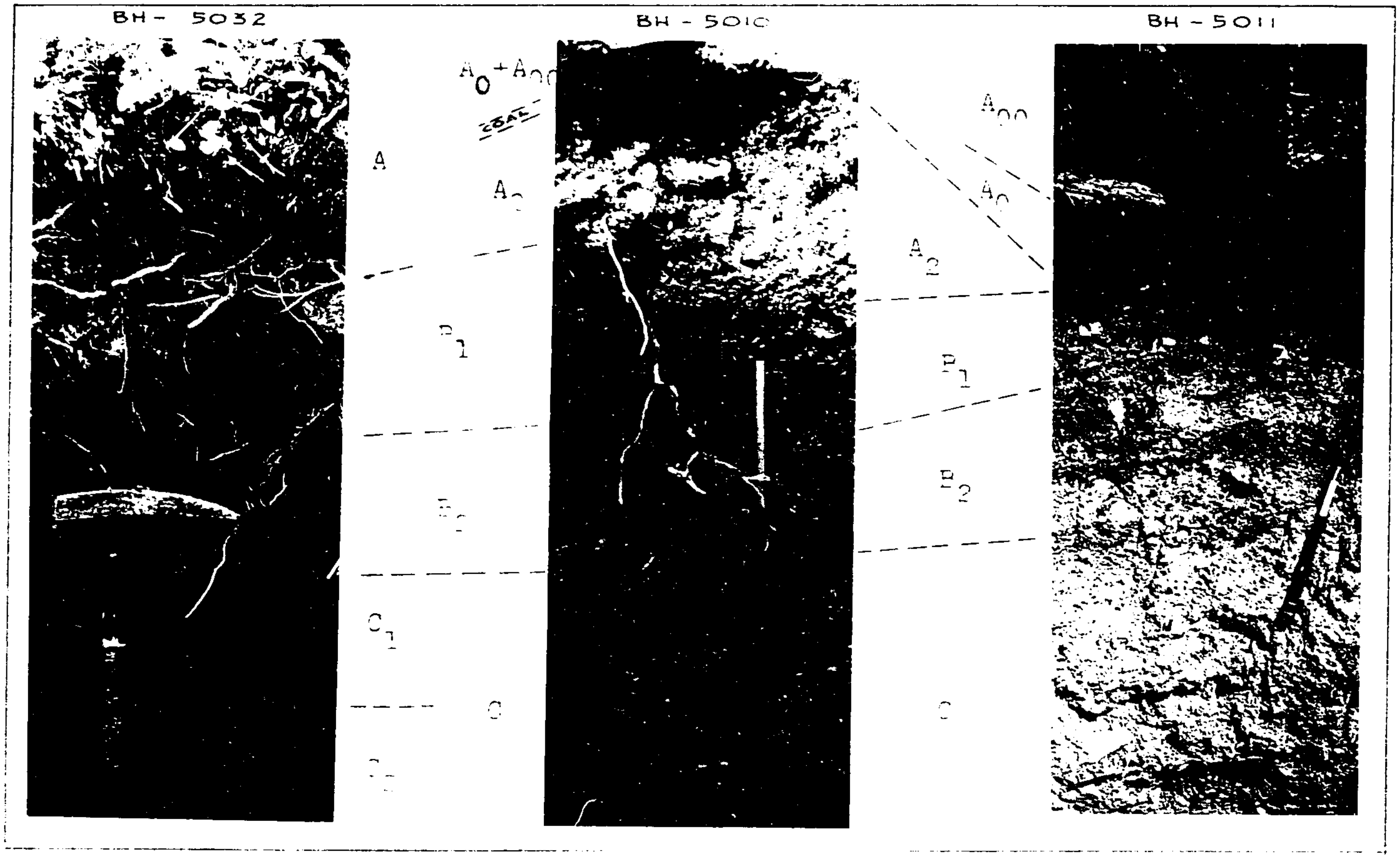


FIGURE 7. General soil profile of the Bathurst district, N.B.



BH-5032 Soil profile [illegible] area
BH-5010 Soil profile [illegible] No. 6 area
BH-5011 Soil profile [illegible] No. 6 area (over the sulphide

PLATE 1. Photographs [illegible] profiles of the Bathurst district.

The A_0 and A_{00} horizons, while constituting zones of organic accumulation, are usually absent in grassland. The A_2 bleached layer, characteristic of the podzolic type of soils, is occasionally not well developed or is absent in areas where immature soils occur.

Since the climatic conditions are the same within the area of study, the variation in the nature of soil profiles is probably attributed to one or a combination of the following factors:

a. Types of parent materials.

b. Types of vegetative cover.

c. Drainage.

In normal areas the parent materials are glacial tills or more rarely glacial outwash deposits such as sand, gravel and till with mixed sand or gravel. Such materials generally give a relatively uniform distribution of molybdenum in their derived soils. Soils overlying massive sulphide deposits as at the Brunswick No. 6 deposit have much iron oxide, and this has an influence on the chemistry of molybdenum. Likewise profiles with much manganese also effect the chemistry of molybdenum in a marked way.

Variations in the vegetative cover presumably could have an effect on the chemistry of molybdenum, but the details are complex and not readily ascertained. Similarly the drainage pattern is of importance since soluble molybdenum will follow the gradient of the water table and will be fixed in the soils down slope from the source of the molybdenum.

Mineralogy of Soils

Work by Present (1963) on the geochemistry of six typical soil profiles in the district provides an adequate knowledge of the mineralogy of the soil. Those interested in the subject should consult the original work.

A general conclusion can be drawn from his study, namely that the qualitiative mineralogical composition of any one profile does not vary greatly from that of others. This is due mainly to the similarity of the resistant minerals present in the underlying rocks, and is probably also the result of a relatively good mixing of the till during Pleistocene glaciation. However, a reflection of the underlying bedrocks can still be observed in the minor differences present in the various soil profiles. For instance profiles from the Nigadoo Mine area differ from others by their lack of epidote and the presence of sphalerite, pyrite, and galena. Profiles developed over the Bathurst batholith are characterized by the presence of apatite, garnet, sphene, andalusite, and topaz. Like those over the Nigadoo deposit, the profiles developed over the Brunswick No. 6 deposit contain some sulphides, in addition to barite and staurolite. Except for apatite, which is present in the A_2 horizons, the minerals just mentioned tend to occur only in the B and C horizons of the profiles.

The following minerals constitute the general mineralogical composition of all soil horizons in the district. In addition there are the usual clay minerals and fragments of undecomposed bedrock.

1. quartz
2. feldspars
3. muscovite
4. rutile
5. zircon
6. biotite
7. ilmenite
8. magnetite
9. epidote
10. hornblende
11. pyroxenes
12. chlorite
13. hematite
14. goethite

These are arranged according to their degree of resistivity, decreasing downward. Of these minerals, hematite, and goethite are thought to be secondary. The soils over the Brunswick No. 6 deposit are generally coated with the secondary ~~the~~ basic salts, jarosite and beudantite.

Result of Analysis

A general review of the geochemistry of molybdenum in soils is presented in Appendix I, pp.I-19 -I-21 . There it is noted that normal soils in different parts of the world contain from 0.08 p.p.m. to 73.8 p.p.m. molybdenum. Generally, however, most soils contain close to 2.0 p.p.m. Mo, the abundance figure for soils quoted by Vinogradov (1959).

The normal soils of the Bathurst district are represented by a total of 266 analysis, with contents ranging from less than 0.2 p.p.m. (below the sensitivity limit of the analytical method) to 4.0 p.p.m. Mo. The average is 1.2 p.p.m. The frequency distribution and the average content of the element in the different soil horizons is generalized in Figure 8. The highest concentration in the 63 complete and incomplete

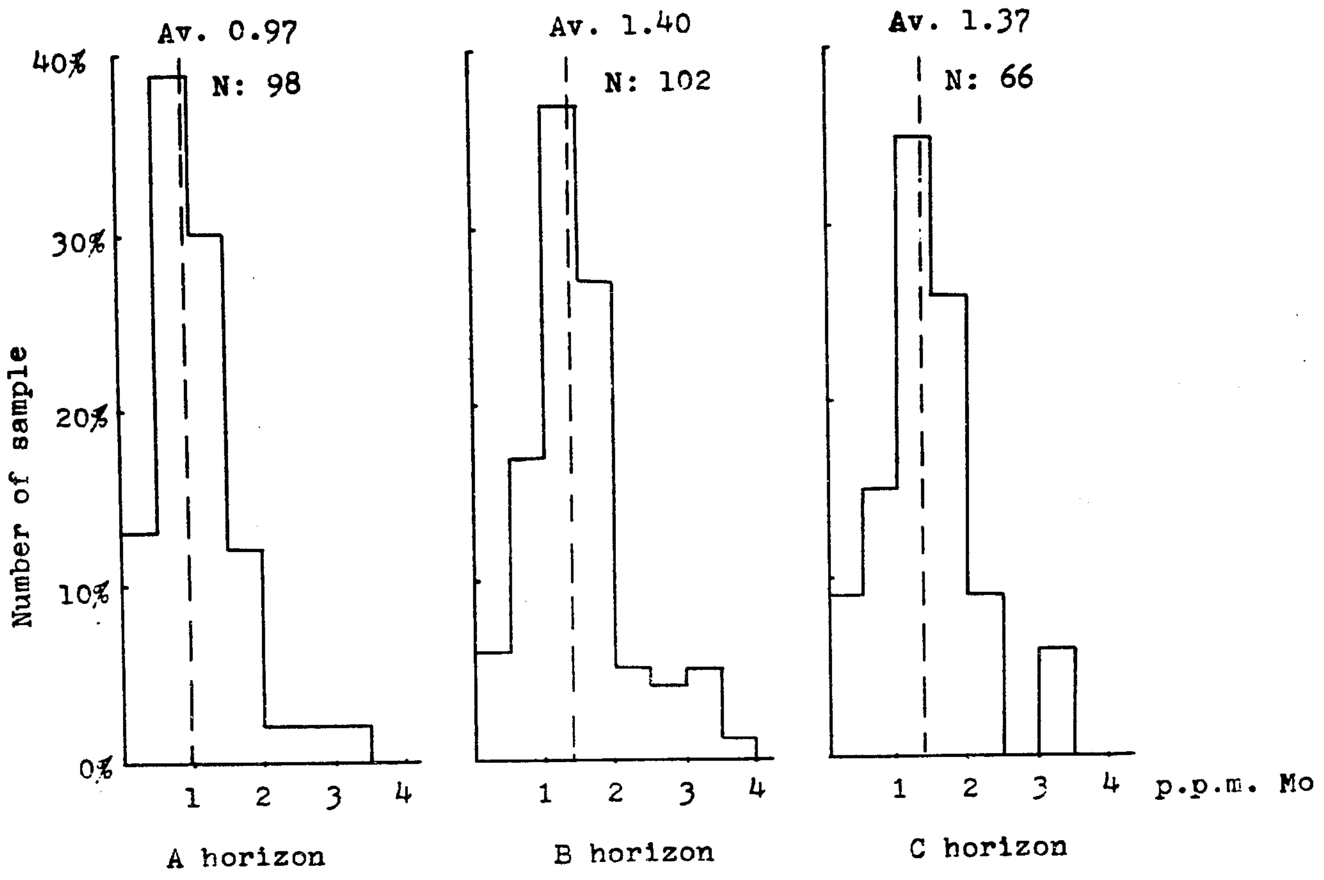


FIGURE 8. Molybdenum distribution in soil horizons.

normal soil profiles of the district is as follows : 16% in the A horizons; 46% in the B horizons; and 38% in the C horizons. Soils developed over mineralized areas and the one which gave an abnormal content are not included in the computations.

Higher than normal molybdenum contents were obtained from profile BH-5084 and a group of soils over the Brunswick No. 6 and Sturgeon River deposits. Analysis of soils developed over the Nigadoo sulphide deposit gave rather erratic results, with some high and some low values. The average is about the same as for the normal soil of the district. Despite the high molybdenum content in the sulphides of the New Larder "U" deposit, the soils from this area gave the lowest average value. The following is a list of the molybdenum contents and pH of the "abnormal" soils (see also Figure 12).

Table 10

<u>Average Molybdenum Content and pH of "Abnormal" Soils from the Bathurst District</u>

Location of soil samples	Molybdenum in p.p.m.	pH value	
		Range	Average
BH-5084 - Upper Rose-hill road	8.1	6.0 - 6.5	6.3
Brunswick No. 6	5.4	3.9 - 6.1	4.9
New Larder "U"	1.1	4.9 - 7.0	5.8
Sturgeon River	1.9	5.0 - 6.2	5.5
Nigadoo	1.2	4.8 - 7.6	6.1

Nature of Occurrence of Molybdenum and Discussion

Our knowledge of the nature of molybdenum in different horizons of soil profiles is uncertain. Most soil scientists are concerned mainly with the availability of the element and the factors and effects of this on plant nutrition (see Appendix I - Molybdenum in Soil and also the Biogeochemistry of Molybdenum). From the limited information available, it is generally thought that molybdenum is concentrated in the B horizons of normal soils. However, there are indications that it accumulates in the humic and C horizons as well.

In the zone of weathering, molybdenum is present in its hexavalent state, probably as MoO_4^{-2}, which forms readily soluble complex molybdates with Na, K, or Mg and less soluble ones with Ca, Pb, Fe, or Al. The process by which molybdenum is concentrated in the various constituents of soil is mainly due to adsorption of molybdates by sesquioxides and clay minerals as shown by Barshad (1951) and Jones (1957). The effectiveness of the various adsorbents according to the experiments by Jones (1957) follows the order : hydrous ferric oxide $>$ aluminum oxide $>$ halloysite $>$ nontronite $>$ kaolinite. The pH of the soil and the availability of molybdenum in the environment decide the amount of sorption. As the pH increases, more molybdenum is adsorbed, and the reverse is so when the pH decreases. Hence in an alkaline soil more of the element present will be available for plant nutrition. These findings are significant in explaining some of the peculiarities found in the soils of the Bathurst district.

The results of the soil analysis of the district indicates that, in most cases the highest concentration of molybdenum in the soil profiles is found in the B and C horizons (84%), with B having the highest percentage. The remaining 16% of the cases favor the A horizons, of which 12% are in the organic layers (A_0 and A_{00}). The pH-Mo concentration graphs of 24 complete soil profiles*, as shown in Figure 9, indicate the following:

Graph 1. Except for two values, this graph suggests that the accumulation of molybdenum in the A_0 and the A_{00} horizons increases with increasing pH.

Graph 2. A similar tendency to that in Graph 1 can be observed for the A_2 horizons, although the points are somewhat more scattered.

Graph 3. For the B_1 and B_2 horizons an inverse relation between the pH and molybdenum content seems to hold.

Graph 4. For the C horizons the relationships are similar to those in Graph 3 but more pronounced.

The tendencies illustrated in Graphs 3 and 4 can be explained as follows. As the pH of the soil decreases, the amount of molybdenum fixed by sesquioxides and clay minerals increases. The differences found in the B and C horizons are probably related to the amount of adsorbents present (see Figure 11 on the relation of the Mo and Fe contents in the different soil horizons).

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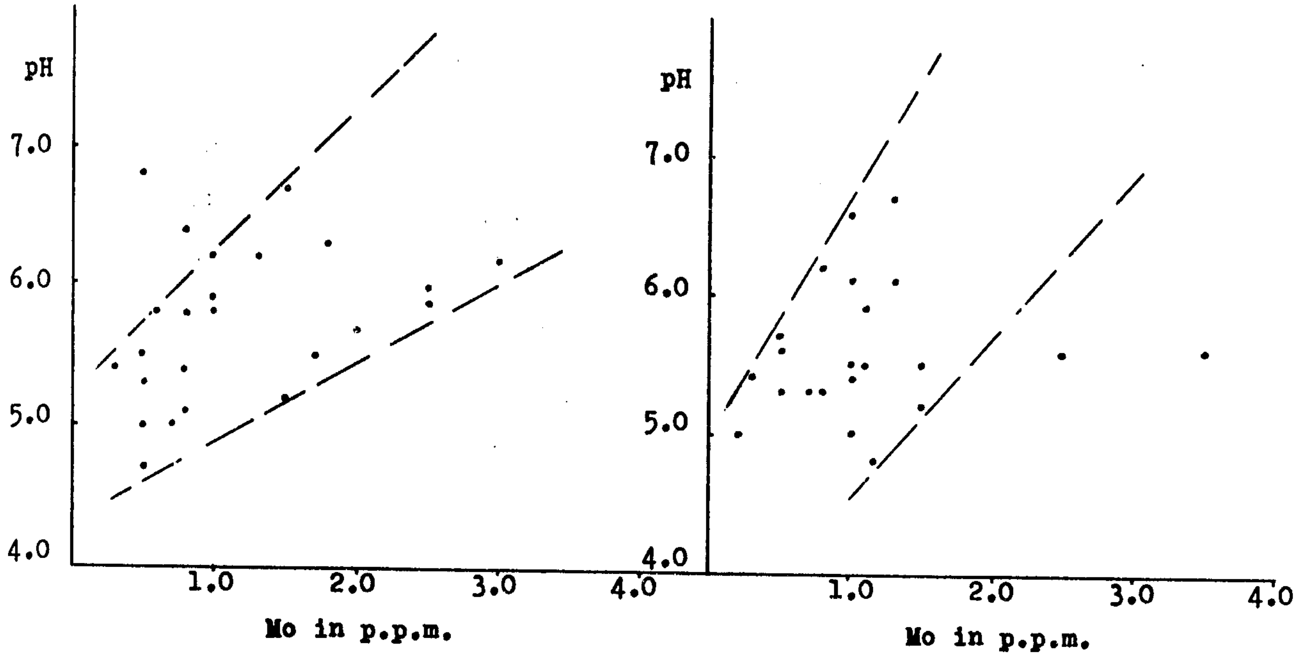
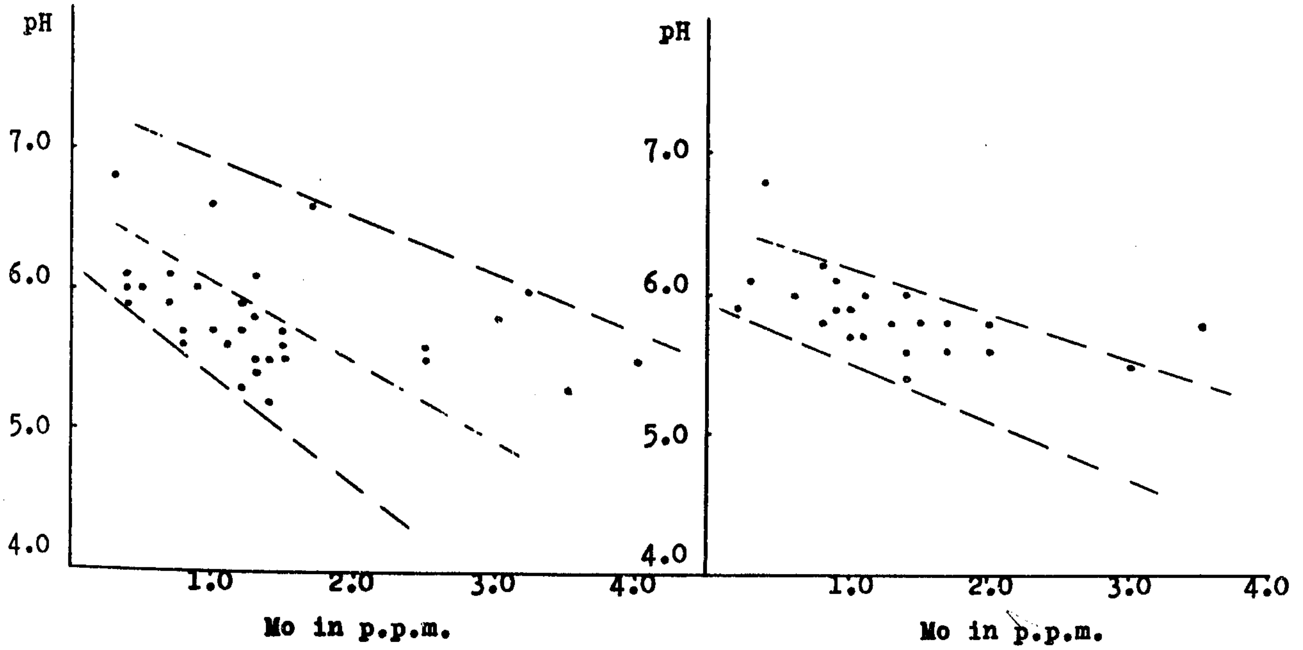
* Soil profiles marked with asterisk sign in Appendix II



Graph 1. For $A_0 + A_{00}$ horizons

Graph 2. For A_2 horizons



Graph 3. For $B_1 + B_2$ horizons

Graph 4. For C horizons

FIGURE 9. pH - Mo concentration diagrams for 24 soil profiles.

