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MERCURY AND ARSENIC LEVELS IN LAKE SEDIMENTS FROM
THE CANADIAN SHIELD

BY

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ABSTRACT

Mercury contamination of particulate drainage system materials, i.e., lake, river and marine sediments, is a major concern of industrial nations. In studies of mercury pollution, it has been difficult to assess what is the natural abundance and variation in concentration of this element. A similar situation exists for arsenic. To date, these two elements, more than most others, have been associated with the new interest in environmental pollution. However, although studies of levels of these elements in polluted sediments have been made, there is a general lack of information on natural concentrations in uncontaminated sediments.

In Canada, the Precambrian Shield has a greater volume of fresh water than any other area of comparable size (about 5M sq. km.) in the world. This water, which represents about $\frac{1}{4}$ of the world's fresh water resources, is contained in millions of lakes, both large and small. Because most areas of the Shield have virtually no population, metal concentrations in these lakes are as yet largely unaffected by human activities. Assessment of levels of toxic elements, such as mercury and arsenic, in the sediments of these lakes provides vital information on the abundance and variation of these elements in uncontaminated environments.

Over the last three years lake sediments have been collected from a variety of geological terrains in the shield, during geochemical exploration programs. In particular, one very large sub-Arctic area of 94,000 square kilometres was systematically sampled during 1972. Lake sediments from this area have now been analysed for mercury and arsenic.

In some districts of the Shield, the concentrations of mercury and arsenic in the bedrock have been related to that in lake sediments. Mean concentrations measured in lake sediments are often higher than those in bedrock of the surrounding area although the latter usually have a more positively skewed distribution. Lake sediments accumulate heavy metals relative to bedrock sources principally because the disseminated sulphides in which the metals are mostly contained, are selectively weathered. Thus relatively more metals accompany rock flour and silts to a lake than were originally present in the bulk bedrock.

This effect is particularly significant in the forested regions of the Shield where accumulation of certain metals by sediments can be further promoted by the presence of organic colloidal materials which effectively scavenge them either directly from streams waters or indirectly via biogeochemical uptake by plants. There are well-defined areas where mercury concentrations in all lake sediments are high. Such areas are normally ones where sulphide ore occurrences are located. Such mineralization is selectively leached, enhancing the metal content of the nearby lake sediments.

Normal concentrations for mercury and arsenic in lake sediments from the northern part of the Shield within the Bear and Slave structural provinces, are commonly in the range of 10 to 50 ppb and 6 to 25 ppm respectively. Even in lakes near to sulphide occurrences, concentrations do not often exceed 100 ppb Hg. Background mercury concentrations rarely exceed 20 ppb; arsenic concentrations rarely exceed 5 ppm. However, maximum Hg and As values of 438 ppb and 58 ppm respectively were recorded in lakes near to a large, iron-rich weathered zone. Mercury anomalies (>20 ppb) were larger and more frequent in areas underlain by Proterozoic rocks. Arsenic anomalies (>5 ppm) were larger and more frequent in areas underlain by older Archean rocks, in particular Archean sedimentary-volcanic complexes.

In the southern part of the Shield, samples of sediments were collected from three mining areas in the Archean Superior and Southern provinces. In the nickel-rich Sudbury basin levels of Hg and As in the lake sediment cores at depth of 15-20 cm are in the range of 100 to 200 ppb and 4 to 8 ppm respectively. Highest levels found in surface sediment samples that are not thought to be related to industrial pollution are about 200 ppb Hg and 10 ppm As. These figures would represent elevated natural background levels characteristic of the region. In the copper-rich Chibougamau area, lake sediments with concentrations of about 100 ppb Hg are common. Here, even lakes in granitic terrain have levels of 30 to 50 ppb, twice greater than similar terrain in the Slave Province. In the Red Lake gold mining area, Hg and As levels are commonly in the range of 70 to 120 ppb and 20 to 40 ppm respectively. The elevated levels of Hg found in most lakes in all three of these widely separated mineral-rich areas in the Superior and Southern Provinces are likely related to the presence of such mineralization.

Detailed sampling of lake sediments carried out in two small lakes of the Grenville Structural Province indicates quite clearly that underlying and surrounding geological formations of differing rock types influence the nature and levels of trace metals found in the sediments. The presence of large accumulations of finely dispersed organic sediments does not override these distinctions but does, nevertheless, produce enhanced levels of mercury and arsenic relative to those found in surrounding host rocks. In the case of Hg, the main source rock appears to be Grenville marble which is known to contain some sulphides elsewhere in the immediate area. Such considerations are very important to the interpretation of metal distribution patterns outlined by regional scale lake sediment surveys.

TENEUR EN MERCURE ET EN ARSENIC DES SÉDIMENTS LACUSTRES DANS LE BOUCLIER CANADIEN

par

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RÉSUMÉ

La contamination par le mercure des matériaux particuliers dans les réseaux hydrographiques, c'est-à-dire les sédiments lacustres, fluviaux et marins, constitue un souci important des nations industrialisées. Il a été difficile dans le cadre des études de la pollution par le mercure d'évaluer la concentration naturelle de cet élément. La même situation existe dans le cas de l'arsenic. Jusqu'à présent, ces deux éléments, plus que tout autre, ont été associés à la pollution environnementale. Cependant, même si on a fait des études sur la teneur de ces éléments dans des sédiments pollués, nous connaissons très peu de chose au sujet de leur concentrations naturelles dans des sédiments non contaminés.

Le Bouclier précambrien au Canada est doté d'une quantité d'eau douce, plus grande que toute autre région de dimension comparable (environ 5,000 km²) sur la terre. Cette eau qui constitue environ un quart de toutes les ressources du monde en eau douce est contenue dans des millions de lacs, grands et petits. Comme la plupart des régions du Bouclier ne sont à peu près pas

habitées, les concentrations de métaux dans ces lacs n'ont pas subi les conséquences des activités de l'homme. La teneur en éléments toxiques comme le mercure et l'arsenic dans les sédiments de ces lac donne une excellente indication des différentes quantités que ces éléments présentes dans des milieux non contaminés.

Au cours des trois dernières années, on a recueilli dans le cadre de programmes d'exploration géochimique des échantillons de sédiments lacustres provenant de divers terrains géologiques du Bouclier. En 1972, on a procédé tout particulièrement à un échantillonnage systématique d'une vaste zone de 94,000 km² au sud de l'Arctique. Les sédiments lacustres de cette région ont maintenant été analysés en vue de déterminer leur concentration en mercure et arsenic.

Dans certaines parties du Bouclier, on a comparé des concentrations de mercure et d'arsenic dans la roche en place à celles des sédiments lacustres. Les concentrations moyennes mesurées dans les sédiments sont habituellement supérieures à celles de la roche en place avoisinante, même si leur répartition est souvent plus irrégulière dans ces dernières. Les sédiments lacustres accumulent les métaux lourds en fonction des sources qui se trouvent dans la roche en place principalement parce que les sulfures disséminés qui renferment la majeure partie des métaux sont altérés de façon sélective. Ainsi une quantité relativement plus grande de métaux que celle qui se trouvait dans la roche en place est transportée vers les lacs avec le silt.

Il s'agit là d'une constatation particulièrement importante dans les régions boisées du Bouclier où l'accumulation de certains métaux par les sédiments peut être accentuée par la présence de certaines matières colloïdales organiques qui à toute fins pratiques les accaparent directement dans les cours d'eau, ou indirectement par voie biogéochimique dans les plantes. Il existe des régions bien définies où les concentrations de mercure sont élevées dans tous les sédiments lacustres; on trouve habituellement dans ces régions des venues de minerais sulfurés. Ces minéralisations sont filtrés de façon sélective, ce qui rehausse la teneur en métal des sédiments de lacs avoisinants. Les concentrations normales de mercure et d'arsenic dans les sédiments lacustres de la partie nord du Bouclier, à l'intérieur des provinces structurales de l'Ours et des Esclaves, sont habituellement dans les 10 à 50 parties par milliard et 6 à 25 parties par million, respectivement. Même dans les lacs situés près de venues de sulfures, il est rare que les concentrations dépassent 100 parties de mercure par milliard. Les concentrations régionales du mercure dépassent rarement 20 parties par milliard, et celles d'arsenic rarement plus de 5 parties par million. On a cependant enregistré dans des lacs situés près d'une grande zone altérée riche en fer, des concentrations de 438 parties par milliard de mercure et de 58 parties par million d'arsenic. Les anomalies de mercure (>20 parties par milliard) étaient plus importantes et fréquentes dans des régions reposant sur des roches du Protérozoïque. Les anomalies d'arsenic (5 parties par million) étaient plus importantes et fréquentes dans des régions reposant sur des roches plus anciennes de l'Archéen, et plus particulièrement les complexes sédimentaires-volcaniques de l'Archéen.

Dans la partie sud du Bouclier, on a recueilli des échantillons de sédiments dans trois régions minières des provinces archéennes Supérieure et du Sud. Dans le bassin de Sudbury, qui est riche en nickel, les carottes de sédiments lacustres d'une profondeur de 15 à 20 centimètres renfermaient de 100 à 200 parties de mercure par milliard et de 4 à 8 parties d'arsenic par million. Les concentrations les plus élevées rencontrées dans des échantillons de surface et qui ne semblent pas être attribuables à la pollution

industrielle étaient d'environ 200 parties par milliard de mercure et de 10 parties par million d'arsenic. Ces données semblent représentatives de teneurs régionales élevées. Dans la région cuprifère de Chibougamau les sédiments lacustres présentent souvent des concentrations de 100 parties par milliard de mercure; dans cette région, même les lacs situés dans un terrain granitique ont des concentrations de 30 à 50 parties par milliard, soit le double des terrains semblables dans la province des Esclaves. Dans la région aurifère du lac Red les teneurs en mercure et en arsenic sont fréquemment de 70 à 120 parties par milliard et de 20 à 40 parties par million respectivement. Les teneurs élevées de mercure que l'on retrouve dans la plupart des lacs de ces trois régions riches en minéraux et éloignées les unes des autres sont sans doute rattachées précisément à la présence de ces minéralisations.