Where molybdenum occurs in some abundance in the A_0 and A_{00} horizons of the soil profiles, it probably occurs as a compound of the soil organic matter. Plants are known concentrators of the element and are often enriched much in excess of that present in the soil substrate. Increase in the soil pH increases the available molybdenum taken up by the vegetation. Hence the greater the pH the more molybdenum that will be taken up by the vegetation. On the death of the plants they accumulate in the A_0 and A_{00} horizons and contribute their molybdenum content to these horizons.

The erratic values found are thought to be due mainly to a variation in the parent materials, the effects of glaciation, and the degree of maturity attained by the soil.

The relation of molybdenum to the major and other trace constituents of soils of the district is presented in Figures 10 and 11. Of particular interest is the parallel behaviour of Mo, Zn, Fe, and Mn. This behaviour would seem to be related to the fixation of molybdenum and zinc by the colloidal hydrated oxides of iron and manganese in the soil.

Geological Control

The geological control of molybdenum concentration in the soil is illustrated in Figure 13. As stated earlier, the molybdenum content in the various types of rocks of the district do not vary greatly. However, slight variations can be detected. The area south of the Rocky Brook - Millstream "Break", which is underlain by rocks of the Tetagouche Group and a variety of basic intrusives, with one exception, is

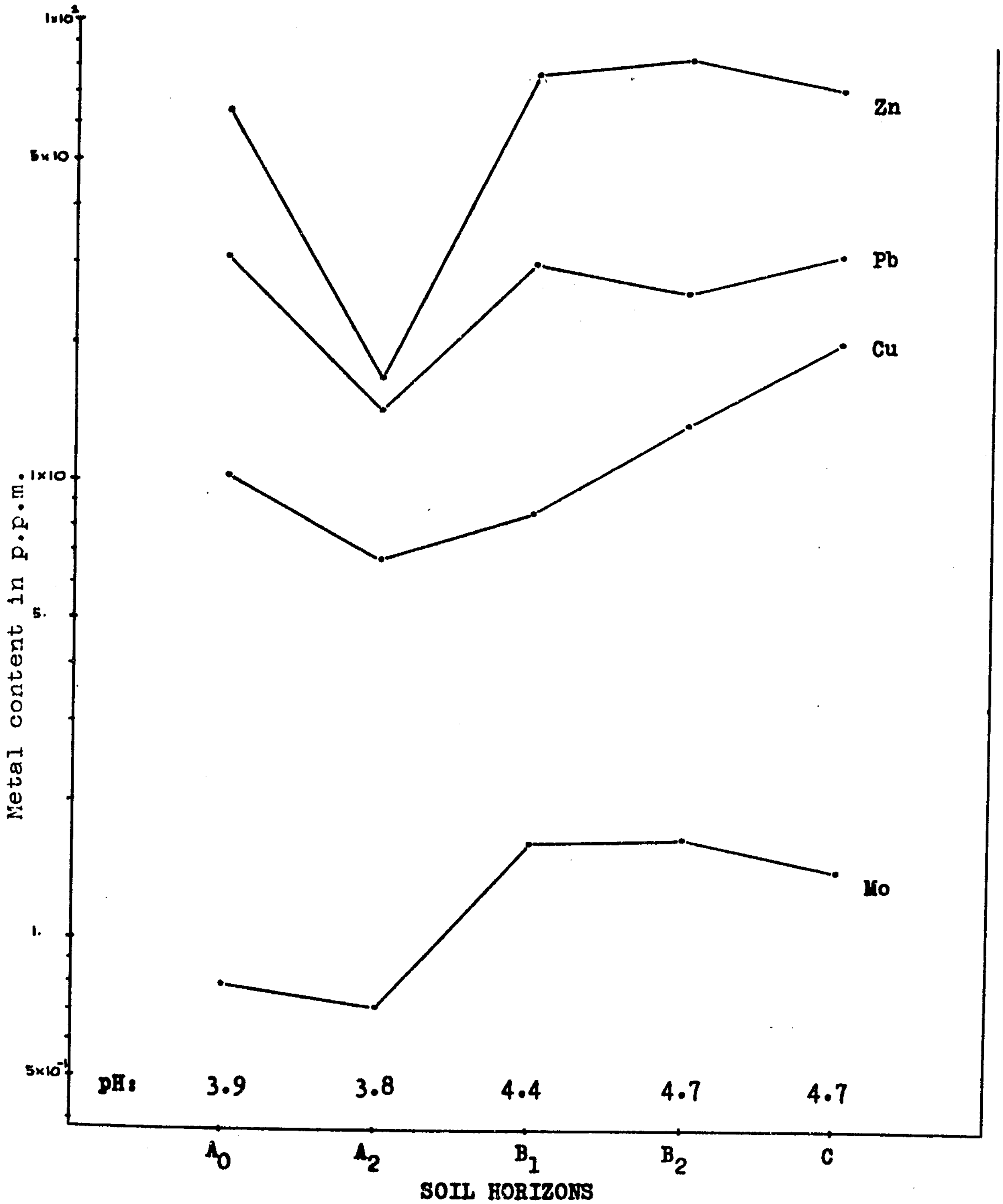


FIGURE 10. **Correlation diagram for Mo-Zn-Pb-Cu contents and pH in 10 soil profiles, metal contents are plotted on a logarithmic scale.**

(Complete and incomplete soil profiles numbered: BH-1848, -1850, -1851, -1852, -1856, -1857, -1861, -1862, -1863, -1864, -1865 are used for the construction of the diagram)

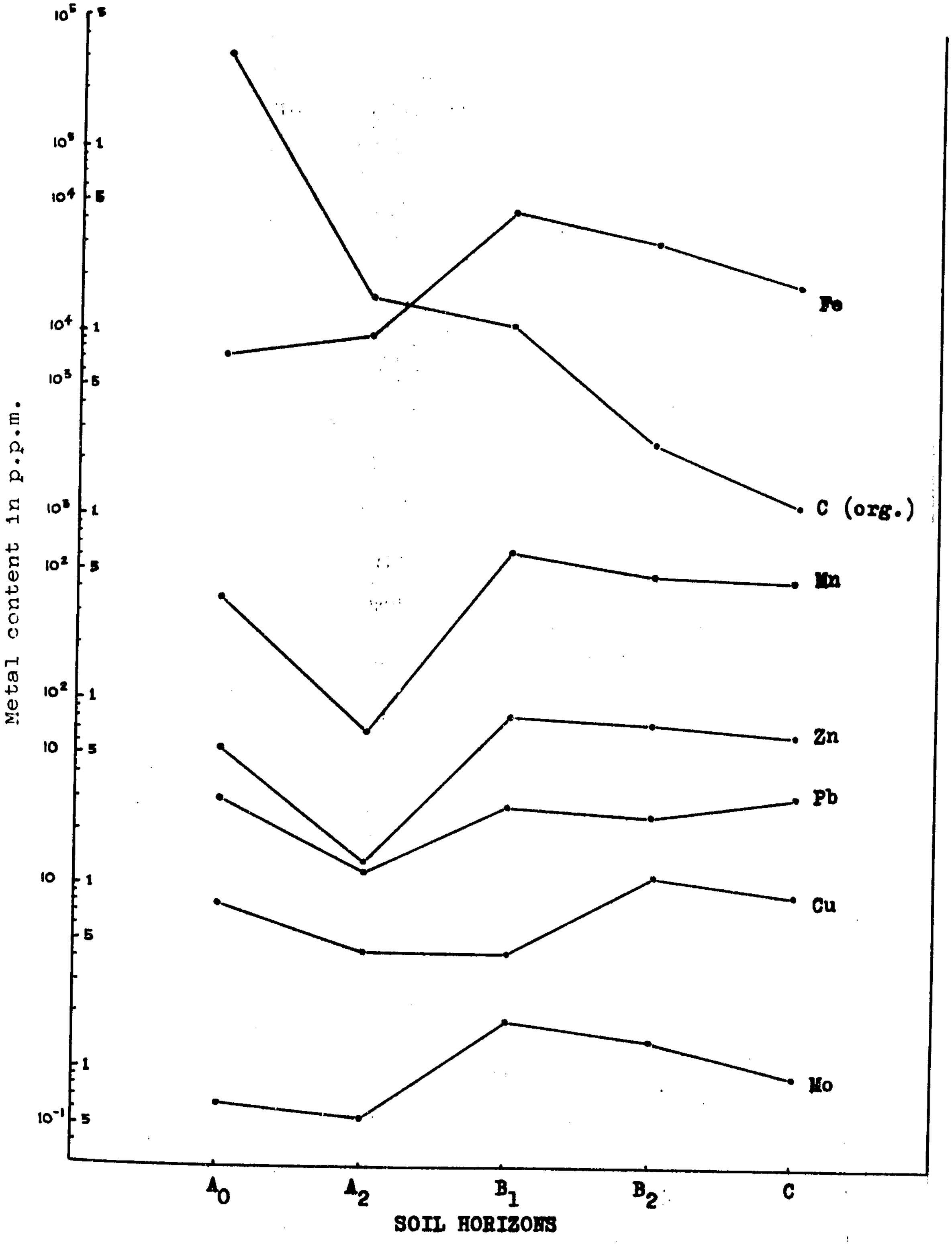


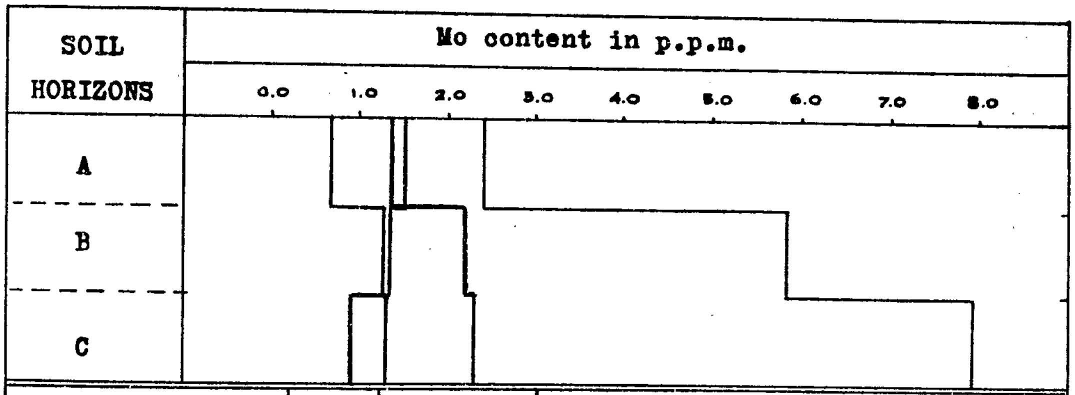
FIGURE 11. Correlation diagram for Fe-C-Mn-Zn-Pb-Cu-Mo contents in 4 soil profiles, metal contents are plotted on a logarithmic scale.

(Complete and incomplete soil profiles numbered: BH-1851, -1852, -1862, -1864 are used for the construction of the diagram) characterized by values ranging from 0.8 p.p.m. to 1.3 p.p.m. molybdenum. The soils developed over the Silurian rocks gave lower values ranging from 0.3 p.p.m. to 1.0 p.p.m. molybdenum. The highest molybdenum values within the area are concentrated in three zones - along the Rocky Brook - Millstream River fault system, over the Nicholas Dénys granite, and in the area northwest of this granitic body. In the first case the high values probably reflect the numerous deposits that occur along the fault. In the second the highest values are related to molybdenite-bearing zones known to occur in the granite. In the third the slightly anomalous values may be due to glacial transport of molybdenum-bearing till from the granitic area.

Profile BH-5084 contains from 2.5 p.p.m. to 19.0 p.p.m. molybdenum with an average content of 8.1 p.p.m. This anomaly appears to be related to the manganese oxide coating on the soil particles. In Table 5 it can be seen that the Tetagouche Falls manganite is also high in molybdenum (average: 12 p.p.m.). The local residents of the area, report that there is a similar manganite occurrence in red slate on the river bank, upstream from where this profile was obtained. It should be also noted that this soil profile was developed on the flood plain material of this river.

The soils overlying the polymetallic sulphide deposits do not always have high molybdenum values. This is probably due to the fact that some sulphide bodies are low in molybdenum and also that some are more deeply buried than others. The molybdenum content in the soil profiles over most deposits,

FIGURE 12. Molybdenum distribution in soil profiles over sulphide deposits.



Sulphide deposit		Number of profiles	Content (range in p.p.m.)		
			A horizons	B horizons	C horizons
Brunswick No. 6	——	6	0.5 - 6.0	2.0 - 15.0	3.5 - 18.0
New Larder "U"	——	6	0.2 - 1.1	0.5 - 1.8	1.0 - 2.0
Sturgeon River	——	8	0.2 - 7.0	1.0 - 4.0	1.0 - 3.8
Nigadoo	——	17	0.0 - 14.0	0.5 - 2.5	0.5 - 2.5

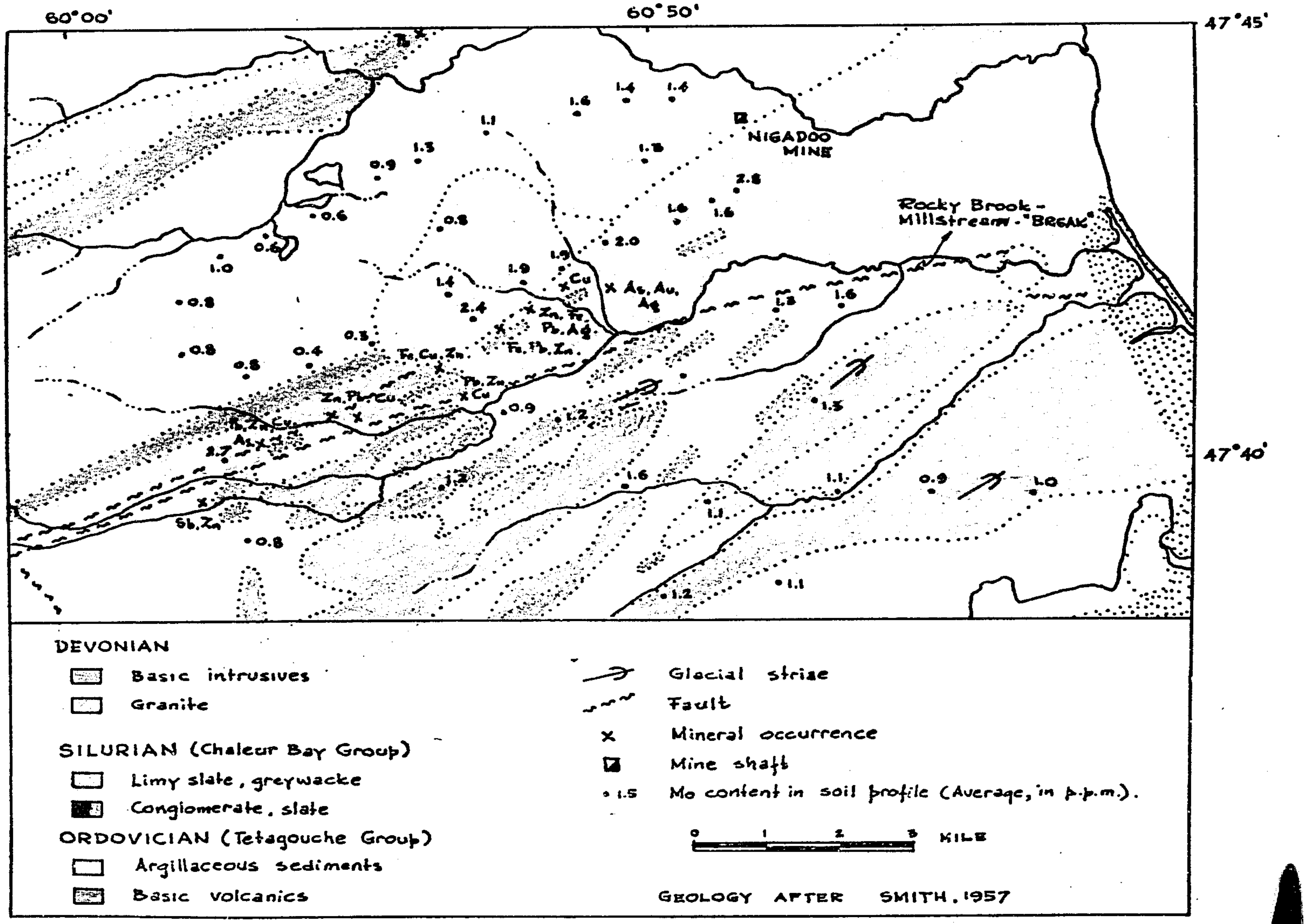


FIGURE 13. Molybdenum content in soils in the vicinity of the Nicholas Denys Granite.

the Nigadoo excluded, increases downward with the C horizons being the richest. Over the Nigadoo deposit and in its vicinity this tendency is reversed. There, the A horizons have the most molybdenum, and there is a decrease downward toward the C horizons (Figure 12). This discrepancy may be explained by the differences in the pH of the soils. Having an average pH of 6.1 (see Table 10), the soils of the Nigadoo Mine area would permit more molybdenum to be taken up by plants which on their death would enrich the upper organic layers of the profiles, a condition that obtains in the area.

CHAPTER VII

GEOCHEMICAL PROSPECTING FOR MOLYBDENUM

General Statement

In the area investigated, numerous large and small sulphide deposits are known, and among these are molybdenite occurrences in the Bathurst granite batholith and Nicholas Dénys area. This offers an ideal situation for a trial study of the application of stream sediment methods using molybdenum as an indicator both for molybdenum deposits and polymetallic sulphide deposits.

The results of the investigation of the geochemistry of molybdenum in the various earth materials of the district, would also appear to be of considerable assistance in geochemical exploration for molybdenum (see Figure 17).

Lithogeochemical Prospecting

Molybdenum analysis of 44 samples of the Bathurst granite turned up 4 samples whose contents equal or are higher than 5.0 p.p.m. Of these, two were collected in the vicinity of known molybdenite occurrences. The other two are probably also indicative of molybdenite in the rocks. It would seem, therefore, that a random geochemical sampling of granites can be used effectively in deciding whether the granites are molybdenum-bearing or not. Furthermore if the samples are taken on a close grid it seems logical to expect that molybdenum-bearing zones can be outlined.

A comparison of the frequency distribution diagrams for molybdenum in granitic stocks is also of considerable help (Figure 3). Thus the diagrams for the Bathurst granite and Nicholas Dénys granite stock show similar distributions. Since it is known that the Bathurst granite contains molybdenite one could predict that the Nicholas Dénys granite was likewise molybdenum-bearing. Such has proved to be the case.