Un échantillonnage détaillé des sédiments de deux petits lacs de la province de Grenville indiquent clairement que les formations géologiques sous-jacentes et avoisinantes de divers genres de roche influencent la nature et la qualité de métaux à l'état de trace trouvés dans les sédiments. La présence d'accumulation importantes de sédiments organiques finement dispersés ne permet pas d'accorder plus d'importance à ces différences, mais produit quant même des teneurs plus élevées de mercure et d'arsenic que celles que l'on trouve dans les roches-mères avoisinantes. Dans le cas du mercure, la roche source principale semble être le marbre de Grenville qui renferme certains sulfures quelque part dans la région immédiate. De telles observations revêtent une très grande importance dans l'interprétation de la répartition des métaux révélée par les études de sédiments lacustres à échelle régionale.

MERCURY AND ARSENIC LEVELS IN LAKE SEDIMENTS FROM THE CANADIAN SHIELD

INTRODUCTION

A considerable amount of surficial geochemical information published in the earth-science literature is relevant to the detection and resolution of contemporary environmental contamination problems. Unfortunately, with its geological emphasis, such data are not readily accessible, or perhaps more specifically, they are not available in a technical form immediately useful to ecologists. Much of the work being carried out in Canada, and for that matter in most industrialized nations, on the toxicological effects of trace metals on fish, game birds, other wildlife and subsequently on man, has been restricted to regions where contamination has clearly resulted from industrial or urban-domestic activities. Examples of such studies in Canada are the investigation by the Department of the Environment (unpublished report) into a mercury pollution problem in certain waterways of the James Bay drainage basin; and a similar study presently continuing in the English River system of Western Ontario. In both cases industrial (chemical and paper-pulp) activities were designated as important sources of mercury contamination. Other research work has centered on air pollution and related soil pollution by heavy metals from ore smelters; for example, in the Sudbury, Noranda and Traill areas (Costescu and Hutchinson, 1972).

In all cases, it has proved very difficult, if not impossible, to accurately gauge the absolute degree and effects of increasing metal levels on environment materials. The point is that an estimate of the amounts of metals which were present in the system of interest before pollution is difficult to make after pollution onset. The elegant and extensive studies made by Thomas (1972; 1973) on mercury pollution in the Great Lakes and their sediments, have certainly defined the extent of that problem clearly; but even in this instance little attention has yet been given to a study of natural sources of mercury. Attention must eventually turn to tracing natural input of heavy metals from drainage systems of the Great Lakes.

The natural average background levels in lake sediments for metals such as mercury and arsenic are not determined so much by their content in economic ore bodies, but rather by their presence in varying amounts in rocks of all types and in the common and widely distributed non-economic sulphides such as pyrite and pyrrhotite. In regions where there is little or no known mining activity there may well be extensive undiscovered economic mineralization. Because actual ore grade accumulations may be deeply buried, they will make relatively little direct contribution by way of trace heavy metals to the drainage systems of the region. However, the science of exploration geochemistry has reached a stage where such concealed mineralization can be detected by sampling surficial materials such as soils, sediments, waters and rocks from within the encompassing drainage basin.

A fundamental assumption, on which reconnaissance geochemical drainage sediment surveys are in part based, is that the presence of many types of mineralization, whether economic or non-economic grade and size, are reflected by increased metal abundance levels. Statistical treatment of data derived from sediment samples collected over a wide area may well reveal favourable host rocks which are distinguished by higher average contents of the metals of interest than found in similar rocks in adjacent areas. In the broadest sense, such areas are sometimes referred to as geochemical provinces.

It is apparent then that the exploration geochemist and the environmental scientist may often be seeking the same information but from an entirely different motivation.

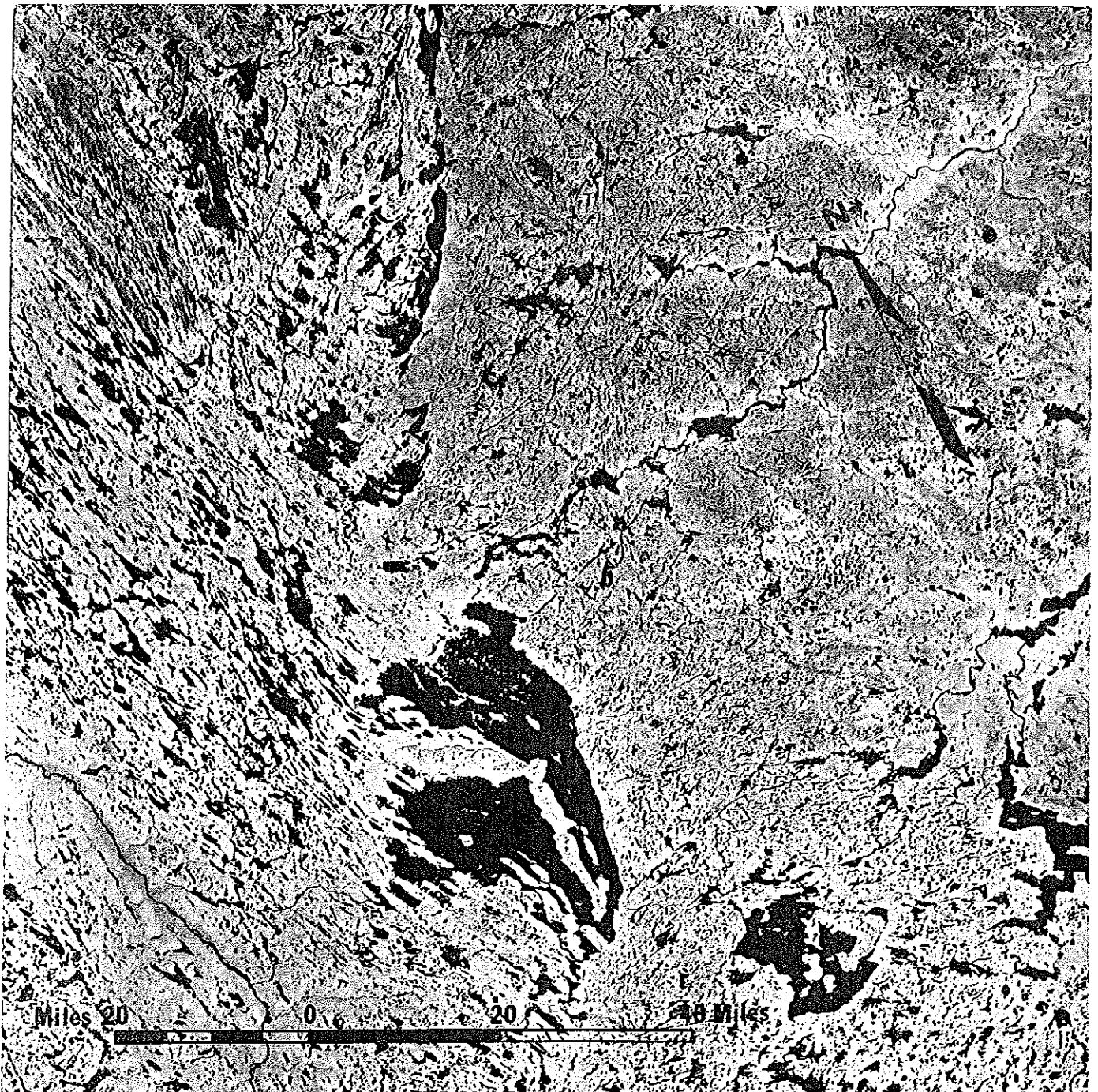


Figure 1. Typical shield terrain - photograph from Earth Resources Satellite of the central part of the Bear Structural Province (pers. comm. R. Slaney, Geological Survey of Canada): Lakes are black.

A knowledge of mean background variations for metal levels in geological materials, on either a large or small areal scale, provides on the one hand information on metal anomalous areas which may enhance chances of finding ore; and on the other hand, provides information on a locality where a threshold contamination situation may presently exist. Should mining eventually commence in this area then it is worthwhile having on file a knowledge of which metals may cause trouble if they were to be released into local water systems. The file would also provide an estimate of the "pollution buffering capacity" of the systems, i.e., how much more of a contaminant can be added before a danger level is reached.

The Canadian Shield contains more fresh water than any other area of the world of comparable size. Much of this water is held in myriads of lakes of all sizes (Fig. 1). Because many parts of the Shield are isolated and have a negligible population, metal concentrations in these lake sediments are subject only to *natural* geochemical processes. In these areas, determination of the abundance of Hg and As in such sediments provides indispensable background data for comparison with drainage sediment metal levels from lakes in the vicinity of long-established mining activity.

In the southern parts of the Shield, this problem of assessing background levels of toxic metals is more prevalent because the principal mining areas are already suspect in terms of heavy metal pollution. However, lake sediment sampling can readily provide the original pre-mining levels if sediment cores are collected and samples are selected from a horizon at a depth well below that which could have accumulated since the onset of mining activity.

STUDY AREAS

Bear and Slave Provinces

During the past three years, sediment samples have been collected from lakes within the Canadian Shield from several areas comprising a variety of geological terrains. During 1971, lake sediment and bedrock samples were collected in six areas, three in the Bear and three in the Slave Structural Provinces (Fig. 2) of the Canadian Shield (Allan, *et al*, 1972). Summary data on the geology and metallogeny of these six areas are given in Table 1.

In 1972, a helicopter based, systematic lake sediment survey which covered an area of 94,000 sq. km. (roughly the size of Portugal) of the sub-Arctic region of the Shield was carried out (Allan, *et al*, 1973).

The survey was designed to delineate metal anomalous areas within the much larger study area, with a view to enhancing the chances of discovering economic ore deposits, and to aid in the assessment of mineral resource potential in the Canadian Arctic. Data on the economically significant elements have been published as maps with marginal notes on interpretation (Allan and Cameron, 1973). Sediments from these six small areas and the one large area (Fig. 2) were further analysed for the accessory metals, mercury and arsenic, as it was realised that this would provide invaluable information on the abundances of these metals in the river and lake systems of a largely pristine environment; perhaps one of the last truly uncontaminated wilderness regions in North America.

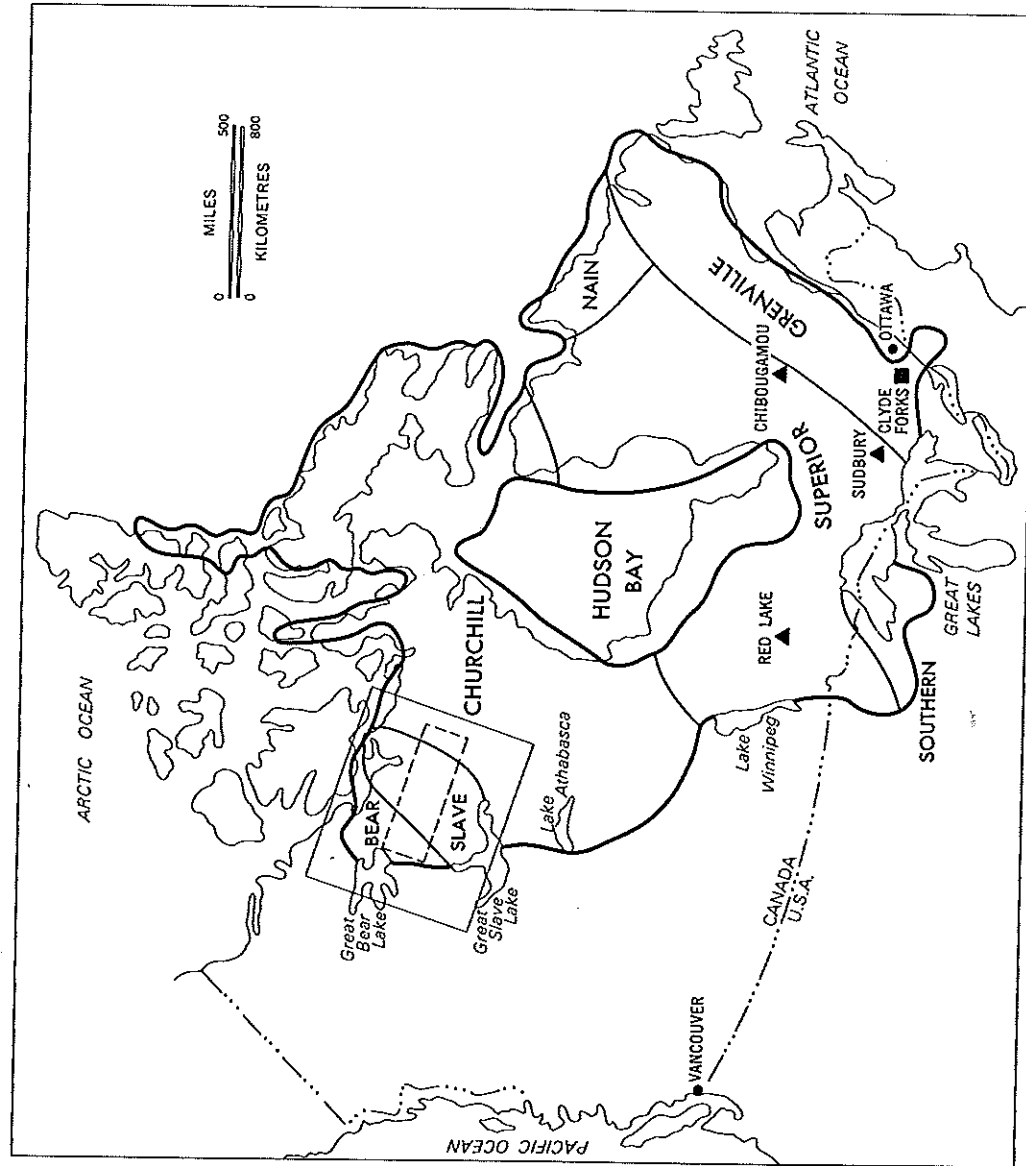
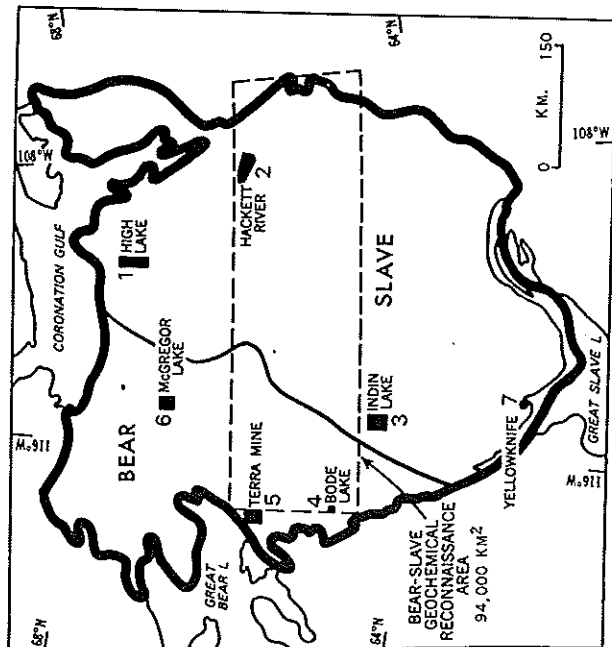


Figure 2. Lake sediment survey areas in the Canadian Shield



Bear-Slave Survey (see map for location)

STUDY AREAS	PROVINCE	AGE IN B.Y.S.
4, 5, 6	Bear	Proterozoic < 2.4
1, 2, 3, 7	Slave	Archean > 2.4
▲	Superior	Archean > 2.4
■	Grenville	Proterozoic < 2.4

Boundary of exposed Canadian Shield rocks...

Structural Province boundaries.....

TABLE 1

Summary geologic and metallogenic data for
selected study sites in the Canadian Shield.¹

BEAR PROVINCE	(Proterozoic)
<p><u>Terra Mines</u> complex mineralization yields native Ag and Bi, and Ni-Co-Fe arsenides, pitchblende (U), some chalcopyrite and sphalerite. Ore zones outcrop in a number of places.</p> <p><u>Bode Lake</u> area is relatively barren of sulphides. Minor sulphide occurrences in volcanic porphyries contain pyrite and chalcopyrite.</p> <p><u>McGregor Lake</u> region is well known for the presence of a layered ultramafic intrusion (Muskox Intrusion) within granitic rocks. Occurrences of Cu and Ni sulphides occur within it and around its periphery.</p>	
SLAVE PROVINCE	(Archean)
<p><u>High Lake</u>, Cu-Zn occurrence in acid-intermediate volcanic rocks. Contains estimated 5,200,000 tons 3.5% Cu and 2.5% Zn. Main sulphides are pyrite, sphalerite, chalcopyrite, galena, arsenopyrite. Oxidized iron cap (gossan) outcrops visible.</p> <p><u>Hackett River</u> area, Zn-Pb-Ag-Cu occurrence in acid volcanic rocks. Contains in excess of 10,000,000 tons 8% Pb-Zn and 300 ppm Ag. Main sulphides are pyrite, sphalerite, galena, arsenopyrite.</p> <p><u>Indin Lake</u> region is essentially devoid of significant sulphide occurrences. Basic intermediate and acid volcanic rocks sometimes display minor Au-pyrite, or chalcopyrite in quartz veins or shear zones. It may be regarded as a barren area.</p>	
SUPERIOR PROVINCE	(Archean)
<p><u>Red Lake</u> A Au mining area since the late 1940's. Au ores are associated with granitic intrusion into Archean sedimentary-volcanic sequence. Massive sulphide deposits of Zn, Cu, Pb, Ag may as yet be undiscovered in this area.</p> <p><u>Chibougamau</u> An area of Cu and Au mining since the 1960's. Ore zones associated with the presence of anorthositic intrusion, are extensive along zones of shearing and alteration. Zinc deposits with local lead concentrations also occur in the area.</p>	
SOUTHERN PROVINCE	(Archean)
<p><u>Sudbury</u> One of largest nickel producing areas of the world since discovery in the 1870's. Complex area of Ni and Cu containing Pt, Pd, Se, Te, Cu, Fe, Au, and Ag. Numerous ore zones extending to great depth associated with the Sudbury ultramafic irruptive, still of debatable origin. Pb and Zn deposits also occur within the basin.</p>	
GRENVILLE PROVINCE	(Proterozoic)
<p><u>Clyde Forks</u> Lake sediments were collected from one small area in the Grenville Province. This area, near Clyde Forks, consists of granites and marbles. The area has a small mercury occurrence of non-economic grade and some small barite veins. Auriferous pyrites and tetrahedrites are also known in the area.</p>	

¹See Figure 2 for location of study sites.

The large survey (referred to hereafter as Bear-Slave Survey) area lies within boundaries defined by latitudes $64^{\circ}30'$ to $66^{\circ}00'N$ and longitudes $106^{\circ}00'$ to $118^{\circ}00'W$. It is two-thirds underlain by continuous permafrost and one-third by discontinuous permafrost; two-thirds of it is tundra and one-third sparsely forested, mainly by spruce. The rocks of the western part are Proterozoic (>2.5 b. yrs.) age (Bear Structural Province) whereas the remainder consists of the older Archean (>2.5 b. yrs.) rocks (Slave Structural Province) (Figs. 2 and 3). Potentially economic heavy metal mineralization in the area is known only in the Hackett River area (Fig. 2) (Pb-Zn-Ag sulphides). Parts of the study area have been prospected for gold, others for uranium, small occurrences of which have been noted in the west.

In the study area relief is moderate to low and drainage generally consists of chains of interconnected lakes, often superimposed upon and controlled by structural geological features such as faults and topographic lineaments.

Superior Province

During 1973, lake sediment cores were taken from three established mining areas--Red Lake, Sudbury, and Chibougamau (Fig. 2)--in the forested, non-permafrost, southern Canadian Shield. These cores were collected with a view to using lake sediments as an exploration geochemical sample medium for such areas (Timperley and Allan, 1974; Allan and Timperley, 1974). Results for mercury and arsenic in lake sediment cores are presented later for selected sites. Mining activity commenced less than one hundred years ago at Sudbury and only recently at Red Lake and Chibougamau. It is unlikely that sediments found in cores at depths of greater than 10 cm. have been affected by industrial activity unless there has been severe downward leaching of surface materials. Summary data on the geology and mineralization in the three areas are given in Table 1.