The lithogeochemical method has an advantage, namely that the sampling can be done while doing geological mapping. The results of a lithogeochemical survey should be regarded, however, as preliminary in nature. Where warranted more detailed survey should be done during the follow-up stage of exploration.

Pedogeochemical Prospecting

The geochemistry of molybdenum in the soils is discussed in Chapter VI. There it was shown that the soils over polymetallic deposits are not always high in molybdenum, and it is doubtful if some of the deposits are reflected by abnormal molybdenum contents in the soil. However, where molybdenite is present in deposits as in the Nicholas Dénys granite higher than average amounts of molybdenum are present in the soil (Figure 16). From this it is logical to assume that zones containing molybdenite can be outlined by soil analysis using molybdenum as an indicator.

As shown in Figures 10 and 11, the content of molybdenum, zinc, lead, copper, and other metals varies somewhat in the different soil horizons. Hence consistency in the sampling of horizons for the different elements is important. For Mo, Zn, and Pb in the podzolic soils of the district the B horizon is preferable. For Cu, it is advisable to sample the lower part of the B and C horizons.

Stream Sediment Sampling

Millstream River System

The system was sampled in 42 places, and the results of analysis for Mo, Zn, Cu, and Pb are shown on Map 2 (in pocket) together with the locations of the known mineral occurrences. The normal background in the area is considered to be : Mo - 1.5 p.p.m. ; Zn - 170 p.p.m. ; Cu - 15 p.p.m. ; and Pb - 25 p.p.m. Assuming these background values a number of areas with higher than normal values can be outlined. These, in general, are related to the known mineral occurrences. However, 4 new areas of interest which are not related to the presently known deposits are outlined on Map 2. These are numbered 1 to 4 and may be described as follows :

1. Higher than normal molybdenum, zinc, lead, and copper values occur in this area. One sample contained up to 12 p.p.m. tungsten. Recent drilling in the area revealed minor molybdenite and other sulphides in the granite.
2. Slightly higher than normal copper values occur in this area.
3. Higher than normal contents of molybdenum are present in this area. Recent drilling in the area

proved the existence of a garnet-diopside skarn with molybdenite and minor scheelite.

4. Slightly higher than normal molybdenum and lead contents occur in this area.

All of these anomalies would seem to call for follow up surveys to ascertain the possibility of the occurrence of hidden molybdenum and polymetallic deposits.

From this survey, it can be concluded that almost all molybdenum values higher than 2.0 p.p.m. correlate well with anomalous values of other metals. It would seem, therefore, that they reflect the presence of molybdenum-bearing polymetallic sulphide deposits. In some cases, however, higher than normal molybdenum contents are not accompanied by higher values of other metals as in the areas of interest 1 and 3. These molybdenum values are generally higher than that of the first group and probably reflect the presence of molybdenum occurrences with few or no zinc, copper, and lead minerals.

Stream Systems Draining the Bathurst Granite

The results of a stream sediment survey over the Bathurst granite batholith are presented in Figure 14 for Mo, and in Figure 15 for Zn, Pb, and Cu. It will be noted that there is a marked difference between the values for zinc and copper in the stream sediments over the granite body and those over its enclosing rocks. Hence, the normal background of these two elements in the area is more or less arbitrary. It is felt however, that values over 200 p.p.m. Zn and 20 p.p.m. Cu are anomalous. The normal background for Mo is 2.0 p.p.m.

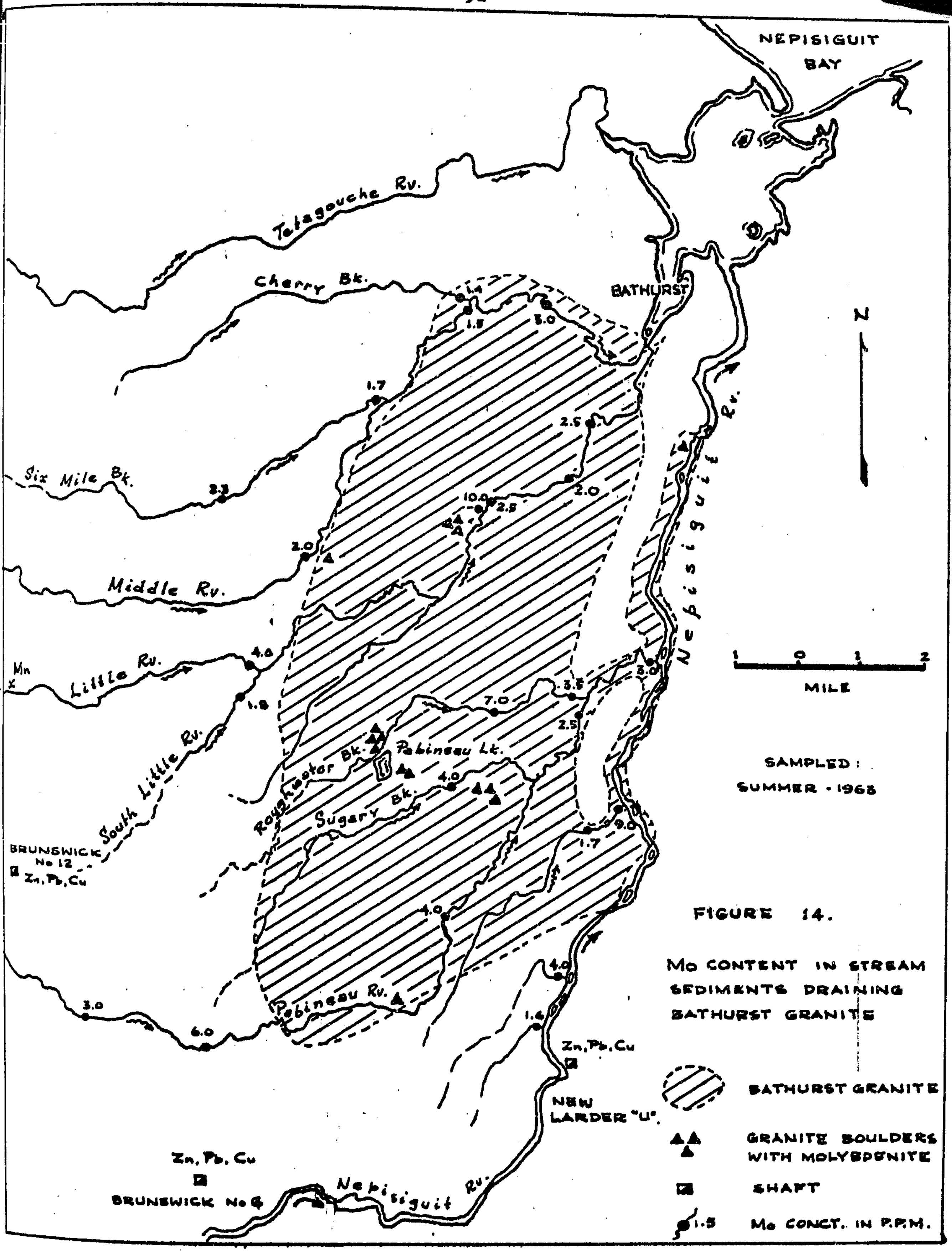


FIGURE 14.

Mo CONTENT IN STREAM SEDIMENTS DRAINING BATHURST GRANITE

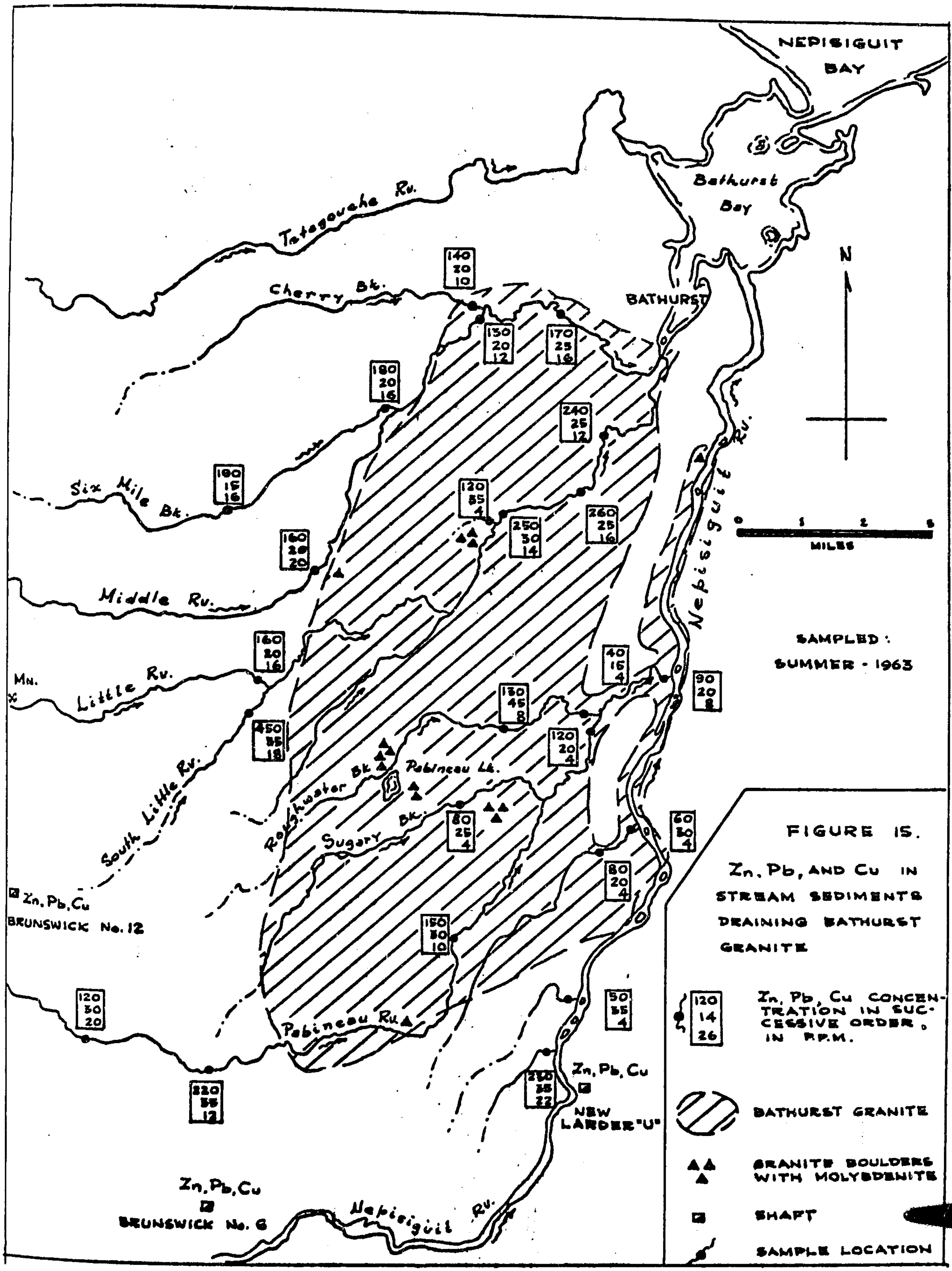


FIGURE 15.

Zn, Pb, AND Cu IN STREAM SEDIMENTS DRAINING BATHURST GRANITE and for Pb, 25 p.p.m.

From this survey, it is clear that most molybdenum values higher than the normal background are associated with known occurrences of molybdenite. Some coincide with higher than normal zinc values, and hence are probably related to polymetallic occurrences. The high molybdenum content obtained from the sediment of Little River is thought to be related to manganese which appears in quantity in a manganese bog upstream. One stream sediment sample from a tributary of Nepisiguit River contained 9.0 p.p.m. Mo. Up to the present the cause of this anomalous value is unknown.

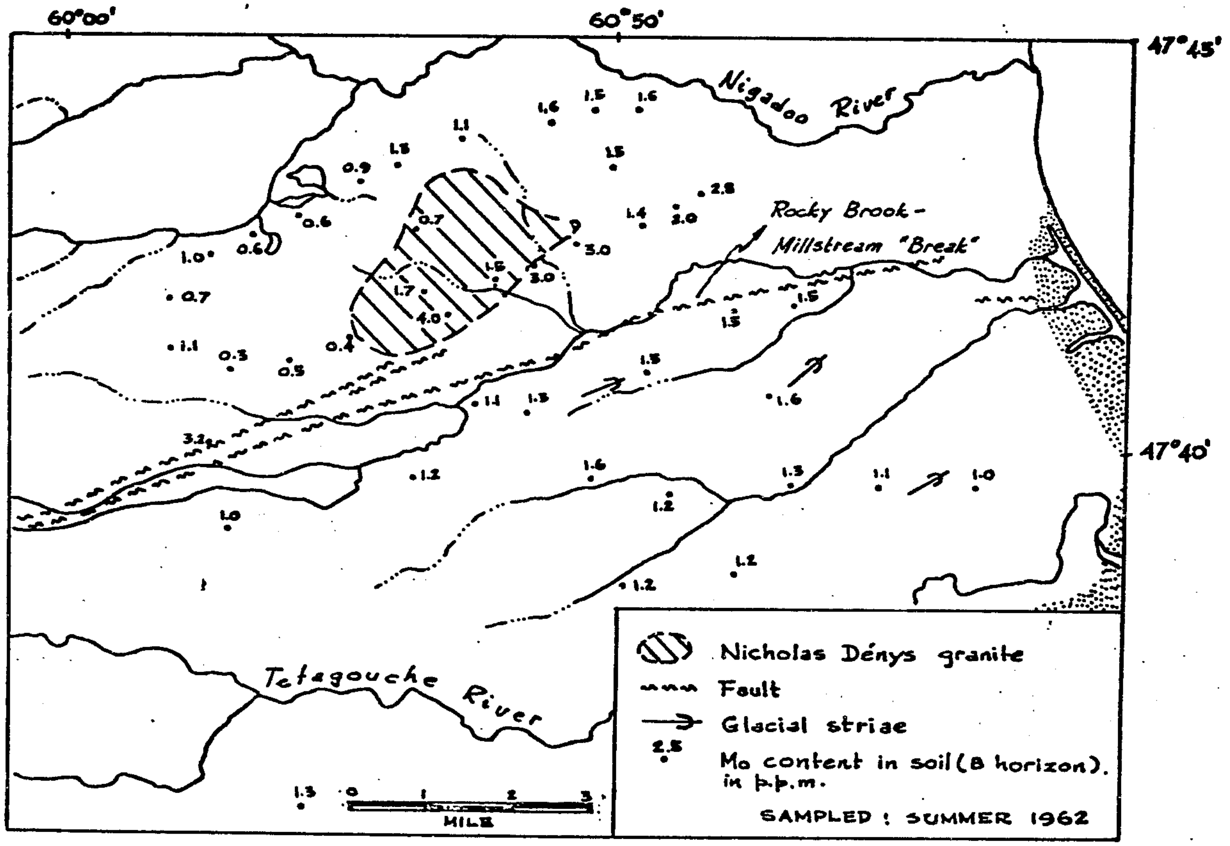


FIGURE 16. Molybdenum content in soils in the vicinity of the Nicholas Denys granite.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

The different types of earth materials in the Bathurst district were sampled and analyzed for their molybdenum, as well as other elemental contents. These samples, depending on their bulk chemical composition, were fused with either potassium pyrosulphate or a mixture of sodium carbonate, sodium chloride, and potassium nitrate. The melt was then leached with either HCl solution or water, and the molybdenum in the resulting solution was reacted with potassium thiocyanate in an acidic solution in the presence of a reducing reagent (SnCl).

The results of the study on the geochemistry of molybdenum in the Bathurst district is diagrammatically summarized in Figure 17. Of notable interest are the following points :

1. The molybdenum content in the rocks of the Tetagouche Group, the Chaleur Bay Group, and the Pennsylvanian sandstones and conglomerates ranges from 0.3 to 3.0 p.p.m. The average for the argillaceous sediments is generally higher than that for sandstones and conglomerates. High molybdenum contents are related to the presence of disseminated sulphides, and high carbon and manganese contents.
2. Four black schists of the Tetagouche Group contained from 1.5 to 15.0 p.p.m. molybdenum with an average of 6.5 p.p.m. The molybdenum content of these rocks is proportional to the sulphur and total carbon contents. This suggests that the molybdenum in the rocks probably originated by two

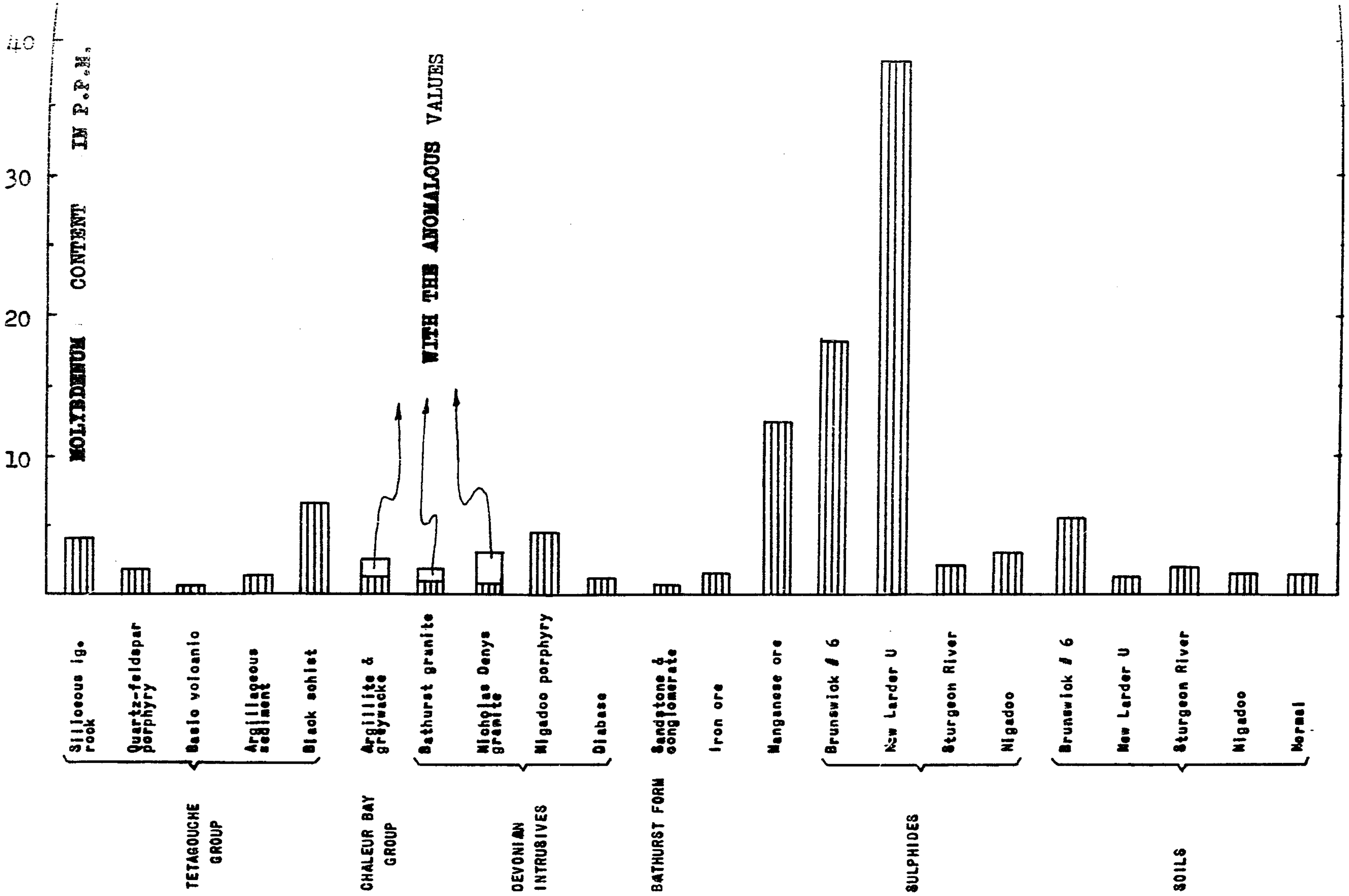


FIGURE 17. GENERAL DISTRIBUTION OF MOLYBDENUM IN THE VARIOUS EARTH MATERIAL OF BATHURST DISTRICT, N. B.

agencies - organisms which on their death contributed their molybdenum to the sediments and by coprecipitation processes during the formation of iron sulphides.