Grenville Province

Although no regional scale surveys have been initiated by the Geological Survey in the lake systems of the Grenville Province, detailed geochemical process studies have been on-going in a small, closed drainage basin in the Clyde Forks area of Lanark County, Eastern Ontario. For the past four years, waters, sediments, soils and rock samples have been systematically collected in and around Lavant Long Lake and Perch Lake which ultimately drain to the Clyde River. From these studies it has proved possible to establish relationships between underlying and surrounding bedrock geology, and metal contents of waters and lake sediments. Mercury is of particular interest in the study area because of the nearby presence of a rare occurrence of cinnabar, HgS , in association with veins of various copper, nickel, zinc and arsenic rich sulpho-salts. The primary host rock consists largely of marble and dolomite. Other than the presence of this and other possibly similar sulphide occurrences, there is no other known source of mercury in what is otherwise a heavily forested wilderness area. Mining activity has been very minor and largely confined to sporadic pitting and trenching about the mercury prospect itself which lies nearly $2\frac{1}{2}$ km. south of Lavant Long Lake. Drainage from the prospect does not reach the lake. Summary information on the local geology of the two lakes is presented in Table 1.

SAMPLING AND ANALYTICAL METHODS

In the regional sampling programmes, helicopters or small fixed wing aircraft were used to reach sample sites. In the northern study areas, sediments were collected from near-shore, shallow water (<2 m deep) sites using an extension auger. Samples came from 3 to 10 cm below the sediment-water interface. In the survey of 94,000 sq. km., sample sites were located systematically at 5 km. centres. Most samples were inorganic, silty sediments. A sieved fraction (sub-63 μ) was recovered from an air dried sample and used for analysis. In the Superior Province, sample sites were reached by small fixed wing aircraft, and were normally located in the

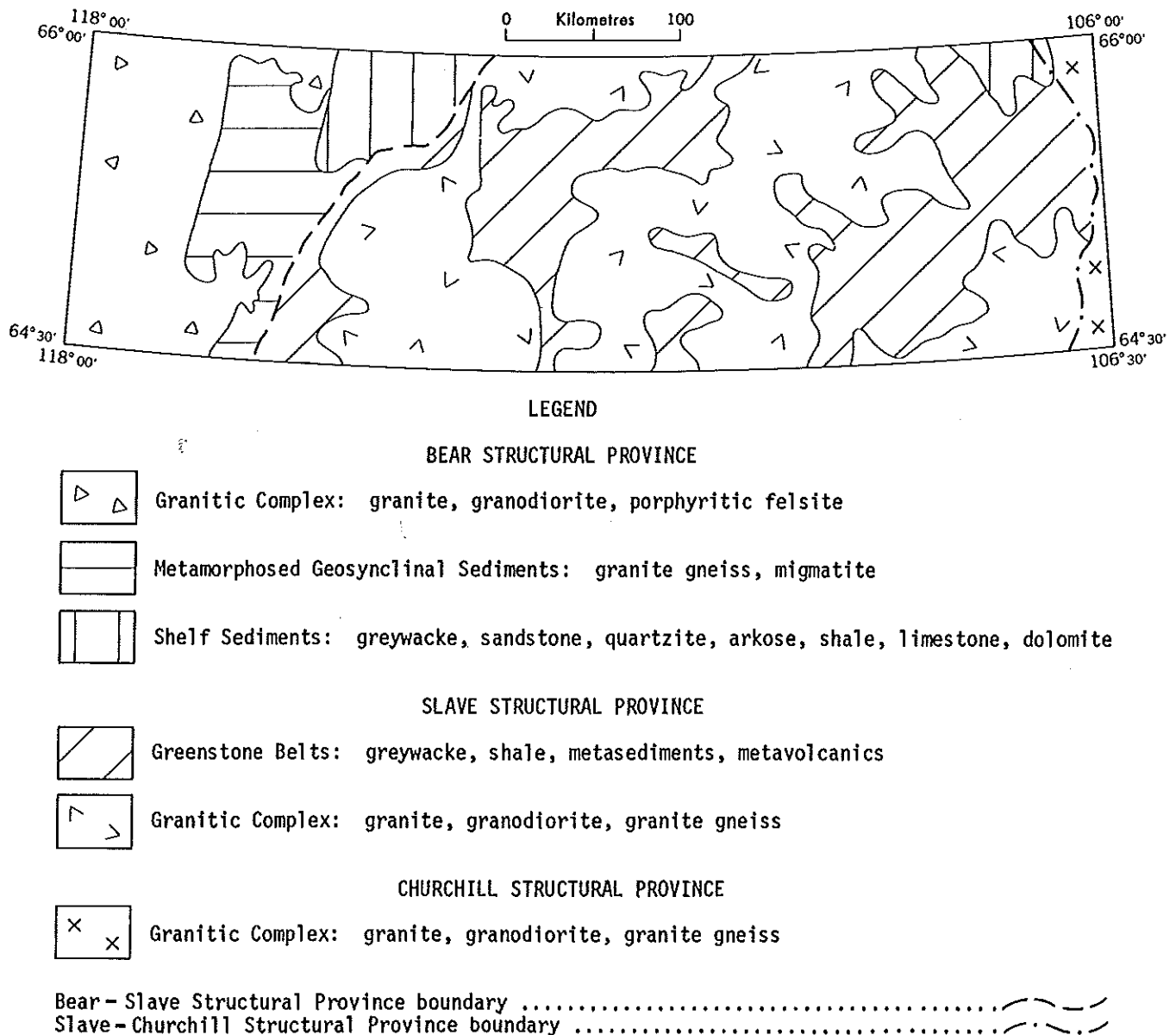


Figure 3. General geology of the Bear-Slave survey area.

centres of lakes. Core samples, collected using a Phleger sampler, were obtained up to 50 cm long. The samples in the southern Shield consisted of silts and clays or of organic oozes, and often of combinations of all these materials. Surface dredge samples of organic ooze and inorganic shoreline sediment were hand collected by scuba divers in the Clyde Forks area. No cores were collected in this area. The gel-like samples were air dried then pulverised before analysis.

Mercury was determined on all samples, sediments and waters, using the methods of Jonasson *et al* (1973). Arsenic was determined colorimetrically as follows. A weighed sample of <63 μ material was leached with 6M HCl at 90° C. for 1.5 hours. The test solution was centrifuged and an aliquot was then removed for As determination wherein As is reduced to the trivalent state with KI and SnCl₂ and then evolved as AsH₃ upon reaction with nascent hydrogen generated by addition of granulated Zn metal to the test solution. The arsine was scrubbed from the hydrogen stream into a solution of silver diethyldithiocarbamate. The color intensity of the arsenic complex so formed was determined at 520 μ using a Bauch and Lomb Spectronic 20 colorimeter and As content was calculated from a calibration curve. In this study, the detection limit for mercury in rock or sediment samples was around 2 ppb compared with a detection limit of 1 ppm for arsenic.

MIGRATION CHARACTERISTICS OF MERCURY AND ARSENIC

General Principles

Schematic illustrations of the principles of geochemical migration of trace metals are given in Figs. 4 and 5. In general, the sequence of events leading to the ultimate dispersion of metals into lake sediments is as depicted. The fate of metal ions, originally derived from chemical weathering and mechanical disintegration of host rock is controlled by innumerable factors involving atmospheric precipitation, water movement, soil movement, changes in redox and pH conditions, absorption-desorption processes, chemical complexation and precipitation and hydrolysis, uptake by and decay of vegetation and biochemical-bacterial interactions. Whether or not a specific flush load of freshly leached metal ions eventually reaches a lake system intact or widely dispersed, depends on the relative interplay of these factors.

Because of the different chemical and physical properties of mercury and arsenic compounds, each of these metals will behave differently with regard to the development and propagation of trace metal dispersion trains in waters, soils and sediments in terms of the above-mentioned factors. The successful detection and measurement of such dispersed metals depends principally on their individual migration characteristics and, very importantly, on their initial abundances in the host rocks or enclosed sulphides. Clearly, if a metal is somewhat rare, e.g., mercury, by comparison with others, e.g., arsenic, then much more sensitive analytical techniques need be employed to indicate its presence and abundance in dispersed sediments with meaningful precision. Table 2 briefly summarized typical abundance levels for mercury (Jonasson and Boyle, 1971) and arsenic (Boyle and Jonasson, 1973) in broad rock types many of which are common in the study areas. It can be seen that Hg is by far the rarer of the two elements in all rock types. This disadvantage is compensated for to a large extent by the existence of very sensitive and precise analytical schemes for mercury.