3. An acid volcanic rock of the Tetagouche Group contained 4.0 p.p.m. molybdenum which is higher than the average for the rocks of the district. This is thought to be due to the presence of disseminated sulphides in the acid rock.
4. The abundance and the pattern of distribution of molybdenum in the Bathurst batholith and the Nicholas Dénys granitic stock are similar. The average molybdenum content of these granitic rocks, excluding the anomalous values, is 0.7 p.p.m.
5. The basic intrusives in the northern part of the district contained an average of 1.0 p.p.m. molybdenum, a value higher than that of the granitic rocks.
6. The Nigadoo quartz-feldspar porphyry, which forms the wall rocks of the Nigadoo sulphide deposit in places, contained abnormally high contents of Mo, Zn, Cu, Pb, As, and Sb. This abnormality is probably due to the presence of disseminated sulphides of some of these elements, such as sphalerite, galena, arsenopyrite, etc.
7. The iron formations of the Tetagouche Group contained normal amounts of molybdenum, whereas the manganese ores in the group have an average molybdenum content of 12.0 p.p.m.
8. The average molybdenum content of the sulphide ores of the Brunswick No. 6, New Larder "U", Sturgeon River, and Nigadoo deposits are - 12.2 p.p.m. ; 38.2 p.p.m. ; 2.0 p.p.m. ; and 2.8 p.p.m. respectively. The molybdenum content in the

oxidized zones of the Brunswick No. 6 deposit reflects the amount of molybdenum in the ore. Binding of molybdenum by clay minerals, iron hydroxide, and secondary salts such as beudantite (in which MoO_4^{-2} replaces AsO_4^{-3} and/or SO_4^{-2}) explains the presence of molybdenum in the supergene zone of the Brunswick No. 6 deposit.

9. The normal podsols of the district contained an average of 1.2 p.p.m. molybdenum (from 266 analysis). In 84% of the soil profiles investigated the molybdenum content is highest in the B and C horizons, with B having the highest percentage frequency (46%). In a few cases, however, molybdenum is also concentrated in the organic layers of the soil profiles (12%).
10. The pH of the soil, the abundance of adsorbents in the different soil horizons (clay minerals and sesquioxides), soil maturity, and the availability of molybdenum in the environment are important factors which govern the amounts of molybdenum taken up by the different horizons of a soil profile.
11. In a number of cases higher than normal molybdenum contents in the soils were observed. These were found in soils developed over some of the sulphide deposits, in an area underlain by molybdenum-bearing granite, and in soils with high manganese contents.
12. The results of a stream sediment survey in part of the district proved successful in locating anomalous zones that are related to the presence of abnormal molybdenum concentrations in the underlying rock formations.

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APPENDIX I

GENERAL GEOCHEMISTRY OF MOLYBDENUM

THE GENERAL GEOCHEMISTRY OF MOLYBDENUM

FORWARD

The purpose of this paper is to provide a background knowledge of the geochemistry of molybdenum. In addition the writer has commented on the various data and opinions and added some of his own.

Molybdenum : Mo ; Atomic No. : 42 ; Atomic weight : 95.95 ; Sp. gr. : 10.28 ; M. P. : 2622° ± 10° C ; Valence : 2, 3, 4, 5, and 6

History

From Aristotle's time (350 B.C.) to the 17th century, the term molybdaena together with plumbago, graphite, and galena were used interchangeably for all naturally occurring minerals with a dark grey metallic lüster. Molybdaena is a latinized form derived from the Greek word "molybdos", meaning lead. In the seventeenth century it was recognized that molybdaena and graphite do not contain lead, and in 1778 C.W. Scheele showed that when molybdaena is heated with nitric acid a white residue, molybdenum trioxide, is formed. Graphite on the other hand remains unaltered under a similar treatment. By heating the white residue with charcoal, P.J. Hjelm in 1782 produced a metal which he called molybdenum. The term molybdenite was then applied to the metal sulphide by A. Brongniart.

Chemical Characteristic

Molybdenum together with chromium, and tungsten belong to subgroup VI B of the Periodic Table. This family of elements is characterized by variable valences, and they form numerous types of stable compounds. Of these the hexavalent compounds are the most stable. The trioxides of the family possess powerful acidic properties and yield well defined salts, namely, chromates, molybdates, and tungstates. Amphoteric properties are also characteristic of these oxides. The lower oxides of the group are however predominantly basic.

Molybdenum is a typical metallic element with many valences. It has six oxidation states, viz. 0, +2, +3, +4, +5, and +6. In nature molybdenum is known only in its tetravalent and hexavalent states, the first characterizes hypogene minerals and the second chiefly supergene minerals. Hexavalent molybdenum forms its most stable compounds with oxygen and fluorine. The principal stable pentavalent molybdenum compound is the chloride. MoS_2 and $MoBr_4$ are the stable sulphide and bromide with tetravalent molybdenum. The simple molybdate ion, MoO_4^{-2}, is generally believed to be the principal molybdenum species in alkaline solution. In acid solution condensation of molybdate ions results in the formation of polymolybdate ions. The following sequence has been proposed by Lindqvist (1951) :

$$MoO_4^{-2} \text{ ---- } Mo_7O_{24}^{-6} \text{ ---- } Mo_8O_{26}^{-4} \text{ ---- larger complexes.}$$

There are three kinds of known complex anions of molybdenum

Table 11

Molybdenum Isotopes

(Source : "Table of Isotopes", D. Strominger, et. al., 1958)

MASS number	ABUNDANCE in %	HALF LIFE s(econd), m(inute) h(our), d(ay), y(ear)
90	-	5.7 h
91	-	66 s --- 15.5 m
92	15.86	stable
93	-	6.8 h --- 10^4 y
94	9.12	stable
95	15.70	stable
96	16.50	stable
97	9.45	stable
98	23.75	stable
99	-	67 h
100	9.62	stable
101	-	14.6 m
102	-	12 m
105	-	2 m

(Killeffer and Linz, 1952). The isopolymolybdates are mostly acid varieties, whereas basic molybdates are rare. The heteropolyacids are highly polymerized complexes of molybdic acid with other acids. Typical are the heteropolyacids of molybdic with phosphoric and silicic acids. Complexes of molybdenum in one of its lower valence states with an element or radical having a pronounced tendency to form anions include the halogen, cyanide, and thiocyanate complexes of molybdenum. Other groups are the complexes or compounds with many organic substances, such as oxalic acid, citric acid, thioglycollic acid, phenyl hydrazine, catechol, EDTA, 1-10 phenantroline, etc.

Seven stable and seven radioactive isotopes of molybdenum and their relative abundances and half lives are listed in Table 11. An eighth stable isotope of relative natural abundance of 2 to 3 per cent has also been claimed (Northcott, 1956).

Molybdenum Compounds

According to Killeffer and Linz (1952), there are only two molybdenum oxides, MoO_2 and MoO_3, whose existence has been confirmed as chemical compounds. Molybdenum trioxide is one the most important of the molybdenum compounds. It behaves as the anhydrite of molybdic acid, and also possesses the power of combining with acids, not as a base, but in a complex way, forming complex heteropolyacids. As regards the familiar molybdenum blue, there has not been any definite answer about its actual nature. Its molybdenum - oxygen ratio suggests the combination of several molybdenum oxides, namely Mo_2O_5 and MoO_3.

overwhelming evidence indicating the colloidal nature of the blue material is also pointed out by Killeffer and Linz.

Although several hydroxides of molybdenum have been mentioned in the literature, only two, $Mo(OH)_3$ and $MoO(OH)_3$, have been isolated. These compounds are precipitated by adding a base to a molybdenum solution. Both hydroxides give up their water readily to form hydrous oxides. By heating, $Mo(OH)_3$ is oxidized and loses its water to form molybdenum trioxide, MoO_3 .

Molybdenum forms binary compounds with the halogens. In contact with water these yield oxy- and hydroxy-halides. Molybdenum hexafluoride, MoF_6, is the only fluoride known with certainty; other lower binary fluorides are also reported but lack confirmation. The well known chloride of molybdenum is the pentachloride, but $MoCl_4$, $MoCl_3$, and $MoCl_2$ are also said to exist. Bromine forms a stable compound with tetravalent molybdenum, whereas the lower bromides are considered to be less significant. There is no certainty as to the existence of a binary compound of molybdenum with iodine.

There are four known sulphides of molybdenum : sesquisulphide, disulphide, dimolybdenum pentasulphide, and trisulphide. Of these, molybdenum disulphide, molybdenite, is the most important, since it is the principal commercial source of molybdenum. Molybdenite, in general, is considered to be stable chemically, but on weathering (oxidation) hydrated molybdenum oxide is formed. Sulphur vapour does not react with MoS_2 to form higher sulphides. Aqua regia will dissolve the mineral, and both hot concentrated H_2SO_4 and HNO_3 will oxidize it to MoO_3 .

No carbonate of molybdenum has been reported.

Geochemical Characteristics

Early data on the crustal abundance of molybdenum varies. Clarke and Washington (1924), though among the earliest contributors to the data, gave a reasonable value of 1 p.p.m. Higher values were given by Noddack and Noddack (1931), who reported 14 p.p.m. for average igneous rocks. Von Hevesey and Hobbie (1933) gave 15 p.p.m. for igneous rocks, and Fersman proposed 10 p.p.m. for the earth's crust. More recent data indicate more consistent figures, though these are much lower than what were given in the past. In 1943, Sandell and Goldich gave 2.5 p.p.m. as the average for igneous rocks, and Vinogradov in 1949 suggested 3 p.p.m. as the figure for the earth's crust. The abundance figure given by Kuroda and Sandell (1954) for the lithosphere (1 ± 0.5 p.p.m.) is in agreement with Vinogradov, et.al. (1958) who quote a value of 1.5 p.p.m. The latter is the generally accepted average for the crustal abundance of molybdenum.

Molybdenum does not occur in the elemental form in nature, and its compounds are among the rarest constituents of the earth's crust. It is siderophilic in nature, with a strong chalcophilic tendency. As a micronutrient, molybdenum is considered essential for living organisms.

Table 12

Energetic Properties of Molybdenum and Common Associated Elements

Source: Green, Jack, 1959, Geochemical Table of the Elements for 1959, Geol. Soc. Am. Bull. Vol. 70, pp. 1127 - 1184

Property Outer electron configuration		Molybdenum (42) $4d^5$ $5s^1$	Rhenium (75) $5d^5$ $6s^2$	Tungsten (74) $5d^4$ $6s^2$	Uranium (92) $5f^3$ $6d^1$ $7s^2$	Titanium (22) $3d^2$ $4s^2$	Aluminum (13) $3s^2$ $3p^1$	Iron (26) $3d^6$ $4s^2$	Silicon (14) $3s^2$ $3p^2$
Ionization potential						Ti^{+3} - 27.6	Al^{+3} - 28.31	Fe^{+2} - 16.24	
		Mo^{+6} - 70	Re^{+7} - 79(?)	W^{+6} - 61		Ti^{+4} - 44.66			Si^{+4} - 44.95
Electronegativity (kilocalories/gram-atom)						Ti^{+3} - 230	- 220	- 245	- 270
		Mo^{+6} - 275	Re^{+7} - 260	W^{+6} - 235	U^{+4} - 190	Ti^{+4} - 260			
Lattice Energy Coefficient			Re^{+4} - 1850			Ti^{+3} - 1160	Al^{+3} - 1280	Fe^{+2} - 580	
		Mo^{+4} - 2170	Re^{+6} - 4500?	W^{+4} - 1684?	U^{+4} - 1800	Ti^{+4} - 2150		Fe^{+3} - 1280	Si^{+4} - 2500
		Mo^{+6} - 4930	Re^{+7} - 6380?	W^{+6} - 4470	U^{+6} - 4250				
Atomic radius, Å (coordination in brackets)				1.26(4)	1.43(4)				1.17(4)
		1.36(8)	1.33(8)	1.31(8)		1.41(8)	1.39(8)	1.24(8)	1.26(8)
		1.40(12)	1.37(12)	1.41(12)		1.45(12)	1.43(12)	1.27(12)	1.30(12)
Ionic radius, Å (coordination in brackets)	M^{-4}								1.98
	M^{+2}							.74(6)	
	M^{+3}				1.12(6);1.16(8)	.76(6)	.49(4);.51(6)	.64(6)	
	M^{+4}	.70(6)	.72(6)	.70(6)	.97(6);1.01(8)	.68(6)			.40(4)
	M^{+5}								
	M^{+6}	.59(4);.62(6)		.59(4);.62(6)	.80(6)				
	M^{+7}		.53(4);.56(6)						
Miscellaneous radii, Å	Oxide	Mo^{+4} - 1.00		W^{+4} - .97	U^{+4} - 1.15	Ti^{+3} - 1.03	Al^{+3} - .85	Fe^{+2} - .90	Si^{+4} - .80
		Mo^{+6} - 1.03	Re^{+7} - .96	W^{+6} - .97		Ti^{+4} - 1.06		Fe^{+3} - .92	
	Sulphide	Mo^{+4} - 1.25						Fe^{+2} -1.10	
	Fluoride						Al^{+3} - .68	Fe^{+2} - .81	
								Fe^{+3} - .81	Si^{+4} - .65

Table 12 lists the energetic properties of molybdenum and other elements with which it is closely associated in nature. In the earth, as already mentioned earlier, molybdenum is generally found in the 4 and 6 oxidation states. The first is typical of hypogene minerals and the latter of minerals formed under weathering conditions or in the zone of hyper-genesis.

It is generally believed, based on its energetic properties (see Table 12), that molybdenum substitutes for Ti^{+4} in the mineral lattices of ilmenite, titano-magnetite, and sphene, for Fe^{+3} in magnetite, biotite, amphiboles, and pyroxenes, and for Al^{+3} and Si^{+4} in feldspars and other alumino silicates. It has also been considered that the element may substitute for magnesium. Isomorphic relationships between molybdenite and other sulphides explains the noticeable amounts in selenolinneite (5%) and colusite (8.8%) (Fersman, 1939). Rhenium is commonly found in the mineral molybdenite, where it replaces molybdenum. This is verified by the experiments of Noddack and Noddack (1931) who found unlimited isomorphism between MoS_2 and ReS_2 . Other elements which have been mentioned as being commonly associated with molybdenum are the remaining elements in the VI B subgroup of the Periodic Table. Thus, it is thought that molybdenum may substitute for chromium in mariposite and for tungsten in scheelite (variety seyrigite).

Molybdenum Minerals

The principal minerals of molybdenum, as well as a number of other complex minerals containing relatively large

Table 13

Molybdenum-bearing Minerals

NAME	COMPOSITION	SOURCE
Molybdenite	MoS_2	1
Wulfenite	$PbMoO_4$	1
Powellite	$CaMoO_4$	1
Ferrimolybdite	$Fe_2(MoO_4)_3 \cdot n\ H_2O$	2
Lindgrenite	$Cu_3(MoO_4)_2(OH)_2$	1
Ilsemannite	$Mo_3O_8 \cdot n\ H_2O$ (?)	1
Jordisite	Colloidal MoS_2 or $MoO_3.SO_3.5H_2O$	1
Chillagite	Tungstenian wulfenite (?)	1
Eosite	Vanadian wulfenite (?)	1
Koechlinite	$(BiO)_2(MoO_4)$	1
Pateraite	Cobalt molybdate (?)	1
Achrematite	Mixture of mimetite & wulfenite (?)	1
Molybdo-sodalite	Sodalite containing ± 2.9 % MoO_3	3

1. Palace, C.; Berman, H. and Frondel, C. 1944, 1951, "Dana's System of Mineralogy", Vol. I and II.

2. Kerr, P.F.; Thomas, A.W. and Langer, A.M., 1963, "The nature and synthesis of Ferrimolybdite", The Am. Min. Vol. 48, pp. 14 - 32.

3. Hey, M.H., 1955, "An Index of Mineral Species and Varieties", Second Edition, London.

amounts of the element, are listed in Table 13 in the approximate order of their importance. Molybdenite and wulfenite are the only two which are of economic interest. The rest of the minerals listed in the table are rare, on account of their metastability and/or their occurrence only as secondary alteration products in molybdenum and polymetallic deposits.

In addition to the minerals mentioned above, molybdenum also occurs in various other minerals in trace amounts. Significant amounts have been reported in alkalic and calcic feldspars, biotites, amphiboles, pyroxenes, olivines, and especially in accessory minerals, namely ilmenite, magnetite, sphene, and zircon. A minute amount of molybdenum may also occur in quartz, although Studenikova <u>et. al</u>. (1957) report as much as 5.5 p.p.m. in this mineral. It should be noted that the amounts of molybdenum reported in any particular mineral seems to vary with the investigator. This makes any generalization about the distribution of molybdenum in minerals rather difficult (see Table 14).

To explain the present of molybdenum in the minerals mentioned above, it is generally suggested that molybdenum substitutes for trivalent aluminum, trivalent iron, tetravalent titanium, and possibly also for magnesium in the mineral lattices because of similar ionic radii (see Table 12). It may also substitute for silicon as a result of other energetic properties. (Kuroda and Sandell, 1954; Studenikova, <u>et. al</u>. 1957; Malyuga, 1958).

Table 14

Molybdenum in Other Minerals

MINERAL	ROCK TYPE	Mo content in p.p.m.		Reported by
		Range	Average	
Quartz	Granite (min)* Igneous rock	0.01 - 5.5 0.0 - 0.1	2.66 -	Studenikova, et.al.(1957) Kuroda & Sandell, (1954)
Feldspar	Acid intrusive Granite (min)* Igneous rock	- 1.2 - 22.5 0.3 - 2.5	0.5 7.5 0.98	Rabinovich, et.al. (1958) Studenikova, et.al.(1957) Kuroda & Sandell, (1954)
Biotite	Granite (min)* Igneous rock	1.8 - 5.8 -	3.3 3.1	Studenikova, et.al.(1957) Kuroda & Sandell, (1954)
Biotite + Hornblende	Acid intrusive	0.5 - 4.0	-	Rabinovich, et. al. (1958)
Pyroxene	Igneous rock Igneous rock	2. - 3. 0.1 - 0.5	- -	Wager & Mitchell, (1951) Kuroda & Sandell, (1954)
Olivine	Igneous rock	-	10.	Wager & Mitchell, (1951)
Accessory Minerals	Granite (min)*	9.63 - 49.2	18.05	Studenikova, et.al.(1957)
Ilmenite	Acid intrusive Igneous rock	trace - 328. -	- 3.	Rabinovich, et.al. (1958) Wager & Mitchell, (1951)
Magnetite	Acid intrusive Igneous rock	1. - 10. -	- 3.	Rabinovich, et.al. (1958) Wager & Mitchell, (1951)
Magnetite+ Ilmenite	Igneous rock	15. - 16.	-	Kuroda & Sandell, (1954)
Sphene	Acid intrusive Igneous rock	34. - 400. 20. - 40.	- -	Rabinovich, et.al. (1958) Nockolds & Mitchell,(1951
Zircon	Igneous rock	-	15.	Nockolds & Mitchell,(1951

* min = mineralized.

Another group of minerals in which molybdenum is usually enriched is the sulphides. Noddack and Noddack (1931) report an average value of 20 p.p.m. for primary sulphides (pyrrhotite, pyrite, pentlandite, and nickeliferous pyrite). Michalek (1958), in his investigation of the distribution of molybdenum in iron sulphide ores, gave the results given in Table 15.