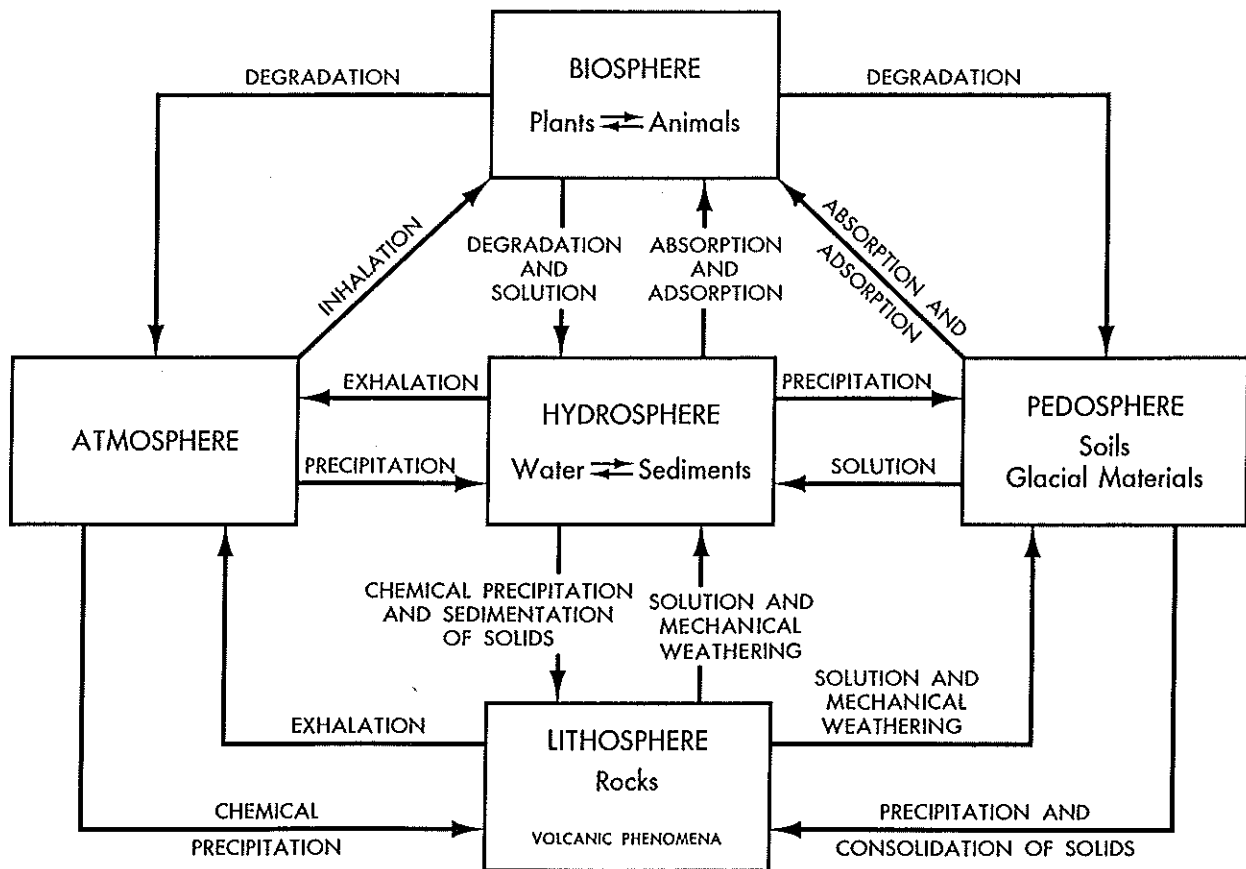
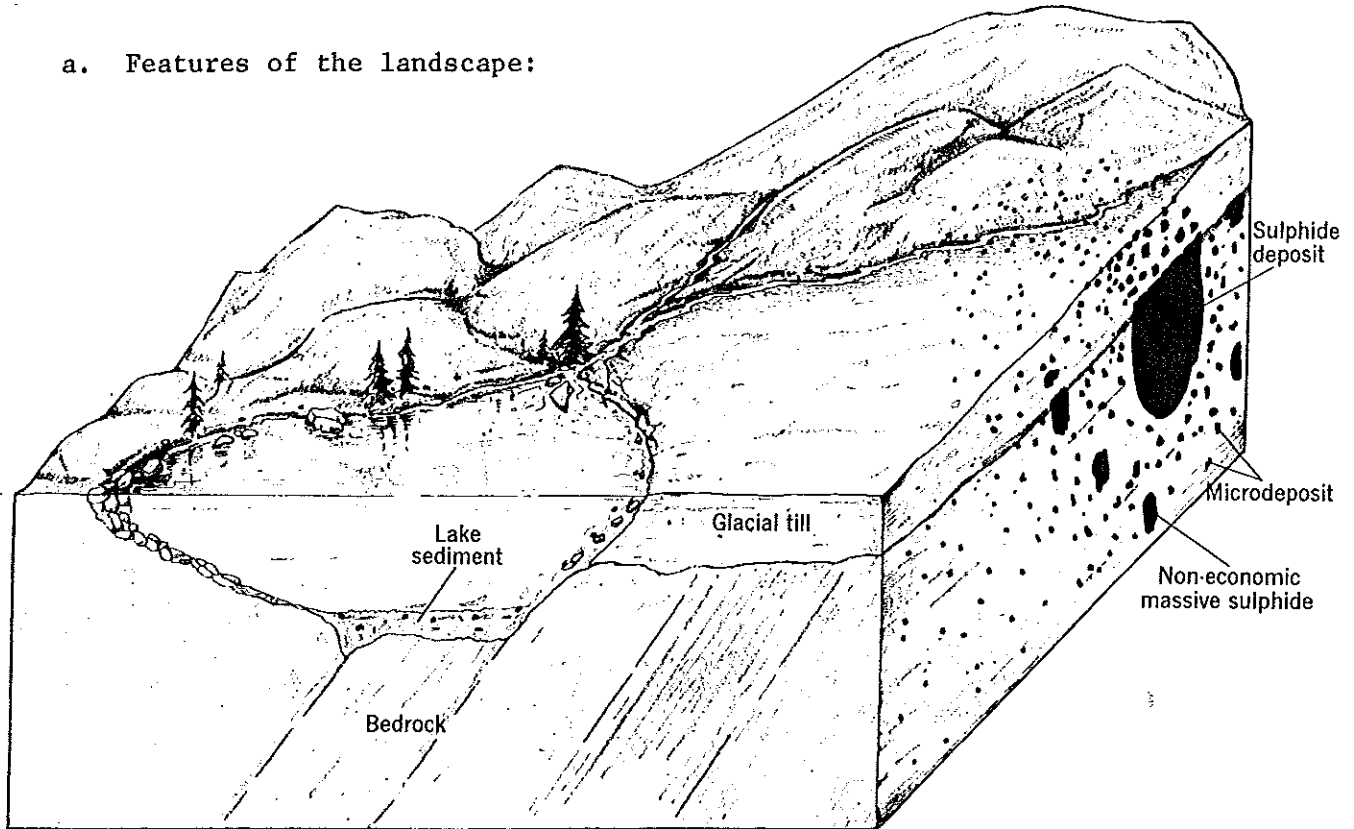


Figure 4. Generalized Heavy Metal Geochemical Cycles.
Influence of permafrost

One further factor which bears upon the migration of trace metals from rock sources to lake sediments is specific to all of the northern Shield study areas. This relates to the effects of freeze and thaw of permafrosted landscape. Most of the study areas can be regarded as being located in an arctic desert. Precipitation is limited to a few feet of snow in winter and an occasional autumn rainstorm. Thus the time of maximum water flow is early spring when normally dry streams replenish the lakes and carry in a good charge of suspended and dissolved materials, including trace metals in various forms.

It has been demonstrated in southern Canada that winter snow cover and the surface soil horizons accumulate soluble trace metal ions which can migrate through the soil surface from underlying unfrozen soils and rocks in quantities which indicate the presence of buried mineralization. The same processes of migration also take place in snow overlying deeply permafrosted ground (Jonasson and Allan, 1972). The overall effect is that build-up of trace metals takes place during winter, particularly so in the vicinity of sulphide mineralization, which is then flushed into stream systems in the spring thaw (Fig. 6). One important consequence is that the upper soil layers, or active zones as they are often referred to, are also leached clean of their winter accumulated trace metals. From the geochemists view-point, the main consequence is that sub-arctic and arctic surface soils or till are poor samples for mineral exploration studies

a. Features of the landscape:



b. The effect of dispersion on relative concentrations:

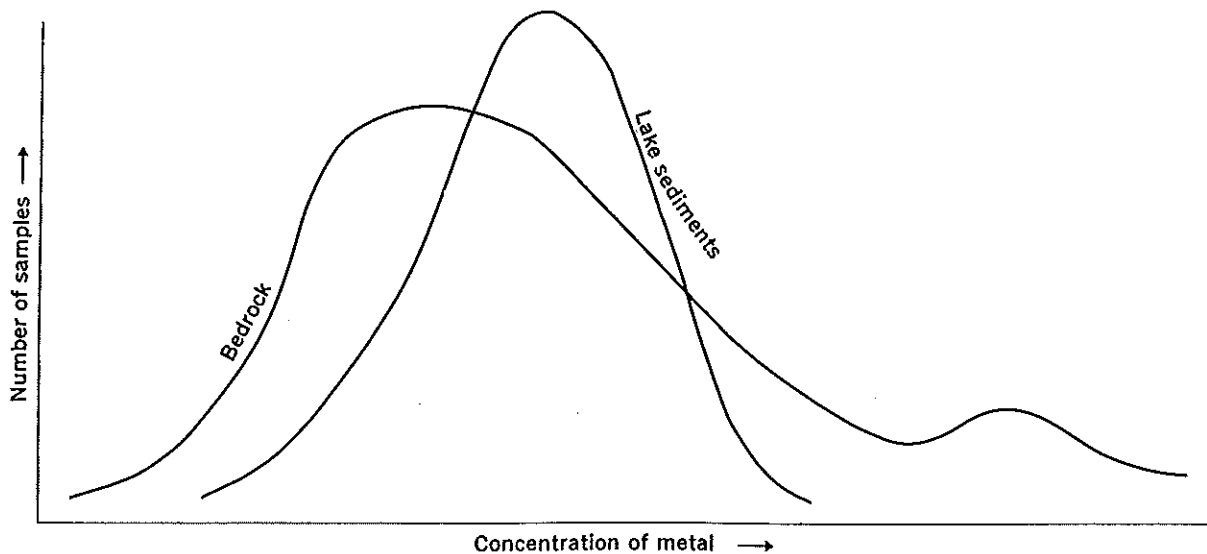


Figure 5. The dispersion process of metals into lake sediments

TABLE 2

Typical Abundance Levels for Hg and As in Rocks

Rock Type	Mercury (ppb)		Arsenic (ppm)	
	Range	\bar{X}	Range	\bar{X}
<u>IGNEOUS</u>				
Ultrabasic rocks (peridotite, pyroxenite, dunite, kimberlite, etc.)	7 - 205	168	0.034 - 15.8	1.5
Basic rocks:				
extrusives (basalt, etc.)	5 - 40	20	0.18 - 113	2.3
intrusives (gabbro, diabase, etc.)	5 - 84	28	0.061 - 28	1.5
Intermediate rocks:				
extrusives (latite, trachyte, andesite, etc.)	20 - 200	66	0.5 - 5.8	2.7
intrusives (granodiorite, syenite, diorite, etc.)	13 - 64	38	0.091 - 13.4	1.03
Acid rocks:				
extrusives (rhyolite, etc.)	2 - 200	62	3.2 - 5.4	4.3
intrusives (granite, aplite, etc.)	7 - 200	62	0.18 - 15.0	1.29
Feldspathoid rocks (nepheline syenite, phonolite, etc.)	40 - 1,400	450	n.d.	n.d.
<u>SEDIMENTARY</u>				
Sandstone, arkose, conglomerate	<10 - 300	55	0.6 - 120	4.1
Shale and argillite	5 - 300	67	0.3 - 500	14.5
Shales, black shales and pyritic shales (Helikian), N. Labrador, Canadian Shield	100 - 3,250	437	<3 - 500	17
Limestone, dolomite, etc.	<10 - 220	40	0.1 - 20.1	2.6
Iron formations and iron-rich sediments	n.d.	n.d.	1 - 2,900	-
Evaporites:				
Gypsum and anhydrite	<10 - 60	25	0.1 - 10	3.5
Phosphorite	n.d.	n.d.	3.4 - 100	14.6
Halite, Sylvite, etc.	20 - 200	30	n.d.	n.d.
<u>METAMORPHIC</u>				
Marble, crystalline, dolomite, etc.	10 - 100	50	n.d.	n.d.
Hornfels	30 - 400	225	0.7 - 11	5.9
Quartzite	10 - 100	53	2.2 - 7.6	5.5
Slate and phyllite	n.d.	n.d.	0.5 - 143	18.1
Schist	10 - 1,000	100	0.0 - 18.5	1.1
Gneiss	25 - 100	50	0.5 - 4.1	1.5
Amphibolite and greenstone	30 - 90	50	0.4 - 45	6.3

Note: \bar{X} is the arithmetic mean; n.d. = no data.