Table 15

Molybdenum in Iron Sulphide Minerals (after Z. Michalek, 1958)

Mineral	Maximum Mo content in p.p.m.	Number of samples showing Mo content in p.p.m.								Number of analysis
		>1000	500 → 1000	100 → 499	50 → 99	20 → 49	10 → 19	1 → 9	1	
Pyrite	1664	1	-	5	2	6	18	44	1	77
Marcasite	54	-	-	-	1	3	4	14	1	23
Pyrrhotite	10	-	-	-	-	-	1	2	1	4
Arsenopyrite	10	-	-	-	-	-	1	4	2	7
Chalcopyrite	1	-	-	-	-	-	-	1	3	4

According to Michalek, there are two different types of pyrite : high temperature pyrite, characterized by its low molybdenum content averaging 2 p.p.m.; and low temperature pyrite having the highest concentration of molybdenum (exceeding 100 p.p.m.).

Additional data on the distribution of molybdenum in sulphide minerals is given by Fleischer (1955), as follows:

Mispickel (arsenopyrite)	60 p.p.m.
Pyrrhotite	20 and 40 p.p.m.
Pyrite	5 and 20 p.p.m.
Chalcopyrite	70 and 900 p.p.m.
Galena	20 p.p.m.

Grip (1951), from an investigation of the sulphide minerals in northern Sweden, gives the molybdenum contents of various sulphides as follows:

Copper rich pyrite	340 p.p.m.
Pyrite mineral	13 p.p.m.
Zinc mineral	8 p.p.m.

A number of minerals of sedimentary origin contain traces of molybdenum as follows: glauconite, with 3.5 p.p.m. Mo; bauxites, with values ranging from 2.0 to 15.0 p.p.m.; and unspecified amounts in some titaniferous iron ores and manganese ores of sedimentary origin.

Molybdenum in Igneous and Igneous type Rocks

The molybdenum content of igneous rocks are tabulated in Table 16. It will be noted that the values given by Vinogradov *et. al*. (1958) are slightly higher than those by Kuroda and Sandell (1954). Both, however, have the same elemental distribution pattern in the various type of rocks.

It is generally thought that the molybdenum content of igneous rocks, like that of tungsten, increases parallel with

Table 16

Molybdenum in Igneous Rocks

ROCK TYPE	No. of analysis	Mo content in p.p.m.		Reference
		Range	Average	
Ultramafic rocks	23 14	0.0 - 1.3 0.05 - 0.7	0.4 0.23	Kuroda & Sandell, (1954) Vinogradov, et.al.(1958)
Mafic rocks	24 11	- 0.78 - 4.4	0.7 2.2	Kuroda & Sandell, (1954) Vinogradov, et.al.(1958)
Gabbros	21	0.1 - 1.5	0.6	Kuroda & Sandell, (1954)
Basalts and diabases	10 37	- 0.2 - 3.1	1.0 1.0	Ishimori, (1951) Kuroda & Sandell, (1954)
Intermediate rocks	10 29 8	- 0.0 - 1.5 0.66 - 1.5	1.2 0.7 1.1	Ishimori, (1951) Kuroda & Sandell, (1954) Vinogradov, et.al.(1958)
Granitic rocks	10 74 8 -	- 0.1 - 6.7 0.95 - 2.3 0.5 - 3.0	3.3 1.1 1.6 -	Ishimori, (1951) Kuroda & Sandell, (1954) Vinogradov, et.al.(1958) Rabinovich, et.al.(1958)

Note-T.Ishimori's results are of Japanese volcanic rocks.

the SiO_2 content. Basalts and diabases do not appear to follow this rule and show a much higher content compared with the intermediate and even the acidic types of igneous rocks. Rabinovich et. al. (1958) investigated the Eastern Transbaikal intrusives and concluded that within the boundaries of every magmatic complex the younger rocks generally contain more molybdenum than the older ones. However, Studenikova et.al. (1957) indicate that the molybdenum content of acidic intrusives does not depend on their age.

As mentioned previously, the bulk of the molybdenum in igneous rocks is concentrated in feldspar, but there may also be significant amounts of the element in biotite and the various accessory minerals (ilmenite, magnetite, sphene and zircon). Contents as high as 400 p.p.m. in sphenes are reported by Rabinovich et. al. (1958). Traces of molybdenum may also be found in amphiboles, pyroxenes, olivines, and quartz.

In contrast to most trace elements in igneous rocks, molybdenum does not follow any major constituent closely in its distribution. It tends to concentrate in the late stage of a differentiating magma particularly in pegmatites and pneumatolitic deposits. Due to its high affinity for sulphur, molybdenum binds the available sulphur to form molybdenite. Replacement of trivalent iron, trivalent aluminum, and tetravalent titanium during the fractional crystallization process, explains the presence of traces of molybdenum in the minerals of igneous rocks.

Molybdenum in Sedimentary Rocks

The general abundance of molybdenum in sedimentary rocks as given by Vinogradov (1956), is 2 p.p.m., a value slightly higher than the average for igneous rocks.

Table 17 gives the distribution of molybdenum in the various types of sediments. Sandstones and carbonate rocks in contrast to shales, contain only minute amounts of the element. High contents of molybdenum are generally recorded for shales rich in organic matter and sulphides. Based on experiments, Korolev (1958) concluded that molybdenum enrichment in shales was the result of coprecipitation with finely dispersed iron sulphide - melnikovite in the form of a sorbed sulphide compound. He is also of the opinion, that an association between organic matter and the content of molybdenum is indirect. A direct precipitation of molybdenum sulphide can be expected where molybdenum-bearing solutions enter a reducing environment, such as in stagnant lakes and shallow seas, especially where muds and sapropelites were being deposited. The Permian Kupferschiefer of central Europe is considered to be one of the best examples of this mode of concentration. In these rocks the content of molybdenum ranges from 100 to 200 p.p.m. over great distances (Goldschmidt, 1954). Other types of sedimentary rocks may contain a considerable amount of molybdenum. Phosphate rocks, for instance, may contain up to 208 p.p.m. MoO_3 (samples from Wyoming), but in other case the MoO_3 content is only 1 or 2 p.p.m. (samples from Tennessee).

Coprecipitation of molybdenum with iron and especially

Table 17

Molybdenum in Sedimentary Rocks

ROCK TYPE	No. of analysis	Mo content in p.p.m.		Reference
		Range	Average	
Shale and clay	32	0.0 - 87	-	Kuroda & Sandell,(1954)
Shale, black	-	10. - 300	-	Krauskopf, (1955)
Shale, light grey	-	-	0.5	Kuroda & Sandell,(1954)
Shale, grey	10	-	2.9	Kuroda & Sandell,(1954)
Shale, dark grey	36	-	4.5	Kuroda & Sandell,(1954)
Sandstone and Arkose	6	0.0 - 1.6	0.75	Kuroda & Sandell,(1954)
Limestone and Dolomite	12	0.1 - 1.2	0.4	Kuroda & Sandell,(1954)
Cherts	7	0.0 - 0.9	0.23	Kuroda & Sandell,(1954)
Radiolarian chert	1	-	4.4	Cressman, (1962)
Bedded chert	9	Av.1.0;11.4;3.2	-	Cressman, (1962)
Nodular chert	7	- 3.4	2.4	Cressman, (1962)
Deep sea sediment	10	0.0 - 29.	9.0	Wedepohl, (1960)
"	-	-	45.0	Goldberg & Arrhenius, (1958)
"	6	2. - 5.	3.3	Kuroda & Sandell,(1954)
"	-	2. - 100.	-	Sugawara, *et.al*. (1961)
Phosphatic rock	-	2; 62;208	-	Robinson, (1948)
Asphalt and Petroleum ash	-	50. - 1500.	-	Krauskopf, (1955)

manganese hydroxides during the sedimentary process explains the high molybdenum contents of certain sedimentary manganese and iron deposits.

Molybdenum in Metamorphic Rocks

Data on the abundance of molybdenum in metamorphic rocks are scarce. In Table 18 are listed the molybdenum contents of various types of metamorphic rocks as reported by Kuroda and Sandell (1954). The metamorphic rock types are more consistent in their contents than are sedimentary rocks. Some contact metamorphic hornfels and skarns are greatly enriched in the element.

Analysis of rocks from the different metamorphic facies of the regionally metamorphosed Thomson Formation in eastern Minnesota, show that there is no apparent parallelism between the degree of metamorphism and molybdenum content (Kuroda and Sandell, 1954).

Table 18

Molybdenum in Metamorphic Rocks

Rock type	Number of analysis	Mo content in p.p.m.		Reference
		Range	Average	
Slate	7	0.2 - 1.7	0.6	Kuroda & Sandell, (1954)
Graywacke	1	-	0.4	
Quartzite	2	-	0.6	"
Graphitic gneiss	1	-	0.8	"
Granite gneiss	2	0.5 ; 1.0	-	"
Phyllite	2	0.2 ; 1.2	-	"
Schists	3	0.2; 0.3; 04	0.3	"
Hornfels	1		5	Nockolds & Mitchell,(1948)

From Table 18, it can be seen that the average content of molybdenum in metamorphic rocks is lower than that of both igneous and sedimentary rocks. Migration of the element during metamorphism, followed by concentration in zones of dilation may be the answer to the above discrepancy. On this theory Lombard (1958) postulated, that the molybdenum in deposits probably came from sedimentary rocks that were metamorphosed.

Molybdenum in Soils

Ordinary soils generally contain from 1 p.p.b. up to several p.p.m. molybdenum. The average value is thought to be about 2 p.p.m., which is slightly higher than that for rocks in general (Vinogradov, 1959).

The distribution of molybdenum in the soils of different regions of the world is generally considered to be uniform, although there are variations as shown in Table 19. These variations are thought to reflect differences in the content of the element in the various types of rocks underlying the soils.

The molybdenum distribution in soil profiles is not well known. Fixation of the element by organic matter (decayed plants) explains the high content in some humic horizons. Similarly the enrichment in the B horizon of certain podzolic soils, may result from fixation by iron and aluminum hydroxides. In some soils, however, an increase of molybdenum near the bottom of the profiles (C horizon) is often noted. Galego and Jolin (1959), from their study on the soils of Spain, state that high contents of molybdenum occur in horizons rich in

Table 19

Molybdenum in Soils

LOCATION	No. of analysis	Mo content in p.p.m.		Reference
		Range	Average	
California, U.S.	36	0.1 - 9.7	2.2	Barshad, (1948)
Wyoming, U.S.	8	0.08 - 20.0	6.0	Stanfield, (1935)
New Jersey, U.S.	18	0.8 - 3.3	1.99	Evans, <u>et. al</u>. (1951)
Hawaii, U.S.	79	7.9 - 73.8	25.8	Fujimoto & Sherman (1948)
Hawaii, U.S.	6	1.8 - 18.6	9.1	Edgington, ( )
Europe	20	4.3 - 69.0	27.8	Bertrand, (1940)
France	8	0.3 - 1.0	0.5	Edgington, ( )
Russia	52	1.0 - 12.0	2.6	Vinogradov & Vinogradova, (1946)
Aberdeenshire, (England)	161	1.0 - 20.	2.0	Swaine, (1955)
Scotland	-	0.0 - 2.0	1.0	Mitchell, (1948)
Ireland	-	-	2.0	Walsh, <u>et.al</u>. (1953)
Spain	54	0.08 - 3.0	1.01	Galego & Jolin (1959)
Italy	-	0.1 - 7.0	2.0	Giovonnini, (1954)
Argentina	238	0.2 - 24.0	2.0	Trelles & Amato, (1949)
New Zealand	20	0.7 - 6.9	1.7	Grigg, (1953)

organic matter, clay, iron, aluminum and manganese oxides.

A deficiency or a high concentration of molybdenum in soil can have a serious effect on the life processes of plants and animals (see Biogeochemistry).

On the nature of molybdenum in soils, Amin and Joham (1958) classified the available molybdenum as follows :

a) Water soluble molybdenum consisting largely of soluble salts of molybdenum that are available to plants.

b) Ammonium hydroxide soluble or readily complexible molybdenum which is not available as such but can become easily available by reacting with the cations present in the soil.

c) Oxidizable molybdenum which is not available to plants as such but must be oxidized before it is converted to a ready available form.

Decomposition of a molybdenum mineral leads to the formation of complex molybdenum-oxygen ions, viz. MoO_4^{-2} . It is in this form that molybdenum is thought to be adsorbed on the clay particles of soils. From his study on molybdenum sorption by the various constituents of soil colloids, Jones (1957) concluded that hydrous ferric oxide plays a more important role than any other constituent. The sorption effect is dependent on pH and molybdenum adsorbed into the crystal lattice of the clay. At pHs below 7.5 molybdenum is adsorbed in small amounts; at pH 7.5 virtually no molybdenum is adsorbed (Barshad, 1951). When the pH exceeds 7.5, however, molybdenum is again adsorbed, but in smaller amounts.

Molybdenum in Natural Waters

Our knowledge of the hydrogeochemistry of molybdenum is limited. The reason for this is the lack of an accurate analytical method for determining the minute amount of molybdenum present in most natural waters.

In Table 20 data on the distribution of molybdenum in various natural waters are tabulated. With the exception of the values given by Ernst and Hormann the molybdenum content of ocean and sea water is rather uniform, although a few explainable exceptions occur. The same situation also obtains for river waters in which the contents generally vary from 0.2 ug/l to 0.6 ug/l. More variable amounts, however, occur in fresh water lakes, where the contents range from 0.05 ug/l to 1.2 ug/l Mo.

According to Goldberg (1961) the molybdenum species in sea water is MoO_4^{-2}.

According to Sugawara et. al. (1960, 1961) there is a slight but indefinite tendency for molybdenum to increase toward the bottom of the sea. Thus the surface layers are often less enriched by molybdenum than the underlying layers. This vertical distribution is more marked in lakes during the period of stagnation, when the increase of molybdenum is parallel with the decrease of oxygen. This phenomenon can be explained by the coprecipitation of molybdenum by flocs of iron, aluminum, and manganese hydroxides. When the flocs sink and reach the reducing anaerobic layers, the colloids liberate molybdenum to the surrounding water as shown by the experiments conducted by Sugawara, et. al. (1961).

Table 20

Molybdenum in Natural Waters

Locality and type of water	No. of analysis	Mo content in p.p.m. Range	Average	Reference
Baltic Sea N. Atlantic Ocean	2 5	0.3 - 0.7	-	Ernst & Hormann, (1936)
20 miles off shore Plymouth, England	2	12. - 16.	-	Black & Mitchell,(1952)
Off shore, Shirahama, Japan	1	-	10.6	Ishibashi et.al. (19)
Pacific Ocean Northern part Temperate & tropic	 - -	 8.9 - 10.0 9.8 - 11.6	 9.3 10.6	Sugawara & Okabe,(1960) "
Indian Ocean	-	11.4 - 12.2	11.8	"
Antarctic Ocean	-	9.8 - 10.6	10.2	"
Ariake Bay, Japan Omura Bay, Japan	-	9.6 - 12.7	11.3	"
Rivers and lakes, Japan	12	0.05 - 0.5	0.24	"
River waters, Japan	10	0.2 - 0.6	-	Sugawara et.al. (1961)
Fresh-water lakes, Japan	19	0.05 - 1.2	-	"
Thermal springs	8	0.8 - 22.9	7.5	"
Rain waters	8	0.02 - 0.11	-	"
Snows	4	0.12 - 0.30	-	"
Sea waters	-	-	10.0	Goldberg, (1961)

Biogeochemistry of Molybdenum

The importance of molybdenum in life processes of both plants and animals is well established. However, clarification as to how this element behaves in life processes requires further investigation.

Molybdenum belongs to the essential groups of trace elements required by animals (Underwood, 1958). In excessive quantities the element is, however, toxic. Concerning its essential qualities, it is known that molybdenum is a component of the following metalloenzymes : xanthine oxidase, aldehyde oxidase, and nitrate reductase (Richert and Westerfeld, 1953; De Renzo, et. al., 1953). A few writers, however, have questioned whether these enzymes are really essential for the well-being and growth of animals. A number of experiments prove that molybdenum is essential for poultry growth (Read, et.al., 1956; Higgins, et. al., 1956; Norris, 1957; and Kurnick, et. al., 1957). Westerfeld, et. al. (1957) have shown that most of the enzymes in rat tissues capable of reducing the nitro group of p-nitrobenzene sulfonamide are molybdenum enzymes.

There is more agreement among experts with respect to toxicity to animals resulting from high concentration of molybdenum. Several cattle diseases are caused by excess molybdenum, especially in Great Britain (Somerset district), United States of America, Canada, New Zealand, Sweden, and Australia. The most common disease reported, called "teart" or molybdenosis, occurs in areas with molybdenum rich soils

(15 to 300 p.p.m. dry weight). The copper-molybdenum ratio is important in the diet of cattle suffering from "peat scours" and copper poisoning (Cunningham, 1950; Bull, 1951; Dick, 1952, 1953, 1954). "Peat scours" develop in cattle confined to pastures which are high in molybdenum and low in copper. This can be controlled merely by rising the copper intake of the animals to normal levels. Copper poisoning of sheep may develop in an area where the pastures are normal or above normal in copper content but exceedingly low in molybdenum (lower than 0.2 p.p.m.). All investigators agree that the effects of molybdenum toxicity are intimately tied up with the copper and inorganic sulphate intake in the diet.

There is good evidence to suggest that molybdenum is essential as a micronutrient in plant growth. However, the only identified role of molybdenum in higher plants, fungi, and algae is its presence in nitrate reductase (as molybdoflavoprotein). There is some evidence to indicate that ~~molybdeønum~~ molybdenum may be replaced by vanadium in its role in nitrogen fixation by bacteria (Burk, 1934). There are, however, cases where the requirement of molybdenum for nitrate reduction is specific and not replaceable by other elements, as in Anabaena (Arnon, 1958) and Neurospora (Nicholas and Mason, 1945a, b). The work of Steinberg (1937) and Nicholas and McElroy (1954) on fungi, and Mulder (1948) and Hewitt and McGready (1954) on higher plants, pointed out that even though the molybdenum requirement was greatly reduced it could not be completely abolished when nitrate reduction is not necessary (where ammonium is used as the sole source of nitrogen).

A deficiency of molybdenum in plants (less than 0.0.1 p.p.m.) produces a variety of effects, such as yellow leaf spot of citrus trees (Stewart and Leonard, 1952), whiptail in cauliflower and broccoli (Davies, 1945; Mitchell, 1945), failure to produce fruit, etc. - conditions that can be corrected by adding trace amounts of molybdenum to the soil.

There is no definite evidence that high concentrations of molybdenum produce toxic effects in plants. A number of investigations show that for concentrations up to at least 300 p.p.m., there is no apparent toxic effect. This is exemplified by corn - 46.8 p.p.m., alfalfa - 20.7 p.p.m., sunflower - 15.9 p.p.m., tomato - 34.0 p.p.m., and cow-peas - 281 p.p.m. (Barshad, 1948). Stiles (1946) also reported the following molybdenum concentrations in plants : clover - 156 p.p.m., timothy - 30 p.p.m., rye-grass - 54 p.p.m., and yorkshire fog - 83 p.p.m.

According to Barshad, the highest molybdenum contents are generally found in the leaves and stems of plants, though in a few exceptional cases molybdenum concentrates in the roots. In legumes, accumulation is centered in the seed pods (Killeffer and Linz, 1952).

Goldschmidt (1954) reported high molybdenum contents in forest litter, which he thinks could be the answer to the high amounts of the element in certain coal ashes. Northumberland coal ashes for instance contain up to 0.05% molybdenum. In addition Goldschmidt also mentioned the high MoO_3 concentration in dammar resin, with 100 p.p.m., and in ambers with values from 80 to 400 p.p.m. MO_3 .

Deposits of Molybdenum

Molybdenite, MoS_2 (59.9% Mo), is the principal mineral in the deposits of the element, although in some places the secondary mineral wulfenite, $PbMoO_4$ (26.4% Mo) has been mined.

The following is a classification of deposits modified from Vokes (1963) and is modelled after that of Klepper and Wyant's classification for uranium deposits (1957).

I. Deposits formed by Igenous and Metamorphic Processes:

A. Syngenetic deposits: In this category belong the occurrences of disseminated molybdenite in acidic and alkalic igneous rocks. These are not commercially important.

B. Pegmatitic and aplitic deposits: These are known mainly in Precambrian terrains.

C. 1. Epigenetic deposits:

a. Pegmatitic quartz veins: These are a transition between feldspar-free quartz veins and normal pegmatites. The Lacorne deposit, Quebec, is a good example for this class.

b. Simple quartz veins: The veins are composed mainly of massive quartz and minor amounts of molybdenite. In addition there may be some pyrite, chalcopyrite, galena, and sphalerite.

c. Gold-bearing veins: Molybdenite occurs as an accessory mineral. These are common in Precambrian terrains.

d. Veins of base-metal sulphides: Molybdenite occurs as an accessory mineral with the other suphides.

The last three groups of veins, as a whole, are not commercially important.

2. Disseminations and Impregnations: In this case molybdenite is often present as the chief economic mineral as in the Climax Mine, Colorado and the Moly Mine in B.C. or as an accessory mineral in the porphyry-copper type of deposit (Bingham, Utah; Braden, Chile; and Cananea, Mexico). The second type are large mineralized bodies of acid to intermediate hypabyssal intrusive rocks. The surrounding country rocks are likewise often mineralized. Molybdenum is won from the porphyry-copper deposits mainly as a by-product.

3. Metasomatic deposits: Two types of deposits are included in this group, the skarn type which consists mainly of garnet, diopside, quartz, magnetite, copper sulphide and molybdenite, and the molybdenite-bearing pyroxenite type common in the Granville rocks of the Canadian Shield.

II. <u>Deposits formed by Sedimentary Processes</u>:

This class is exemplified by the well known Permian Kupferschiefer of Germany. Molybdenum is generally recovered as a by-product of copper smelting. An association with vanadium is also common in some deposits.

III. <u>Deposits formed by Weathering Processes</u>:

Wulfenite is the common mineral in this class of deposits. It occurs as extensive impregnations in limestones or as fillings in vugs and fractures (Central Europe, Arizona).

Of the three major classes I is the most important at the present time. Most of the known world resources of molybdenum belong to this group.

Oxidation of Deposits

Oxidation of molybdenite-bearing deposits leads to the formation in some places of ferrymolybdite and powellite, in others to wulfenite, lindgrenite, and molybdenum-bearing limonite. Other secondary minerals of molybdenum are rare. Blanchard and Boswell (1935) described two "limonite" products of molybdenite derivation, which can be distinguished from limonite derived from rock disseminated with copper sulphides. One has a foliated boxwork structure and the other is granular. Dolukhanova (1960) states that among the secondary minerals wulfenite is characteristically found in polymetallic deposits, whereas ferrymolybdite and powellite are most common in copper deposits containing molybdenum.

Oxidation of molybdenite yields a molybdenum sulphate complex, from which various molybdates may be derived. The processes, as suggested by Khitarov and Ivanov (1937), and Smirnov (1955) can be illustrated by the following reaction:

$$2\ MoS_2 + 9\ O_2 + 2\ H_2O === 2\ (MoO_2SO_4) + 2\ H_2SO_4$$

Where carbonates or bicarbonates are present in the environment, the mineral powellite may be formed,

$$2\ CaCO_3 + MoO_2SO_4 === \underline{CaMoO_4} + \underline{CaSO_4} + 2\ CO_2$$

or

$$Ca(HCO_3)_2 + MoO_2SO_4 === \underline{CaMoO_4} + H_2SO_4 + 2\ CO_2$$

$$Ca(HCO_3)_2 + H_2SO_4 === \underline{CaSO_4} + 2\ H_2O + 2\ CO_2$$

In addition to the molybdenum sulphate complex, the oxide ion, MoO_4^{-2} , may also occur. Both complexes are readily soluble in water and are stable in the absence of reducing agents. The molybdate of lead, wulfenite, is the first to form in the presence of lead ions. In the presence of soluble copper ions it is followed by lindgrenite, $Cu_3(MoO_4)_2(OH)_2$. Insufficient amounts of lead and copper in the environment give rise to the formation of molybdates of other metals. Stcherbina (1956) points out that, in the molybdate group, copper is able to displace calcium from powellite to form lindgrenite. The scarcity of lindgrenite in the oxidized zones of copper-molybdenum and polymetallic deposits is explained by the replaceability of copper by ferric ion, which in general is very abundant in such environments. This gives rise to the formation of ferrymolybdite and malachite. Ferrymolybdite is unstable where lead ions are available, and wulfenite and limonite are formed in its place.

The high mobility of molybdenum in the supergene zone of molybdenum deposits is proven by the relatively large amounts of the element present in the ground and surface waters leaching the deposits. Contents ranging from $n \times 10^{-5}$ g/l to $n \times 10^{-2}$ g/l of molybdenum has been reported by Vinogradov (1957), which is much above the general content of $n \times 10^{-6}$ g/l in natural waters distant from the deposits. Chukrov (1945) lists the following factors which determine the removal and migration of molybdenum from deposits:

1. The type of mineralization.
2. The acidity of the percolating solutions.
3. The presence of neutralizers (such as carbonates) in the ore, gangue, and wall rocks.

4. The amount of precipitates such as iron hydroxides which form in the environment.
5. The length of time during which the district has been exposed to weathering processes.

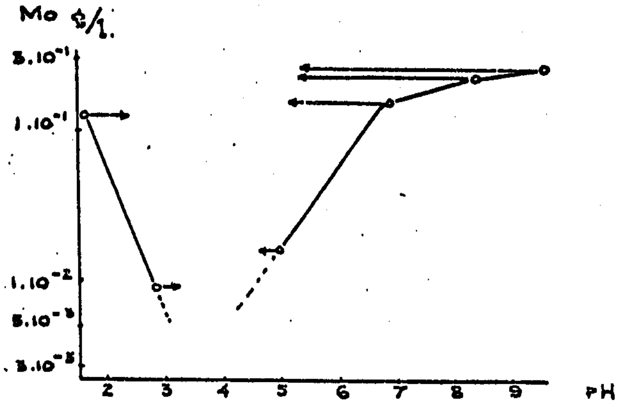
In Figure 18 are shown the solubility of ferrymolybdite and powellite as a function of the pH value of the initial solution. Wulfenite is highly insoluble, but as the pH of the solution approaches 1 or lower, considerable amounts are dissolved.

Prospecting for Molybdenum

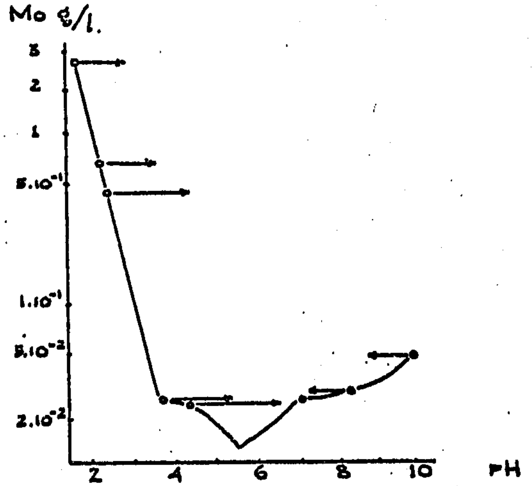
In prospecting for molybdenum it is important to realize that whereas molybdenite is known as a rather common constituent of many rock types, it is rather rare in high concentrations. Lombart (1958) gives the following geological environments as favorable areas in which to find molybdenite deposits. 1) Metamorphic complexes of granites of Precambrian type, 2) Regional areas where an orogenic phase has given rise to intrusions of the monzonitic or dioritic types, 3) Evidence of intense potassic metasomatism together with local silicification, and 4) Brecciated areas within any favorable environment. Other environments which have been overlooked are : oxidized zones of low grade deposits, where concentrations of wulfenite or other secondary molybdenum minerals may occur, and sedimentary rocks of the Kupferschiefer and black shale types.

Molybdenum has a high mobility in ground and surface water in the oxidized zones of molybdenum and other polymetallic deposits. Hence hydrogeochemical prospecting for the element as well as for other less mobile metals with which it is often

FIGURE 18



Solubility of Ferrimolybdite as a function of the pH of the initial solution. Arrows show change in pH toward the end of the experiment. The Mo content is plotted on a logarithmic scale (after V. I. Vinogradov, 1957).



Solubility of Powellite as a function of the pH of the initial solution. Arrows show change in pH toward the end of the experiment. The Mo content is plotted on a logarithmic scale (after V. I. Vinogradov, 1957).

associated, such as tungsten and copper, has proven to be effective in locating molybdenum-bearing zones (Vinogradov, 1957; Belyakova, 1957, 1958; Dolukhanova, 1960). The parallelism of the molybdenum content with sulphate ions as well as an inverse relationship with carbonate ions may be of importance in using this method.

The effectiveness of using pedogeochemical methods in prospecting for molybdenum has been demonstrated by the following investigators: Tikhamirov and Miller (1946), Baranova (1957), Malyuga (1958), Mather (1959), and Dolukhanova (1960). Another important method is the use of stream sediments (Kvashnevskaya, 1957; Mather, 1959; Tauchid, 1964). The fact that plants generally concentrate more molybdenum than the underlying soil suggests that biogeochemical prospecting for molybdenum deposits may be a more effective method than methods based on analysis of residual and other types of soil. The metal concentration in plants is determined by the soil pH, the content of exchangeable and other ions, the plant type, the age of the plant and organ, translocation phenomena, the season of the year when sampling is done, and the molybdenum content in the soils (Carlisle and Cleveland, 1958; Warren, _et. al._, 1953; Baranova, 1957; Malyuga, 1958; Malyuga, _et. al._, 1959).

Stream sediment and water sampling is probably the best approach in geochemical regional reconnaissance prospecting for molybdenum. These methods should then be followed by biogeochemical and pedogeochemical methods if higher than normal contents of molybdenum are found in any given area.

Production and Uses of Molybdenum

Over seventy per cent of the world's molybdenum production comes from the United States. Of this Climax, Colorado, supplies more than two thirds. Other principal molybdenum producing countries are : Russia, Chile, China, Canada, Japan, and Norway (see Table 21).

Table 21

Principal Producing Countries in Molybdenum

Countires	1958 %	1959 %
U.S.A.	71.2	72.1
(Climax)	(43.0)	(60.0)
Russia	16.1	14.0
Chile	5.2	5.4
China	3.8	4.6
Canada	1.5	1.2
Japan	1.2	1.2
Norway	.8	.6
Total	99.8	99.4

About 90 per cent of the world's production of molybdenum is used in the manufactures of iron and steel. The melting point of molybdenum is exceeded only by that of rhenium, tantalum, and tungsten. This fact makes molybdenum one of the best alloying elements in the manufacture of steel. Some of the advantages are : the intensification of the effect of other alloying elements such as nickel, chromium, and vanadium; increasing the tensile and torsional strength and elasticity of steel without decreasing the ductility; and the avoidance of temper-brittleness and the maintenance of high temperature properties. Molybdenum compounds used in the steel industries are molybdenum oxide, ferro-molybdenum, and calcium molybdate. These compounds constitute about 70 per cent of the total molybdenum used in industry.

Sheet molybdenum is used in radio and power valves, in electrodes in mercury vapour lamps, in heating elements in electric furnaces, in dry cells as anodes, and in parts of X-ray tubes.

The following are some of the chemical uses of molybdenum compounds:

1. As chemical reagents for the determinations of phosphorous, alkaloids, uric acids, xanthine, creatinine, etc.; also as oxidation-reduction indicators.
2. In vitreous enamel, for coating iron and steel.
3. Ammonium molybdates are used in disinfecting and fireproofing textiles.
4. Sodium molybdates are used as blue dye for silk and wool.
5. Molybdenite powder is used as a dry lubricant under high temperature conditions.
6. A combination of sodium molybdate with orthophosphate is used as a corrosion inhibitor.
7. As a catalyst.
8. In medicines.
9. In fertilizers.

APPENDIX II

RESULT OF ANALYSIS

General Statement

The following is a tabulation of the complete analytical data of the rocks, gossans, soils, and stream sediments collected during the investigation. To avoid duplication, the data presented in the main text is not repeated. The limited space in the tables prevents the writer from including available information on any particular sample. Should anyone be interested in the details of the samples, he can obtain these from the files of the Geochemical Section, Geological Survey of Canada, Ottawa.

The molybdenum analysis were done by the author using the method described in Chapter V of this thesis. Messrs J.J. Lynch and G. Mihailov of the Geological Survey of Canada determined the Cu, Pb, Zn, As, and Sb in the samples. The results of the analysis on soils done by E.W. Presant are taken directly from his thesis. These are numbered from BH-1847 to BH-1866.

The sample locations are shown on Map No. 1 (in pocket).

ROCKS

SAMPLE #	DESCRIPTION	Mo in p.p.m.
	Tetagouche Group	
BH-5515-62	- grey slate	0.3
BH-5517-62	- light grey phyllite	1.2
BH-5518-62	- maroon argillite	0.5
BH-5519-62	- light grey phyllite	0.5
BH-5520-62	- basalt ~~[illegible]~~ porphyry	0.5
BH-5533-62	- red slate to argillite	1.8
BH-5535-62	- dark grey siliceous argillite	0.5
BH-5537-62	- siliceous argillite, disseminated pyrite	1.1
BH-5540-62	- quartz-feldspar augen schist	0.8
BH-5541-62	- quartz chlorite schist	1.0
BH-5542-62	- meta-volcanics, with feldspar and minor quartz phenocrysts	0.7
BH-5543-62	- acid volcanics, rusty weathering	4.0
BH-5544-62	- yellowish grey phyllite, disseminated with sulphides	3.0
BH-5551-62	- quartz chlorite schist	1.2
BH-5523-62	- dark grey quartzite, disseminated with sulphides	2.0
BH-5665-63	- grey quartzite, disseminated with sulphides	3.0
	Chaleur Bay Group	
BH-5507-62	- dark grey argillite, disseminated with sulphides	7.0
BH-5525-62	- greenish grey greywacke	0.5
BH-5526-62	- meta-conglomerate	1.0
BH-5527-62	- grey slate	1.5
BH-5530-62	- cherty argillite	1.5

ROCKS

SAMPLE #	DESCRIPTION	CONTENT IN P.P.M.					
		Mo	Zn	Cu	Pb	As	Sb
	Bathurst Granite						
BH-5546-62	- biotite granite; coarse to medium grained	0.5	-	-	-	-	-
BH-5547-62	- pink aplitic granite	0.4	-	-	-	-	-
BH-5549-62	- pink biotite granite	1.1	-	-	-	-	-
BH-5564-62	- pink porphyritic granite	0.5	30	4	nd	nd	1
BH-5565-62	- xenolith; comp: feldspar, hornblende, and quartz	0.5	130	24	5	nd	nd
BH-5566-62	- pink biotite granite, coarse	1.0	40	nd	5	nd	nd
BH-5567-62	- pink porphyritic biotite granite	0.7	30	4	5	nd	1
BH-5568-62	- pink aplite dykes in granite	0.5	20	nd	5	nd	1
BH-5569-62	- pink syenite (dyke)	0.5	80	nd	nd	nd	1
BH-5570-62	- pink aplite (dyke)	0.4	30	nd	10	1	nd
BH-5571-62	- porphyritic granite	0.4	30	4	nd	nd	nd
BH-5572-62	- porphyritic granite (altered, greenish)	0.5	20	4	nd	nd	1
BH-5573-62	- pink, fine crystalline granite	0.7	20	nd	10	nd	1
BH-5574-62	- pink, medium grained granite	0.5	30	4	nd	nd	nd
BH-5575-62	- pegmatite	0.5	20	4	nd	5	nd
BH-5576-62	- pink porphyritic granite	1.5	50	4	5	nd	nd
BH-5577-62	- pink porphyritic granite	0.7	40	4	25	nd	nd
BH-5578-62	- altered granite	0.3	50	12	nd	nd	1
BH-5579-62	- pink biotite granite	0.6	30	nd	nd	nd	nd
BH-5580-62	- pink biotite granite	0.8	40	40	nd	nd	nd
BH-5581-62	- grey biotite granite	2.0	30	4	nd	nd	nd
BH-5582-62	- pink porphyritic granite	1.0	30	nd	nd	nd	nd
BH-5583-62	- aplite (dyke)	0.5	20	4	10	nd	nd
BH-5584-62	- pink porphyritic granite	0.5	20	4	5	nd	nd

ROCKS

SAMPLE #	DESCRIPTION	CONTENT IN P.P.M.					
		Mo	Zn	Cu	Pb	As	Sb
	Bathurst Granite (cont'd)						
BH-5585-62	- light grey biotite granite	1.7	30	nd	nd	nd	nd
BH-5586-62	- pink granite (boulder)	9.0	30	nd	15	nd	1
BH-5587-62	- pink biotite granite	1.0	20	nd	nd	22	nd
BH-5588-62	- porphyritic biotite granite	0.5	30	nd	nd	nd	nd
BH-5589-62	- pink porphyritic biotite granite	0.6	40	nd	5	nd	nd
BH-5590-62	- pink porphyritic granite	0.3	50	4	10	nd	nd
BH-5591-62	- pink granite (boulder)	5.0	30	4	10	1	nd
BH-5592-62	- grey granite (boulder)	1.5	30	nd	5	nd	nd
BH-5593-62	- pink porphyritic granite	0.5	30	nd	nd	nd	nd
BH-5594-62	- semi porphyritic granite	0.3	40	nd	5	nd	nd
BH-5595-62	- pink porphyritic biotite granite	0.3	60	4	nd	nd	nd
BH-5596-62	- pink porphyritic granite	0.2	40	4	nd	nd	nd
BH-5597-62	- pink coarse crystalline granite	0.5	40	nd	15	1	nd
BH-5598-62	- pink, semiporphyritic granite	0.5	50	4	15	nd	nd
BH-5599-62	- pink aplite	29.0	30	8	15	26	nd
BH-5600-62	- pink porphyritic granite	0.3	30	nd	5	3	nd
BH-5601-62	- pink porphyritic granite	2.5	20	4	nd	nd	nd
BH-5669-63	- grey medium crystalline granite	8.5	-	-	-	-	-
BH-5670-63	- medium grained granite and granodiorite	0.5	-	-	-	-	-
BH-5671-63	- semi-porphyritic biotite granite	2.0	-	-	-	-	-

ROCKS

SAMPLE #	DESCRIPTION	CONTENT IN P.P.M.					
		Mo	Zn	Cu	Pb	As	Sb
	Nicholas Denys Granite						
BH-5528-62	- medium crystalline granite	0.7	-	-	-	-	-
BH-5529-62	- grey altered granite, disseminated with pyrite	2.5	-	-	-	-	-
BH-5553-62	- greyish biotite granite	0.6	-	-	-	-	-
BH-5554-62	- fine grained biotite granite	0.6	-	-	-	-	-
BH-5556-62	- coarse cryst. granite	28.0	30	nd	nd	nd	nd
BH-5557-62	- biotite granite,med.gr.	0.7	30	nd	nd	nd	nd
BH-5558-62	- hornblende granite	0.3	30	nd	nd	nd	nd
BH-5559-62	- biotite granite,med.gr.	0.3	30	nd	nd	nd	nd
BH-5560-62	- biotite granite,med.gr.	0.7	30	nd	nd	nd	nd
BH-5561-62	- biotite granite,med.gr.	0.5	30	nd	nd	nd	nd
BH-5562-62	- pinkish aplite	0.5	40	160	nd	nd	nd
BH-5563-62	- porph. biotite granite	0.6	40	nd	nd	nd	nd
	Nigadoo Porphyry						
BH-5502-62	- Q-F[1] porphyry, disseminated with sulphides	2.0	-	-	-	-	-
BH-5503-62	- Q-F porphyry, altered	1.4	-	-	-	-	-
BH-5504-62	- dark grey Q-F porphyry	1.2	-	-	-	-	-
BH-5602-62	- Q-F porphyry, weathered	3.0	+1200	140	+1000	51	2.5
BH-5603-62	- Q-F porphyry, fractured	3.0	+1100	120	+4000	+170	+15.0
BH-5604-62	- Q-F porphyry	4.0	+1600	100	150	25	+ 2.5
BH-5605-62	- Q-F porphyry	4.5	+1100	150	+ 600	+150	+ 2.5
BH-5606-62	- Q-F porphyry + pyrite	5.5	40	130	25	84	+ 2.5