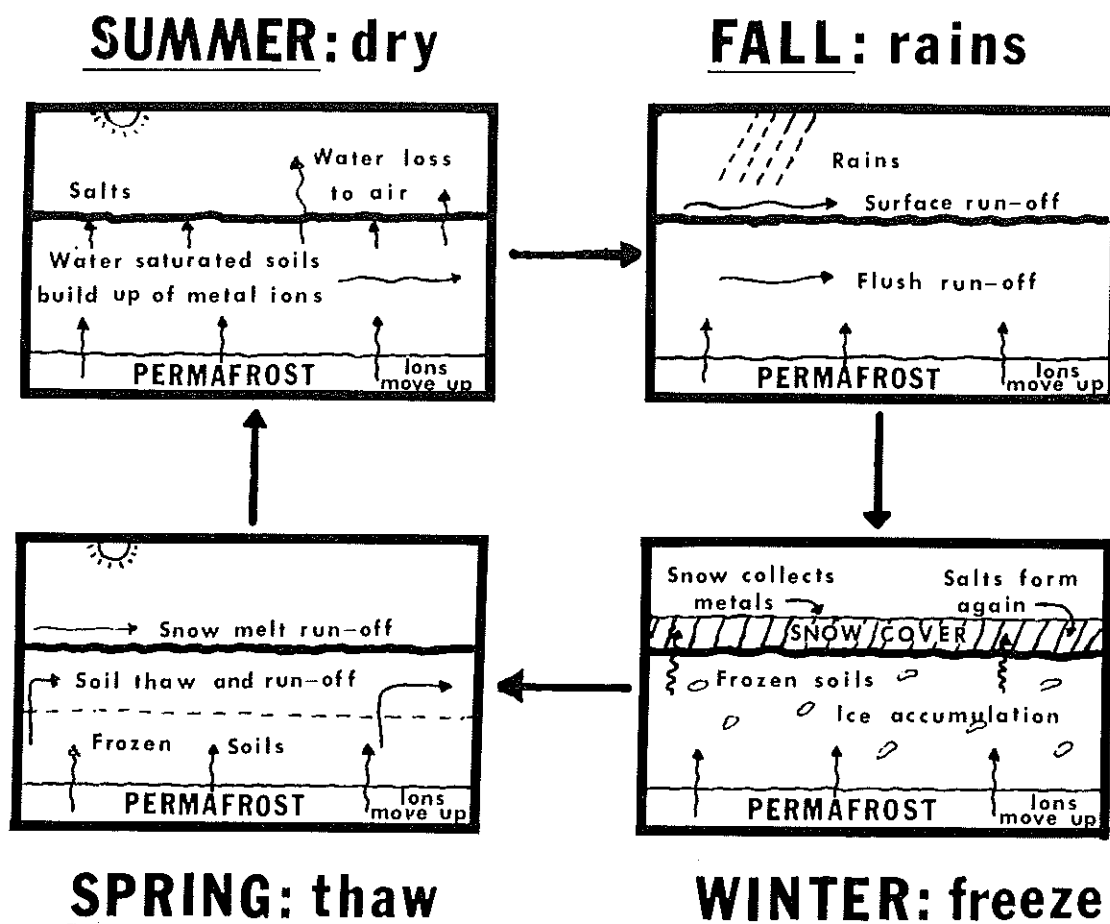
(Shilts and Ridler, 1973) certainly for the mobile elements. For the purposes of this discussion the main point to make is that certain trace metals are rapidly mobilized in essentially soluble form and subsequently deposited along with sediments into streams and lakes by the flush run-off waters. In northern Canada, there is a little by way of plant growth or humic complexing material to impede these processes. Soluble fulvic acid materials derived from tundra vegetation (Smirnov, 1972) undoubtedly are important in sustaining some trace heavy metals in solution during their mobilization (Bugel'skii, 1965; Bugel'skii and Tsimlyanskaya, 1966).

Influences of Environment

For the purposes of discussing environmental effects on dispersion of metals, the Canadian Shield can be divided into three major physiographic regions, on the basis of two dominant factors. The two factors are permafrost and vegetation. The three regions are tundra with continuous permafrost; coniferous forest with discontinuous permafrost; and coniferous-deciduous forest with no permafrost. Each region occupies about one third of the Shield area. In the northern two thirds, the effects of permafrost on the metal dispersion process are the most significant. These effects have been discussed above. However, even here, the increased organic contents of lake sediments, in moving from a treeless to a forested landscape, do influence drainage basin geochemistry. A more significant change is to be found in the southern third of the Shield, the area of coniferous-deciduous forests. Here, the major factor in metal dispersion in drainage systems is no longer the influence of permafrost related processes, but the presence of large quantities of organic debris, which owe their origin to the appearance to deciduous trees. There are several important consequences of these differences in vegetation cover. The first is that ground cover greatly restricts flow of metal ions and silts from rocks to streams to lakes. The same flush run-off effects characteristic of barren permafrost areas, will be dampened in tree-covered terrain. In the non-permafrost Shield the effect is further reduced. Soils and particularly humus soak up metals such as mercury, zinc, copper and to a lesser extent arsenic. Whether or not good dispersion patterns can be generated in lakes and streams in the Southern Shield begins to depend greatly on terrain relief. The higher the relief, the better the drainage, and the better the dispersion. A good flow of water will still transport significant quantities of fine silts derived from bedrock considerable distances.

The second consequence and at present of unknown significance is the contribution the decay of vegetation makes to materials which ultimately constitute significant percentages of the sediments in a lake. Plants take up metals from sub-surface sources and add them to the soils in the form of maturated dead-fall and leaves. Thus a biogeochemical accumulation of metals can result.

The third consequence which to some extent is dependent on the second concerns the fact that lake sediments in the southern parts of the Shield are largely organic-rich types containing usually 5 to 20% but occasionally as much as 40% carbon in some cases as opposed to the almost pure silt sediments of northern Shield lakes. The point is, however, that these organic materials become the principal transporters and scavengers of heavy metals, being especially efficient because of their colloidal form when washed out of soils into streams. By quite analogous processes which lead to the accumulation of metals in humic soil A horizons relative to the



Metal ion migration in permafrost: effects of season changes. The basic process by which ions move from permafrost upwards is probably ionic diffusion in solution. There is sufficient moisture in permafrost to allow capillary type migration to take place. In winter the advance of the freeze front down from the surface and up from the permafrost base causes metal cations (and anions) to concentrate in the frozen soils and subsequently to be moved to the surface, where carbonate and sulphate crusts may form; and to be moved into overlying snow. There is a continuous accumulation over the winter months in the upper soil layers. In spring the thaw flushes out a pulse of ions in the early runoff. Thaw occurs only from the surface down, so these processes may take several weeks to leach the frozen soils. In summer surface runoff has ceased, but subsurface migration may continue and carry dissolved material to the surface, where an ion build-up occurs again if the drought is long. Fall rains complete the cycle, resulting in a flush runoff which may be as intense as the spring thaw under certain conditions.

Figure 6. The effects of permafrost on metal dispersion processes

iron-rich inorganic B horizons, so do organic fractions of lake sediments accumulate metals preferentially. An enhancement relative to silt fractions for mercury in particular is therefore expected for trace metals in sediments which contain a few percent of organic matter. Arsenic which does not bind to organic matter as selectively as it does to iron-rich silts is much less likely to be affected. Only in extreme situations where the sediment consists of virtually nothing but organic matter will arsenic values rise significantly above local bedrock concentrations. Conversely, mercury (and zinc, uranium, copper, etc.) values in highly organic lake sediments will not be expected to closely resemble values found in surrounding source rocks. In the field situations described later the influences of organic matter, where they apply, will be noted.

One further point related to sediment transport which bears particularly upon the sampling of sediment cores in southern Shield lakes is that it is desirable to know something of sedimentation rates in typical Shield lakes. The following results are presented (R.J. Mott, G.S.C., - pers. comm.): for sediment accumulation over the last 100 years. During this time the areas were logged and subjected to agricultural development.

Lake Name	Location	Structural Province	Depth ¹
Pink Lake	Gatineau Park, Quebec	(Grenville)	8 cm
Quadrangle Lake	Sault Ste. Marie, Ontario	(Superior)	<10 cm
Thaneh Lake	Wawa, Ontario	(Southern)	<10 cm
Nungesser Lake	Red Lake, Ontario	(Superior)	<10 cm
Nineteen Mile Lake	Kirkland Lake, Ontario	(Superior)	<10 cm
Lac Louis	Temiscaming, Quebec	(Superior)	<10 cm

¹The depth given is for sediments accumulated in the lake since the surrounding area was first logged.

So it seems likely that in all the lakes where sediments were collected that samples taken from >10 cm beneath the surface probably pre-date mining or agricultural activity.

Migration of mercury and arsenic via sediments and natural waters

Mercury can move freely in surface water systems where pH typically ranges between 6.0 and 8.0. Most probably, uncomplexed metal is present as partly hydrolysed aquo-ions firmly adsorbed to fine clay, silicate and iron oxide rich particles. Limited amounts only will be free in solution because adsorption-desorption equilibria favour the solid phases. Organic colloids or similar fine particles, as well as soluble organic acids, will be competing for both free and surface-bound "ions" as well as their hydrolysates.

Mercury forms quite stable cationic coordination complexes with organic ligands whilst arsenic will more readily assume anionic forms under the same chemical conditions. Arsenates are rapidly precipitated by iron ions and iron-organic colloids which also act as adsorption traps for other metals. Thus dispersion of arsenic from its source rocks is likely to be more limited in extent than for mercury, unless locally high acidity in the waters prevails, when arsenic will be equally mobile. This latter case occurs when oxidizing sulphide mineralization is encountered by ground waters which wash out free sulphuric acid along with the liberated metal ions. These solution phase processes are commonly grouped together under the loose term "hydromorphic dispersion".