[1] - Q-F = Quartz-feldspar

ROCKS

SAMPLE #	DESCRIPTION	CONTENT IN P.P.M.					
		Mo	Zn	Cu	Pb	As	Sb
	Nigadoo Porphyry - cont'd						
BH-5607-62	- Q-F porphyry, disseminated with sulphides	7.0	130	180	90	31	+ 7.5
BH-5608-62	- Q-F porphyry, weathered	8.0	+ 300	110	+ 320	+1100	+13.0
BH-5609-62	- Q-F porphyry + hematite	7.5	+4800	400	+ 380	+4200	+ 7.5
BH-5610-62	- Q-F porphyry + pyrite, altered	5.0	+ 620	120	+ 720	+ 180	+ 7.5
BH-5611-62	- Q-F porphyry	3.5	+5200	170	+4000	+ 230	+15.0
BH-5612-62	- Q-F porphyry, disseminated with sulphides	5.0	+ 320	65	+ 200	+ 170	+ 7.5
BH-5613-62	- Q-F porphyry, coarse	5.0	150	210	+ 450	+ 270	+ 5.0
BH-5614-62	- Q-F porphyry, altered	3.0	+2100	190	+2500	+ 360	+10.0
BH-5615-62	- Q-F porphyry, altered	3.3	370	240	+ 240	+ 150	+ 5.0
BH-5616-62	- Q-F porphyry	3.7	+1000	200	+1100	44	+ 2.5
BH-5617-62	- Q-F porphyry disseminated with pyrite	2.2	80	70	40	+ 200	+10.0
BH-5618-62	- Q-F porphyry disseminated with pyrite	2.7	+ 700	140	+ 420	+ 360	+23.0
BH-5619-62	- Q-F porphyry, altered	2.5	290	110	+ 240	39	2.5
BH-5620-62	- Q-F porphyry disseminated with sulphides	6.5	+2300	210	+ 420	+2100	+ 7.5

ROCKS

SAMPLE #	DESCRIPTION	Mo in p.p.m
	Basic Intrusive	
BH-5510-62	- fine crystalline diabase, with semi-ophitic texture	0.2
BH-5511-62	- serpentinized diabase, disseminated with pyrite	0.5
BH-5512-62	- highly serpentinized diabase	0.4
BH-5513-62	- medium to coarse crystalline diabase with ophitic texture	1.0
BH-5514-62	- medium to coarse crystalline diabase	1.2
BH-5516-62	- dense to fine crystalline diabase	1.7
BH-5531-62	- coarse crystalline diabase, disseminated with pyrite	1.2
BH-5532-62	- fine crystalline diabase, with semi-ophitic texture	1.6
BH-5536-62	- medium crystalline diabase	1.2
	Pennsylvanian Rocks	
BH-5534-62	- greenish yellow sandstone	0.7
BH-5548-62	- red conglomerate, not well cemented	0.3
	Gossan Profile (detail)	
BH-5004a-62	- red to brownish brecciated gossan (transported)	12.0
BH-5004b-62	- brown leached till (unconsolidated)	19.5
BH-5004c-62	- yellow leached till, brecciated (unconsolidated)	11.0
BH-5004d-62	- yellow brecciated leached till (unconsolidated)	17.5
BH-5005a-62	- reddish yellow leached till (unconsolidated)	23.0
BH-5005b-62	- grey, sandy residual gossan	12.0

ROCKS

SAMPLE #	DESCRIPTION	Mo in p.p.m.
	Gossan Profile (detail) cont'd	
BH-5005c-62	- black residual gossan	20.5
BH-5006a-62	- maroon, yellow, and brown brecciated gossan (transported)	10.5
BH-5006b-62	- yellowish brown, conglomeratic leached till (unconsolidated)	10.0
BH-5006c-62	- grey, yellow, conglomeratic leached till (unconsolidated)	7.5
BH-5006d-62	- light brown leached till	9.5
BH-5006e-62	- yellow conglomeratic residual gossan	9.5
BH-5006f-62	- greyish yellow residual gossan, conglomeratic (unconsolidated)	13.0
BH-5007a-62	- maroon, yellow and brown, brecciated gossan (transported)	1.6
BH-5007b-62	- brown leached till (unconsolidated)	9.0
BH-5007c-62	- yellow residual gossan	8.6
BH-5007d-62	- yellowish brown residual gossan	14.5
BH-5007e-62	- maroon residual gossan	33.0
BH-5008a-62	- yellow, maroon and brown, brecciated gossan	1.0
BH-5008b-62	- red leached gossan	28.0
BH-5008c-62	- maroon residual gossan	33.0
BH-5009a-62	- maroon, yellow and brown, brecciated gossan (transported)	4.0
BH-5009b-62	- brown leached till (unconsolidated)	11.0
BH-5009c-62	- red leached till (unconsolidated)	15.0
BH-5009d-62	- yellowish brown leached till	31.0
BH-5009e-62	- yellow, conglomeratic residual gossan	4.0

SOILS

SAMPLE #	LOCATION	HORIZON	pH	in %		in P.P.M.								
				C	Fe	Mo	Zn	Cu	Pb	Mn	As	Sb	Ag	Sn
BH-1851-a	Bathurst Mine	A_0	4.3	24.45	1.04	1.0	80	15	35	780	ND	1	7.8	.9
-b	"	A_2	3.8	2.34	1.28	.5	20	5	25	80	5	2	.2	2.5
-c	"	B_1	4.2	1.05	4.31	1.8	120	5	30	1160	10	1	.2	1.6
-d	"	B_2	5.1	.20	3.54	1.5	110	10	15	700	10	1	.2	1.7
BH-1852-a	Bathurst Mine road	A_{00}	3.0	-	.09	.5	60	5	20	1000	ND	2	.9	ND
-b	"	A_0	2.7	-	.64	.3	20	5	40	80	ND	4	.9	1.3
-c	"	A_1	2.8	-	.88	.2	20	5	10	80	ND	3	.4	7.8
BH-1860-b	Brunswick No. 12 Mine area	A_2	3.6	.27	6.05	3.0	120	120	95	80	300	11	.3	2.6
-c	"	B_1	4.1	.91	7.38	1.7	150	150	180	80	250	8	1.2	17.0
-d	"	B	4.4	.49	8.65	2.0	110	110	270	390	150	6	4.0	5.9
-e	"	C	4.8	.24	11.27	1.8	210	210	370	310	340	11	.9	7.4

SOILS

SAMPLE #	LOCATION	HORIZON	pH	in %		in P.P.M.								
				C	Fe	Mo	Zn	Cu	Pb	Mn	As	Sb	Ag	Sn
* BH-1862-a	Brunswick No. 6 Road	A_0	4.1	30.77	.96	.5	70	5	25	390	ND	3	1.4	-
-b	"	A_2	3.7	1.79	.98	.4	10	5	10	80	ND	2	.2	7.8
-c	"	B_1	4.2	1.34	5.30	1.5	70	5	30	540	15	2	.3	2.7
-d	"	B_2	4.5	.41	3.23	1.5	60	10	25	470	5	2	.2	7.8
BH-1862-f	Brunswick No. 6 Road	C	4.4	.16	3.04	.6	70	5	25	470	ND	2	.2	4.6
* BH-1864-a	Brunswick No. 6 Road	A_0	3.4	35.11	.28	.8	60	10	20	230	ND	1	.5	9.1
-b	"	A_2	3.7	.62	.83	.9	15	5	5	80	ND	1	1.7	4.6
-c	"	B_1	4.5	1.16	4.70	2.4	70	5	25	390	20	3	.5	5.6
-d	"	B_2	4.7	.20	3.53	1.5	70	15	35	390	5	1	.4	11.0
-e	"	C	4.7	.10	1.05	1.3	70	15	40	540	5	2	.2	7.8

SAMPLE #	LOCATION	HORIZON	pH	Content in p.p.m.			
				Mo	Zn	Cu	Pb
*BH-1848-a	Road to Brunswick # 6	A_0	4.7	1.2	80	30	50
-b	"	A_2	4.7	.8	30	8	25
-c	"	B_1	4.7	1.0	70	15	20
-d	"	B_2	4.5	1.2	60	20	ND
-e	"	C	4.9	1.5	60	20	15
BH-1850-a	Austin Bk. area	A_0	3.9	1.0	120	5	40
-b	"	A_2	3.7	1.5	20	10	15
-c	"	B_1	4.3	1.7	50	10	20
-d	"	B_2	4.5	1.5	60	8	20
-e	"	C	4.5	1.7	50	10	20
BH-1856-a	Road to Brunswick # 6	B_2	4.9	1.8	140	5	20
-b	"	C	4.9	1.7	70	25	20
BH-1857-a	"	A_0	3.7	.7	30	5	20
-b	"	A_2	4.2	.5	10	5	10
-c	"	B_1	4.4	1.4	60	5	10
-d	"	C	4.8	1.0	70	15	20

SAMPLE #	LOCATION	HORIZON	pH	Content in p.p.m.			
				Mo	Zn	Cu	Pb
* BH-1861-a	Near Brunswick # 12	A_0	3.4	.5	50	5	25
-b	"	A_2	3.6	.5	20	5	10
-c	"	B_1	4.2	1.2	90	5	20
-d	"	B_2	4.6	2.0	100	8	20
-e	"	C	4.7	2.0	90	25	20
* BH-1863-a	Road to Brunswick # 6	A_0	3.7	1.0	60	10	20
-b	"	A_2	3.5	1.1	20	8	25
-c	"	B_1	4.1	2.2	110	20	110
-d	"	B_2	5.0	2.4	150	30	90
-e	"	C	5.0	1.8	150	55	105
BH-1865-a	Road to Brunswick # 6	A_0	3.8	1.0	60	15	35
-b	"	A_2	3.8	.5	10	5	5
-c	"	B_1	4.8	1.7	80	5	15
-d	"	B_2	4.7	2.0	50	20	20

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5001	a	Brunswick No. 6 Mine	0 - 1	A_{00}	4.8	1.7
	b	"	1 - 7	A_0	4.7	2.0
	c	"	-	A_1	4.8	1.4
	d	"	7 - 7.5	coal	4.6	2.0
	e	"	7.5 - 9.5	A_2	4.7	2.0
	f	"	9.5 - 14.5	B_1	5.2	2.0
	g	"	14.5 - 20.5	B_2	6.1	7.8
	h	"	20.5 - 27.5	C_1	5.7	3.5
	i	"	27.5 -	C_2	5.5	3.5
BH-5002	a	Brunswick No. 6 Mine	0 - 8	A_0	4.6	2.5
	b	"	8 - 8.5	A_1	5.0	1.0
	c	"	8.5 - 9	A_2	4.7	1.2
	d	"	9 - 15	B_1	4.9	4.4
	e	"	15 - 21	B_2	5.2	4.0
	f	"	21 - 29	B_3	4.9	15.0
	g	"	29 -	C	4.8	-

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5003	a	Brunswick No. 6 Mine	0 - 7	A_0	4.6	1.0
	b	"	7 - 9	A_2	4.4	0.5
	c	"	9 - 17	B_1	4.7	4.0
	d	"	17 - 25	B_2	5.9	2.0
	e	"	25 -	C_1	5.6	5.8
BH-5010	a	Brunswick No. 6 Mine	-	A_0	4.7	6.0
	b	"	0 - 1	coal	4.9	2.0
	c	"	1 - 5	A_2	4.9	3.0
	d	"	5 - 12	B_1	4.9	10.0
	e	"	12 - 20	B_2	5.2	9.5
	f	"	20 -	C	5.6	8.7
BH-5011	a	Brunswick No. 6 Mine	0 - 4	A_{00}	4.6	2.0
	b	"	4 - 6	A_0	4.6	1.5
	c	"	6 - 15	B_1	4.7	5.0
	d	"	15 - 24	B_2	4.7	7.0
	e	"	24 -	C	4.4	18.0
BH-5012	a	Brunswick No. 6 Mine	0 - 6	A_0	4.2	.6
	b	"	-	A_1	4.3	.5
	c	"	6 - 9	A_2	4.1	.5
	d	"	9 - 19	B_1	4.0	.5

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5012 e	Brunswick No. 6 Mine	19 - 26	B_2	3.9	3.5
f	"	26 -	C	3.9	1.0
BH-5013 a	Brunswick No. 6 Mine	0 - 1	A_{00}	4.8	4.0
b	"	1 - 2	A_0	4.7	3.5
c	"	0 - 2	A_2	4.6	6.0
d	"	2 - 8	B	5.5	4.0
e	"	8 - 13	C	5.6	7.5
* BH-5014 a	Road to Brunswick No. 6 Mine (see Map)	0 - 2	A_0	4.7	0.5
b	"	2 - 5	A_2	5.0	0.2
c	"	5 - 10	B	5.7	0.8
d	"	10 - 20	C	5.8	0.8
* BH-5015 a	Road to Brunswick No. 6 Mine(see Map)	0 - 2	A_0	5.2	1.5
b	"	2 - 4	A_2	4.2	0.5
c	"	4 - 7	B_1	5.6	0.8
d	"	7 - 14	B_2	5.7	1.0
e	"	14 -	C	5.7	1.2
BH-5016 a	Youghall Beach Area	0 - 6	A	6.2	1.5
b	"	6 - 14	B_1	5.8	0.5
c	"	14 -	B_2	6.0	0.6

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5017	a	Nigadoo Mine Area	0 - 3	A_{00}	7.1	.5
	b	"	3 - 10	A_0	7.4	1.0
	c	"	10 - 18	A_2	7.5	.5
	d	"	18 - 21	B_1	7.5	.5
	e	"	21 - 29	B_2	7.5	.5
	f	"	29 -	C	7.6	.5
BH-5018	a	Nigadoo Mine Area	0 - 3	A_{00}	7.0	.5
	b	"	3 - 9	A_0	6.8	3.0
	c	"	9 - 11	A_1	6.8	1.0
	d	"	11 - 14	A_2	6.9	.5
	e	"	14 - 19	B	7.3	.5
	f	"	19 -	C_1	7.6	.7
BH-5019	a	Nigadoo Mine Area	0 - 4	A_{00}	5.0	0.0
	b	"	4 - 5	A_0	4.8	.5
	c	"	5 - 6	A_2	5.1	.0
	d	"	6 - 13	B_1	5.7	1.0
	e	"	13 - 19	B_2	6.2	.5
	f	"	19 -	C	6.4	.5
BH-5020	a	Nigadoo Mine Area	0 - 6	A_0	5.9	1.0
	b	"	6 - 11	A_2	5.5	.5
	c	"	11 - 19	B	5.8	1.5
	d	"	19 - 23	C_1	5.8	1.0

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5021 a	Nigadoo Mine Area	0 - 1	A_0	5.3	.0
b	"	1 - 2	A_2	5.4	.0
c	"	2 - 5	B	5.5	2.0
d	"	5 - 8	C_1	5.7	.5
e	"	8 - 16	C_2	5.7	.5
BH-5022 a	Nigadoo Mine Area	0 - 5	A_{00}	5.5	.4
b	"	5 - 12	A_0	5.6	.7
c	"	12 - 14	A_2	5.9	2.0
d	"	14 - 18	B	6.3	2.0
e	"	18 -	C	6.4	.5
BH-5023 a	Nigadoo Mine Area	0 - 3	A_{00}	5.4	.4
b	"	3 - 6	A_2	5.6	.4
c	"	6 - 10	B	6.3	1.0
d	"	10 - 20	C	6.2	1.5
BH-5024 a	Nigadoo Mine Area	0 - 6	A_0	5.4	1.0
b	"	6 - 8	A_2	5.4	.0
c	"	8 - 16	B	6.1	2.0
BH-5025 a	Nigadoo Mine Area	0 - 5	A_{00}	4.8	.5
b	"	5 - 9	A_0	6.0	2.6
c	"	9 - 15	-	6.2	4.5
d	"	15 - 18	A_2	6.4	14.0
e	"	18 -	B	6.8	2.0

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5026	a	Nigadoo Mine Area	0 - 3	A_0	7.3	1.0
	b	"	3 - 6	A_2	7.5	.9
	c	"	6 - 10	B	7.1	.9
	d	"	10 -	C	7.1	.6
BH-5027	a	Nigadoo Mine Area	0 - 5	A	6.3	2.8
	b	"	5 - 9	B_1	6.7	1.0
	c	"	9 - 15	B_2	6.8	2.1
BH-5028	a	Nigadoo Mine Area	0 - 4	A_1	5.5	2.0
	b	"	4 - 6	A_2	5.5	2.1
	c	"	6 - 16	B	5.6	2.5
	d	"	16 -	C	5.7	2.5
BH-5029	a	Nigadoo Mine Area	0 - 4	A_0	5.6	2.8
	b	"	4 - 5	A_1	5.7	2.2
	c	"	5 - 8	A_2	5.9	1.0
	d	"	8 - 15	B	6.2	2.2
	e	"	15 -	C	5.8	1.1
BH-5030	a	Nigadoo Mine Area	0 - 2	A_0	5.1	.8
	b	"	2 - 3	A_2	5.1	.6
	c	"	3 - 10	B_1	5.6	.9
	d	"	10 - 15	B_2	5.7	.8
	e	"	15 - 21	C	5.9	.8

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5031 a	Nigadoo Mine Area	0 - 5	A_{00}	6.1	1.8
b	"	5 - 8	A_0	6.1	5.4
c	"	8 - 11	A	6.3	1.2
d	"	11 - 0	B	6.5	1.4
BH-5032 a	Nigadoo Mine Area	0 - 3.5	A_0	5.7	1.0
b	"	3.5 - 5.5	A_2	6.1	.5
c	"	5.5 -11.5	B_1	6.1	1.3
d	"	11.5 -18.5	B_2	6.2	1.1
e	"	18.5 -25.5	C_1	6.7	.7
f	"	25.5 -33.5	C_2	7.0	.7
BH-5033 a	Nigadoo Mine Area	0 - 3	A_0	5.5	1.0
b	"	3 - 7	A_2	5.8	.5
c	"	7 - 12	B_1	5.8	1.5
d	"	12 - 16	B_2	5.6	1.4
e	"	16 - 21	C	5.6	1.4
BH-5034 a	Sturgeon River Mine Area	0 - 8	A_1	5.4	.7
b	"	8 - 12	A_2	5.5	.5
c	"	12 - 16	B	5.4	1.6
d	"	16 - 21	C	5.4	1.5

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5035 a	Sturgeon River Mine Area	0 - 5	A_0	5.2	1.0
b	"	5 - 7	A_2	5.2	.3
c	"	7 - 15	B	5.4	1.0
d	"	15 - 22	C	5.5	1.0
BH-5036 a	Sturgeon River Mine Area	0 - 3	A	5.8	1.5
b	"	3 - 12	B	6.2	1.5
c	"	12 - 17	C	5.7	2.5
BH-5037 a	Sturgeon River Mine Area	0 - 4	A_0	6.0	0.5
b	"	4 - 8	A_1	6.0	1.0
c	"	8 - 11	A_2	6.0	0.5
d	"	11 - 17	B	5.9	1.0
e	"	17 - 21	C	5.8	1.5
BH-5038 a	Sturgeon River Mine Area	0 - 2	A_0	5.6	3.5
b	"	2 - 3	A	5.4	7.0
c	"	3 - 11	B	5.7	4.0
BH-5039 a	Sturgeon River Mine Area	0 - 5	A_0	5.2	2.0
b	"	0 - 0	A	5.2	1.5
c	"	0 - 3	B	5.3	1.5
d	"	3 - 10	C	5.7	2.0

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5040 a	Sturgeon River Mine Area	0 - 2	A	5.0	2.5
b	"	2 - 7	B	5.4	3.0
c	"	7 - 13	C	5.7	3.8
BH-5041 a	Sturgeon River Mine Area	0 - 2	A	5.2	3.4
b	"	2 - 13	B	5.5	3.8
c	"	13 - 22	C	5.6	3.7
BH-5042 a	Nigadoo - Nicholas Dénys Road	0 - 5	A	5.7	1.5
b	"	5 - 10	B_1	5.7	2.5
c	"	10 - 15	B_2	5.7	3.0
d	"	15 - 21	C_1	5.4	3.5
e	"	21 -	C_2	5.5	3.5
* BH-5043 a	Nigadoo - Nicholas Dénys Road	0 - 7	A_0	5.4	0.5
b	"	7 - 10	A_2	5.2	1.5
c	"	10 - 14	B_1	5.5	1.5
d	"	14 - 18	B_2	5.6	2.5
e	"	18 - 23	C	5.6	2.0
* BH-5044 a	Nigadoo - Nicholas Dénys Road	0 - 2	A_0	5.9	1.0
b	"	2 - 4	A_2	5.4	1.0
c	"	4 - 8	B_1	5.6	1.5

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
* BH-5044 d	Nigadoo - Nicholas Dénys Road	8 - 15	B	5.8	1.3
e	"	15 - 20	C_1	5.8	3.5
f	"	20 -	C_2	5.8	1.5
* BH-5045 a	Nigadoo - Nicholas Dénys Road	0 - 2	A_0	5.5	1.7
b	"	2 - 4	A_2	5.5	1.5
c	"	4 - 10	B	5.8	3.0
d	"	10 - 17	C_1	5.8	2.0
e	"	17 -	C_2	5.8	2.0
* BH-5046 a	Nigadoo - Nicholas Dénys Road	0 - 0	A_0	5.8	1.0
b	"	0 - 1	A_2	5.3	0.7
c	"	1 - 4	B_1	5.3	3.5
d	"	4 - 10	B_2	5.5	2.5
e	"	10 - 15	C	5.6	1.7
* BH-5047 a	Nicholas Dénys Road	0 - 2	A_0	5.9	2.5
b	"	2 - 5	A_2	5.9	2.5
c	"	5 - 11	B	5.7	1.5
d	"	11 - 17	C	6.0	1.1
* BH-5048 a	Nicholas Dénys Road	0 - 0	A_0	6.0	2.5
b	"	0 - 4	A_2	4.8	1.2
c	"	4 - 7	B	5.5	4.0
d	"	7 - 12	C	5.5	3.0

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5049	a	Nicholas Dénys Area	0 - 4	A_0	6.3	1.8
	b	"	4 - 8	A_2	6.7	1.3
	c	"	8 - 11	B_1	6.6	1.7
	d	"	11 - 16	B_2	6.6	1.0
* BH-5050	a	Nicholas Dénys - Sturgeon River Road	0 - 2	A_0	6.8	.5
	b	"	2 - 5	A_2	5.9	.0
	c	"	5 - 10	B_1	6.1	.4
	d	"	10 - 16	B_2	6.0	.4
	e	"	16 - 20	C	5.9	.2
* BH-5051	a	Nicholas Dénys - Sturgeon River Road	0 - 3	A_0	5.4	.3
	b	"	3 - 4	A_2	5.7	.5
	c	"	4 - 8	B_1	5.9	.4
	d	"	8 - 15	B_2	5.9	.7
	e	"	15 - 19	C	6.1	.3
BH-5052	a	Nicholas Dénys - Massabielle Road	0 - 4	A_0	6.7	1.5
	b	"	4 - 6	A_2	6.6	1.0
	c	"	6 - 11	B	6.8	.3
	d	"	11 - 17	C	6.8	.4
BH-5053	a	Massabielle Area	0 - 2	A_0	6.2	3.0
	b	"	2 - 6	A	5.6	3.5
	c	"	6 - 11	B	6.0	3.2
	d	"	11 - 17	C	5.8	1.0

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5054	a	Massabielle Area	0 - 3	A_2	5.4	.5
	b	"	3 - 7	B_1	5.8	1.2
	c	"	7 - 13	B_2	5.9	1.1
	d	"	13 - 20	C	5.9	.3
BH-5055	a	Massabielle Area	0 - 3	A_0	6.2	1.0
	b	"	3 - 5	A_2	6.2	.8
	c	"	5 - 10	B	6.1	.7
	d	"	10 - 16	C_1	6.0	.6
	e	"	16 -	C_2	6.2	.8
BH-5056	a	Free Grant Road	0 - 2	A	5.2	1.0
	b	"	2 - 6	B	5.3	1.0
	c	"	6 - 10	C_1	5.5	.5
	d	"	10 -	C_2	5.5	1.5
BH-5057	a	Free Grant Road	0 - 3		5.0	.3
	b	"	3 - 8		5.2	.7
	c	"	8 - 16		5.3	.5
	d	"	16 - 23		5.4	.5
	e	"	23 - 30		5.6	.7

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5058	a	Free Grant Road	0 - 3	A	5.9	1.0
	b	"	3 - 7	B_1	5.9	.4
	c	"	7 - 12	B_2	5.8	.9
	d	"	12 -	C	5.9	.3
BH-5059	a	Free Grant Road	0 - 4	A_2	5.7	.2
	b	"	4 - 9	B_1	5.9	1.0
	c	"	9 - 14	B_2	6.0	.9
	d	"	14 -	C	6.0	1.6
BH-5060	a	Nicholas Dénys - Free Grant Road	0 - 2	A_0	5.5	.5
	b	"	2 - 5	A	6.1	1.3
	c	"	5 - 10	B_1	6.0	.5
	d	"	10 - 15	B_2	6.0	.9
	e	"	15 -	C	6.1	.9
* BH-5061	a	Free Grant Road	0 - 2	A_0	6.2	1.3
	b	"	2 - 8	A_2	5.9	1.0
	c	"	8 - 13	B	6.1	1.3
	d	"	13 - 19	C	5.8	1.5
BH-5062	a	Free Grant Road	0 - 1	A	5.7	.8
	b	"	1 - 5	B_1	5.7	1.0

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5062 c	Free Grant Road	5 - 12	B_1	5.6	1.2
d	"	12 - 18	C_1	5.6	1.5
BH-5063 a	Free Grant Road	0 - 6	A	5.8	1.2
b	"	6 - 10	B_1	5.9	1.5
c	"	10 - 13	B_2	5.9	1.8
d	"	13 -	C	5.9	1.7
BH-5064 a	Madisco Road	0 - 5	A	5.7	1.2
b	"	5 - 8	B_1	5.7	1.4
c	"	8 - 12	B_2	5.8	1.7
d	"	12 -	C	5.8	1.2
BH-5065 a	Nigadoo Mine Road	0 - 4	A_2	5.8	1.0
b	"	4 - 9	B_1	5.6	1.5
c	"	9 - 13	B_2	5.8	1.7
d	"	13 -	C	5.9	1.3
BH-5066 a	Madisco Road	0 - 4	A_2	5.8	.5
b	"	4 - 8	B_1	6.0	1.7
c	"	8 - 12	B_2	6.1	1.3
d	"	12 -	C_1	6.1	1.5
BH-5067 a	Robertville Road	0 - 4	A	6.0	1.8
b	"	4 - 10	B	6.0	1.5
c	"	10 - 14	C_1	5.8	1.5

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5068 a	St. Rosette Road	0 - 3	A	5.2	1.5
b	"	3 - 6	B	5.4	1.5
c	"	6 - 9	C_1	5.4	1.2
d	"	9 - 14	C_2	5.5	1.1
BH-5069 a	Robertville Road	0 - 2	A_1	5.5	1.0
b	"	2 - 5	A_2	5.7	1.2
c	"	5 - 9	B_1	5.5	1.5
d	"	9 - 14	B_2	5.6	1.5
e	"	14 -	C	5.6	1.5
* BH-5070 a	Sormany Road	0 - 2	A_0	5.4	.8
b	"	2 - 4	A_2	5.5	1.0
c	"	4 - 10	B	5.5	1.3
d	"	10 - 14	C	5.8	1.7
* BH-5071 a	Nicholas Dénys Road	-	A_0	5.8	.6
b	"	0 - 3	A_2	5.6	.5
c	"	3 - 4	B_1	5.6	1.1
d	"	4 - 9	B_2	5.7	1.2
e	"	9 - 14	C	5.8	1.3
* BH-5072 a	Sormany Road	0 - 1	A_0	6.4	.8
b	"	1 - 4	A_2	6.0	1.1

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
* BH-5072 c	Sormany Road	4 - 8	B_1	5.9	1.2
d	"	8 - 13	B_2	6.3	1.2
e	"	13 - 18	C	5.8	1.5
* BH-5073 a	Sormany Road	0 - 1	A_0	5.0	.7
b	"	1 - 5	A_2	5.3	.5
c	"	5 - 10	B	5.7	1.0
d	"	10 - 15	C	5.7	1.2
BH-5074 a	1.5 miles South East of Sormany	0 - 5	A	6.1	1.2
b	"	5 - 10	B_1	6.2	1.7
c	"	10 - 14	B_2	6.3	1.4
d	"	14 - 18	C	6.3	2.0
BH-5075 a	Ste Louise Road	0 - 5	A	5.7	.5
b	"	5 - 10	B_1	5.8	1.6
c	"	10 - 14	B_2	5.5	1.6
d	"	14 - 19	C	5.5	1.5
BH-5076 a	1 mile South East of Ste Louise	0 - 3	A	5.3	.5
b	"	3 - 8	B	5.0	1.4
c	"	8 - 12	C_1	5.6	1.2
d	"	12 - 17	C_2	5.9	1.1
BH-5077 a	St. George	0 - 6	A	5.9	.9
b	"	6 - 10	B_1	6.3	1.0

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5077 c	St George	10 - 14	B_2	6.1	1.4
d	"	14 - 18	C	6.0	1.2
* BH-5078 a	Sormany	0 - 2	A_0	5.1	.8
b	"	2 - 5	A_2	5.5	1.1
c	"	5 - 10	B	5.8	1.3
d	"	10 - 15	C_1	6.0	1.4
BH-5079 a	Tetagouche North Side	0 - 3	A	5.5	.6
b	"	3 - 9	B_1	5.5	1.0
c	"	9 - 13	B_2	5.4	1.4
d	"	13 - 18	C	5.7	1.3
BH-5080 a	Robertville	0 - 3	A	5.8	.3
b	"	3 - 7	B_1	5.7	1.0
c	"	7 - 11	B_2	5.8	1.2
d	"	11 - 16	C	5.9	1.1
BH-5081 a	North West of Bathurst	0 - 2	A	6.0	.6
b	"	2 - 11	B_1	5.5	1.0
c	"	11 - 14	Gravel	5.6	1.1
d	"	14 - 19	B_2	5.6	1.0
e	"	19 -	C_1	5.6	1.3
* BH-5082 a	West of Ste Anne	0 - 2	A_0	5.8	.8
b	"	2 - 5	A_2	5.3	.8

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
* BH-5082	c	West of Ste Anne	5 - 11	B	5.6	.8
	d	"	11- 18	C	5.9	.9
BH-5083	a	Tetagouche Falls	0 - 8	Transp. top soil	6.0	.7
	b	"	8 - 11	A	6.2	.9
	c	"	11 - 15	B	6.1	.8
	d	"	15 - 20	C	6.1	1.1
BH-5084	a	Upper Rosehill Road (River Bank)	0 - 5	A	6.0	2.5
	b	"	5 - 10	B	6.4	5.4
	c	"	10 - 14	C_1	6.4	5.6
	d	"	14 - 18	C	6.5	18 - 19
* BH-5085	a	Upper Rosehill Road	0 - 1	A_0	5.3	.5
	b	"	1 - 6	A_2	5.1	1.0
	c	"	6 - 10	B_1	5.4	1.3
	d	"	10 - 14	B_2	5.2	1.4
	e	"	14 -	C	5.4	1.4
BH-5086	a	West of Imhoff	0 - 1	A_0	5.7	2.0
	b	"	1 - 2	A_2	5.4	.3
	c	"	2 - 12	B	5.5	1.4
	d	"	12 - 17	C	5.6	1.4

SOILS

SAMPLE #		LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5087	a	New Larder "U" Mine Area	0 - 7	A	6.1	.7
	b	"	7 - 12	B_1	5.8	.5
	c	"	12 - 17	B_2	6.1	1.1
	d	"	17 -	C	6.4	1.0
BH-5088	a	New Larder "U" Mine Area	0 - 3	A	5.8	.5
	b	"	3 - 9	B	6.7	1.0
	c	"	9 - 23	C_1	7.0	1.1
BH-5089	a	New Larder "U" Mine Area	0 - 3	A	5.9	.3
	b	"	3 - 8	B_1	6.0	1.2
	c	"	8 - 14	B_2	6.2	1.2
	d	"	14 -	C	6.2	1.0
BH-5090	a	New Larder "U" Mine Area	0 - 2	A_0	6.2	1.0
	b	"	2 - 4	A_2	5.9	.2
	c	"	4 - 8	B_1	6.1	1.3
	d	"	8 - 13	B_2	6.1	1.4
	e	"	13 -	C	5.9	1.6
BH-5091	a	New Larder "U" Mine Area	0 - 2	A_0	5.5	.6
	b	"	2 - 7	A_2	5.4	1.1
	c	"	7 - 12	B	5.6	1.4
	d	"	12 -	C	5.8	1.2

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5092 a	New Larder "U" Mine Area	0 - 3	A_0	4.9	.6
b	"	3 - 9	A_2	5.2	1.0
c	"	9 -	B	5.2	1.5
BH-5093 a	New Larder "U" Mine Area	0 - 3	A	4.9	.6
b	"	3 - 5	B_1	5.3	1.6
c	"	5 - 13	B_2	5.4	1.8
d	"	13 -	C_1	5.8	2.0
BH-5094 a	Brunswick No. 6 Road	-	A_2	-	.5
b	"	-	B	-	3.5
BH-5095 a	Little River Area	0 - 3	A_0	-	1.0
b	"	3 - 6	A_2	-	2.0
c	"	6 - 10	B	-	2.7
d	"	10 - 17	B	-	2.3
BH-5096 a	Legresley Road	0 - 3	A	-	-
b	"	3 - 8	B_1	-	.6
c	"	8 - 11	B_2	-	.6
d	"	11 - 17	C	-	1.3
BH-5097 a	Legresley	0 - 3	A_0	-	-
b	"	3 - 7	B_1	-	.6

SOILS

SAMPLE #	LOCATION	DEPTH in inches	HORIZON	pH	Mo in p.p.m.
BH-5097 c	Legresley	7 - 11	B_2	-	.4
d	"	11 -	C	-	.4
* BH-5098 a	East of Legresley	0 - 1	A_0	-	-
b	"	1 - 3	A_2	-	.3
c	"	3 - 8	B_1	-	1.3
d	"	8 - 12	B_2	-	1.5
e	"	12 -	C	-	1.5

STREAM SEDIMENTS

SAMPLE #	LOCATION	METAL CONTENT IN P.P.M.			
		Mo	Zn	Cu	Pb
BH-5101-62	Millstream River System	1.0	70	6	10
BH-5102-62	"	1.4	120	8	15
BH-5103-62	"	1.5	160	10	20
BH-5104-62	"	1.0	70	6	15
BH-5105-62	"	3.3	190	36	35
BH-5106-62	"	2.6	170	16	30
BH-5107-62	"	1.8	190	18	35
BH-5108-62	"	1.4	250	34	30
BH-5109-62	"	2.3	180	20	30
BH-5110-62	"	2.6	180	18	25
BH-5111-62	"	5.0	190	16	45
BH-5112-62	"	1.4	230	22	50
BH-5113-62	"	2.5	190	18	15
BH-5114-62	"	1.5	240	16	35
BH-5115-62	"	2.3	350	28	75
BH-5116-62	"	2.1	650	34	130
BH-5117-62	"	9.0	260	24	25
BH-5118-62	"	9.0	230	12	20
BH-5119-62	"	1.0	160	26	20
BH-5120-62	"	1.0	120	12	15

STREAM SEDIMENTS

SAMPLE #	LOCATION	METAL CONTENT IN P.P.M.			
		Mo	Zn	Cu	Pb
BH-5121-62	Millstream River System	1.7	120	4	15
BH-5122-62	"	.5	120	14	15
BH-5123-62	"	32.0	220	52	25
BH-5124-62	"	20.0	800	36	280
BH-5125-62	"	3.0	170	16	15
BH-5126-62	"	.5	120	10	15
BH-5127-62	"	1.5	120	14	15
BH-5128-62	"	1.2	110	10	15
BH-5129-62	"	3.0	1200	170	1200
BH-5130-62	"	4.0	1200	38	160
BH-5131-62	"	1.5	460	24	50
BH-5132-62	"	1.0	220	54	50
BH-5133-62	"	1.5	180	20	25
BH-5134-62	"	.5	450	42	170
BH-5135-62	"	7.0	260	82	25
BH-5136-62	"	- No fine fraction -			
BH-5137-62	"	3.0	180	20	35
BH-5138-62	"	1.8	160	6	20
BH-5139-62	"	1.3	220	10	30
BH-5140-62	"	2.0	140	14	20
BH-5141-62	"	.5	90	12	15

STREAM SEDIMENTS

SAMPLE #	LOCATION	METAL CONTENT IN P.P.M.			
		Mo	Zn	Cu	Pb
BH-5142-62	Millstream River System	1.5	120	14	15
BH-5143-63	Middle River	1.5	130	12	20
BH-5144-63	Cherry Brook	1.4	140	10	20
BH-5145-63	Six Mile Brook	1.7	180	16	20
BH-5146-63	"	2.3	190	16	15
BH-5147-63	Middle River	2.0	160	20	20
BH-5148-63	Little River	4.0	160	16	20
BH-5149-63	South Little River	1.8	450	18	35
BH-5150-63	Pabineau River	3.0	120	20	30
BH-5151-63	"	6.0	220	12	35
BH-5152-63	"	4.0	150	10	30
BH-5153-63	Sugary Brook	4.0	80	4	25
BH-5154-63	Roughwater Brook	7.0	130	8	45
BH-5155-63	Pabineau River	3.0	90	8	20
BH-5156-63	Trib. of Nepisiguit River	9.0	60	4	30
BH-5157-63	"	4.0	50	4	35
BH-5158-63	"	1.6	230	22	35
BH-5159-63	"	1.7	80	4	20
BH-5160-63	Pabineau River	2.5	120	4	20
BH-5161-63	Roughwater Brook	3.5	40	4	15
BH-5162-63	Little River	2.5	250	14	30

STREAM SEDIMENTS

SAMPLE #	LOCATION	METAL CONTENT IN P.P.M.			
		Mo	Zn	Cu	Pb
BH-5163-63	Trib. of Little River	10.0	120	4	35
BH-5164-63	Middle River	3.0	170	16	25
BH-5165-63	Little River	2.5	240	12	25
BH-5166-63	"	2.0	260	16	25