Alternatively, precipitation and irreversible adsorption processes are often lumped together under the term "mechanical dispersion". The common use of these terms unfortunately implies that two separate and completely unrelated dispersion processes are operative. The transportation of fine, unweathered sulphide particles and of rock flour also comes under the category of mechanical dispersion. Because mercury is the less abundant of the two elements and because of its relatively higher mobility, the already low amounts of mercury leached from source rocks will be so diluted that the detection of these specific sources becomes difficult. On the other hand, arsenic dispersion is considerably more local with regard to locating specific sources in the drainage basin.

Some recent work in our laboratories (Timperley, personal communication) has shown that dilute acid extractable zinc in sediments from all parts of the Bear-Slave study area accounts for some 80% of the total zinc in sediments as determined spectrographically. It has not yet been practicable to make a similar study for mercury, but in view of the close relationship of zinc to mercury mineralogically, similarities in migration behavior, and because of the similarity in dispersion patterns, a comparably high figure would be anticipated.

A number of other workers have made analogous studies on the distribution of certain metals between suspended loads and waters and find that high proportions of the total metal in question are carried on the suspensions. Kvashnevskaya and Shablovskaya (1963) showed that suspensions from rivers of Central Asiatic USSR draining mineralized areas containing Hg and As ores carried these elements in a distribution pattern which reflected the composition of the ores in the drainage basin. Stream dispersions enriched in metals were found at distances up to 35 km from ore deposits. In particular, the mercury content of suspensions in one river in Tadzhikistan near a mineralized zone ranged from 0.06 to 0.01% Hg in the vicinity of the ore zone. Skiba (1963) reported that mercury was carried in river suspensions mainly in the very fine fractions of the particulates and was therefore very mobile.

Chemical transformation of mercury

Mercury has been extensively studied with regard to its ability to form very stable organic complexes and organometallic compounds, but much less work has been done on its forms of occurrence in primary geological materials such as rock forming minerals. Even less data are available on its migration with the various intervening geochemical phases between parent rock and lake sediments. For the purposes of this discussion it is sufficient to merely note the work of Jensen and Jernelov, (1969) and

Wood, *et al* (1968) on the biogenesis of organomercurials in lake bottom muds. But even in the sediments of Arctic lakes which are relatively inactive biochemically (firstly, because of near-freezing water conditions and secondly, because the lake bottoms themselves are frozen solid for much of the year) it is likely that some conversion of inorganic forms of mercury to alkylmercury takes place. These effects may well be indicated by reported observations of above-average levels of mercury in fish from some very isolated lakes and rivers from other parts of the Northwest Territories (from unpublished data of the Fisheries Research Board of Canada). The origin of this mercury is almost certainly natural and local. It would be interesting to check mercury levels in fish from some of the lakes within the study area where the highest "mercury in sediment" values were found. Perhaps a correlation between biota levels and sediment levels may be found which can be interpreted unambiguously in terms of locally derived geochemical sources of the metal as outlined in this study.

Chemical transformation of arsenic

Studies of the natural chemistry of arsenic are much less advanced than in the case of mercury. Some very recent work by McBride and Wolfe, (1971), suggests that arsenic (III) can be methylated by bacteria and perhaps also by enzymic chemical means. But except in unusual circumstances of very high arsenic concentrations in organic-rich lake muds it is unlikely that arsine or its methyl derivatives could be detected and identified. In areas isolated from industrial or urban effluent, such as the Canadian Arctic, it is not anticipated that alkylarsines would represent a significant proportion of lake sediment arsenic. Rather, arsenic forms in lake sediments are probably confined to iron-rich oxide phases rendered inactive and quite immobile by precipitation and absorption processes. The amount of arsenic available, i.e., in soluble form, to biota is likely very limited in most natural systems. Arsenic is not known for its ability to form stable coordination complexes although there is some evidence that there may be some interaction between decomposing humic matter and arsenic in sediments which leads to remobilization of the element in river estuaries (de Groot, 1973). However, such abruptly changing conditions of water chemistry do not apply in more quiescent lake systems where the major chemical changes in arsenic geochemistry probably relate to shifts in the Eh regime between oxidizing and reducing conditions during spring and autumn turnovers of the hypolimnion. Arsenic held in iron oxide precipitates or other iron rich particulates would be converted into sulphide form, also immobile, under reducing conditions where hydrogen sulphide can be generated from organic matter. Ferromanganese nodules which may be generated by such fluctuations in redox potential are quite likely to collect arsenic, amongst other metals, if it is available in the lake system.

RESULTS AND DISCUSSION

The Shield is divided into structural provinces or geological provinces (Stockwell, 1971) which are considered to be of distinctive geological character. These major divisions are shown in Fig. 2 along with their respective age relationships. All parts are, by definition, of Precambrian age (i.e., older than 600 m.y.). Fig. 2 also shows the location of selected test sites and of areas surveyed on a regional basis, within the various geological structural provinces.

TABLE 3

Mercury and Arsenic Contents of Shales and Volcanic
Rocks from the Southern Canadian Shield.

Age	N	Hg. ppb				$\bar{X}C\%$	$\bar{X}S\%$	As, ppm	
		\bar{X}	G	M	S			\bar{X}	
<u>Archean</u>									
Red Lake	12	54	52	54	15	1.73	4.6	-	38
Atikokan	27	60	59	57	12	0.20	0.22	-	38
Lac des Iles	48	60	53	51	30	0.21	0.35	}	- 32
Beardmore	7	122	120	110	27	0.10	0.10		
Geralton	48	99	94	89	33	0.10	0.15		
Michipicoten	7	187	181	172	47	1.76	10.3	}	- 75
Oba	5	286	254	255	55	7.6	10.9		
Timmins	141	208	141	120	386	1.27	1.93	-	75
Matachewan	9	64	62	59	15	0.48	0.74	}	- 50
Larder Lake	47	100	89	78	57	0.19	0.17		
Kenojevis Rv.	11	82	80	76	19	0.16	0.14		
Desmeloizes	6	43	42	39	12	0.12	0.28	}	- 25
Amos-Barraute	9	87	79	63	44	0.39	0.10		
Chapais	29	80	76	79	24	0.30	0.16	-	25
Total Archean	406	129	94	86	238	0.74	1.25		
<u>Proterozoic</u>									
Whitewater	16	548	367	251	463	1.83	0.29	-	25
Gowganda	24	100	88	72	57	0.10	0.15	-	4
Gunflint	46	749	599	598	581	1.90	2.02	-	50
Rove	137	282	231	226	186	0.77	0.47	-	25
Albanel	38	400	308	274	391	5.1	3.71	-	38
Temiscamie	14	672	628	617	285	0.73	1.29	-	25
Attikamagen	50	649	545	596	415	2.05	2.07	-	25
Ruth	10	1021	1017	1030	97	1.09	0.12	-	38
Menihek	61	845	770	745	367	1.57	1.83	-	25
Total Proterozoic	396	513	368	408	426	1.61	1.37		
Archean volcanics									
Noranda, Quebec	98	8.4	7.2	5.5	6.0	-	-	-	-

Note: C is "organic" carbon (total carbon minus carbonate carbon).
 \bar{X} = arithmetic mean; G = Geometric mean; M = median; S = standard deviation; N = number of samples.

Previous studies of rock geochemistry within the Shield have shown that black shales of Archean age (>2.5 b. yrs.) have a distinctly lower Hg content than shales of Proterozoic age (<2.5 b.yrs.) (Cameron and Jonasson, 1972) (Table 3). Accordingly, because of the possible changes in average mercury and arsenic levels between various structural segments of this Precambrian block, the study areas are discussed below in terms of the Provinces in which they lie.

Bear and Slave Structural Provinces

Sampling at selected test sites

A geochemical orientation survey was conducted in 1971 at selected sites of areas between 150 and 750 sq. km. in the Bear and Slave Provinces (Fig. 2). The principal objective was to ascertain the abundance of trace metal levels in lake sediments and waters collected from points in the vicinity of known mineralization, as well as from several zones which are presently considered to be relatively barren of sulphides. Consequently, trace metal levels in lake sediments and waters representative of "natural contamination" situations and of normal low background situations are available. This work has been described in detail by Allan, *et al* (1972).

Information on mercury and arsenic levels in the sediments collected during this operation is summarized in Tables 4, 5, and 6.

The main features of these data are best illustrated by making comparisons between mineralized regions and unmineralized or "barren" regions. For example, mercury is higher in the mineralized High Lake region than in the unmineralized but geologically similar Indin Lake area (Table 5).

Inspection of Table 6 enables similarly relevant comparisons to be made for the water samples. Hg levels remain largely unaffected by the presence of nearby ore, a feature of some significance in a potential natural contamination system as represented by these ore showings. However, there appears to be a higher mean mercury content in waters from sites within the Proterozoic rock sequences than in the Archean, e.g., in the Terra Mine area and at McGregor Lake. This observation, which has been made for rocks and waters in other parts of the Precambrian Shield (Cameron and Jonasson, 1971; Hornbrook and Jonasson, 1971) is supported by higher average values for Hg in lake sediments derived from the Proterozoic rocks at Bode Lake (44.7 ppb), Terra Mines (31.6 ppb) and McGregor Lake (21.0 ppb) (Table 4), compared with sediments derived from Archean rocks at High Lake (25.2 ppb), Hackett River (19.7 ppb) and Indin Lake (14.3 ppb) (Table 5).

Thus, two geological influences on mercury levels are apparent. The first concerns the age and nature of the rocks involved and the second is whether or not sulphide mineralization is present. Both have significant impact and require the correct interpretation to yield meaningful data for exploration geochemists and environmental protection scientists alike.

Of additional interest is the presence of some elevated mercury values in unfiltered waters in the vicinity of Terra Mines, viz., 0.018-0.183 ppb, mean 0.056 ppb ($\mu\text{g/l}$). In general water samples from these regions contain about 0.01 ppb (Table 6). Analyses of selected samples from the native Ag-Bi ores show that the mercury content is of the order of 0.5% and in copper rich sulphides the average content is about 0.1%. The content in silver-rich ramellbergite, a nickel arsenide, is somewhat less at 8 ppm. The mercury contents of nearby lake waters may well reflect the relatively high mercury values noted in the ores and possibly their host rocks.

TABLE 4

Mercury (ppb) and Arsenic (ppm) in rocks and lake sediments from areas in the Bear Structural Province of Proterozoic age.

Element	Area and rock type	Number of samples	Arithmetic mean	Standard deviation	Geometric mean	Range
Hg	Terra Mine, rocks	65	7.4	2.6	6.9	-
	lake sediments	39	31.6	19.7	28.3	12 - 138
As	Terra Mine, rocks	65	6.2	9.1	4.1	-
	lake sediments	36	<6	-	<6	<6
Hg	McGregor Lake, rocks	-	-	-	-	-
	lake sediments	12	21.0	6.6	20.1	13 - 35
As	McGregor Lake, rocks	-	-	-	-	-
	lake sediments	12	-	-	-	<6
Hg	Bode Lake, rocks	57	6.0	2.0	5.6	-
	lake sediments	12	44.7	17.3	52.2	31 - 87
As	Bode Lake, rocks	57	3.1	0.4	3.0	-
	lake sediments	10	<6	-	<6	<6

The environmental effects on mercury and arsenic contents of lake sediments are superimposed upon contributions from mineralization in the Terra Mines area. Both Terra Mines and Bode Lake lie below the tree-line and the comparison between mercury in rock data and sediment data reflects this. However, the rock data for mercury may not be a true reflection of the mercury potential of the area because the mineralization is of a vein-type rather than a stratabound type with which disseminated sulphides are more commonly associated. Consequently, lake sediment sampling is more likely to give a reflection of mineralization because of the averaging nature of the processes which generate the samples, than do rock samples for reasons noted earlier. Similar considerations may apply for Bode Lake where the mineral potential is still largely unknown. Terra and Bode areas lie within a regionally higher mercury area [locate Terra and Bode areas (Figure 2) on Figure 8].

In the High Lake area, it was possible to determine mercury levels in a lake near a series of recently outlined but as yet undeveloped ore deposits. The presence of deeply weathered, sulphide mineralization is often visible in northern Canada as bright red, or orange coloured, soils and crusts. Nearly all of the known ore zones in the northern parts of Canada have associated with them such weathered zones which, consequently are often targets for detailed exploration activity. This activity usually involves trenching with bulldozers, or diamond drilling. Trenching greatly increases the surface area of weathered material exposed to natural leaching processes. Drilling, even in permafrost areas, can result in ground water

TABLE 5

Mercury (ppb) and Arsenic (ppm) in rocks and
lake sediments from areas in the Slave
Structural Province of Archean age.

Element	Area and rock type	Number of Samples	Arithmetic mean	Standard deviation	Geometric mean	Range
Hg	High Lake, all volcanics	94	20.8	57.6	9.7	-
	basic	22	15.9	29.6	8.5	-
	intermediate	54	11.0	7.1	9.3	-
	acid	16	41.3	112.7	10.2	-
	lake sediments	31	25.2	14.2	22.4	11 - 775
As	High Lake, all volcanics	94	5.5	7.9	3.8	-
	basic	22	5.0	6.2	3.8	-
	intermediate	54	4.7	7.1	3.5	-
	acid	16	6.9	8.5	4.7	-
	lake sediments	35	7.0	-	-	<6 - 25
Hg	Hackett River, all rocks	37	17.5	18.6	14.6	-
	lake sediments	28	19.7	11.7	17.4	10 - 53
As	Hackett River, all rocks	37	4.9	11.0	3.3	-
	lake sediments	28	<6	-	<6	<6 - 6
Hg	Indin Lake, all volcanics	109	10.5	5.9	9.2	-
	basic	55	8.5	5.9	7.4	-
	intermediate	21	12.3	6.9	11.1	-
	acid	31	13.3	2.7	13.0	-
	sedimentary	81	10.3	3.7	9.8	-
	granites	5	4.0	2.8	3.3	-
	lake sediments	35	14.3	5.0	13.8	10 - 40
As	Indin Lake, all volcanics	109	3.8	3.6	3.3	-
	basic	55	4.0	4.5	3.3	-
	intermediate	21	3.9	3.0	3.4	-
	acid	31	3.5	2.2	3.2	-
	sedimentary	81	16.9	11.7	12.4	-
	granites	5	3.4	0.9	3.3	-
	lake sediments	33	9.0	-	-	<6 - 50

TABLE 6

Some typical trace metal data for Hg in
unfiltered lake waters from Sub-Arctic Canada.

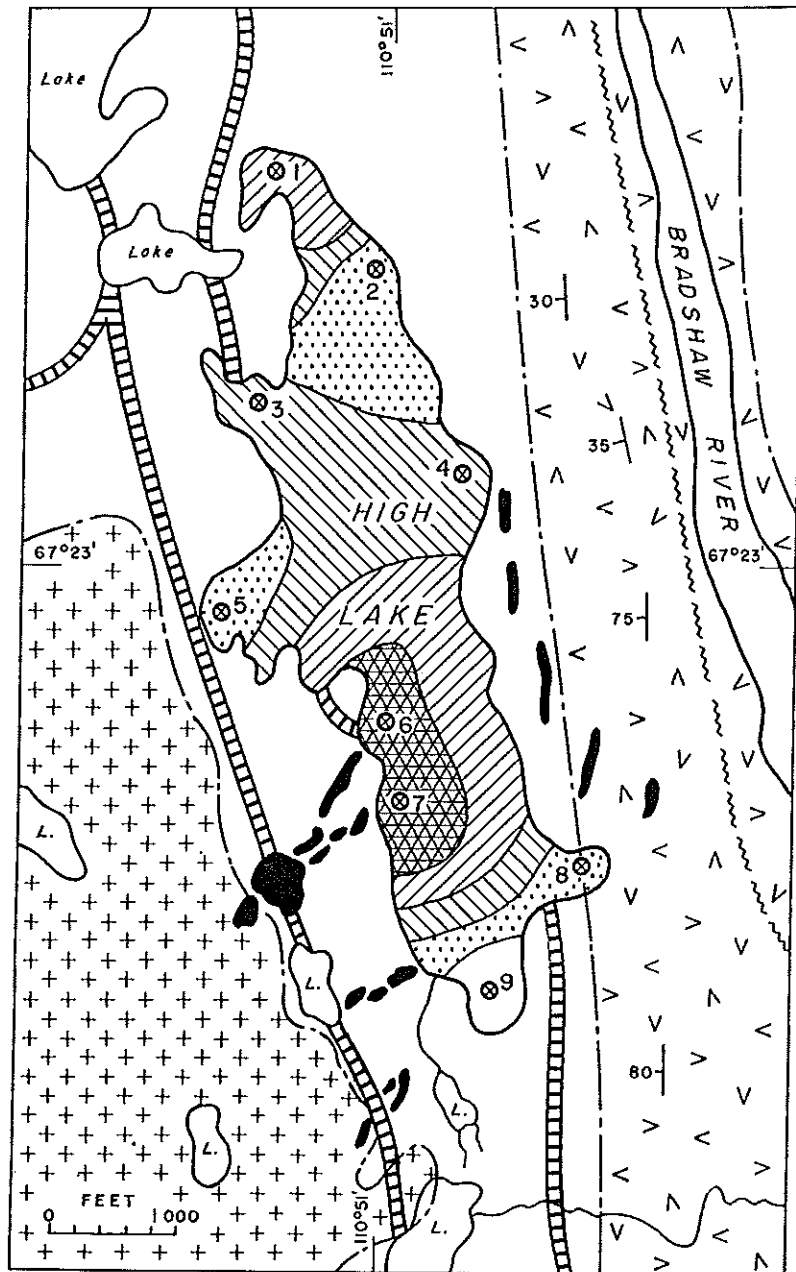
Sample area ¹ location	Mean metal content (ppb): lake waters near ore zones		Mean metal content (ppb): lake waters remote from ore zones	
	No. samples	Hg	No. samples	Hg
Hackett River	3	.016	28	.021
High Lake	9	.022	32	.010
Indin Lake	-	-	35	.007
Terra Mines	15	.056	25	.006
Bode Lake	-	-	12	
McGregor Lake	-	-	12	.024

¹See Table 2 for description of geology and mineralization.

reaching the surface via the drill holes. Because of the vast number of lakes found in the Canadian Shield, these weathered zones are never far from water and in many cases appear to be on the edge of a lake and to drain directly into it. Such a zone exists at High Lake (lat. 67°33'N; long. 110°51'W) where a Cu-Zn ore deposit of some 5 million tons of 3.5% Cu and 2.5% Zn has been outlined.

The very high concentrations of several trace elements in High Lake itself could well be due to any or all of the following factors: the presence of the ore deposit; the occurrence of ore zones beneath High Lake which could supply highly mineralized groundwaters to the lake; the increased flow of trace elements into the lake due to man's exploration activities. Relative to surrounding lakes in the same area, the levels of trace elements such as copper (Fig. 7) in High Lake in both sediment and water are very high. However, as shown in Fig. 7 the mercury levels although higher than many regional concentrations in the Slave Province (Table 5), only exceed the highest level found at Indin Lake, a non-mineralized area, by 44 ppb Hg. Some recent work on the mercury content of base metal sulphides in the Shield (Jonasson and Sangster, 1974) indicates that mercury is present in ores from High Lake at quite low levels (e.g., 5.1 ppm in copper sulphides). In fact the mercury content is typically low for such Archean ores. It is not unexpected therefore that mercury does not attain greatly elevated levels in nearby lake sediments, particularly in view of the fact that there is little organic material available in tundra terrain to provide a medium for accumulation of mercury. This latter observation is supported by the similar mercury data found for rock samples and lake sediments. The same case can be put for the Hackett River area described below.

In 1973, several of the mercury and arsenic anomalies outlined in the Hackett River area in the east of the Slave Province (Figs. 8 and 9) were resampled in greater detail by Cameron and Durham, (1974). This work revealed that the concentrations detected previously by the reconnaissance survey were reproducible and moreover, showed that yet higher values were common in areas of suspected mineralization. Levels of mercury and arsenic



COPPER CONCENTRATIONS IN PARTS PER MILLION
 [Cross-hatched] >7000 [Diagonal lines] >5000 [Horizontal lines] >3000 [Dotted] >1000 [White] <1000

ROCK TYPE
 [Box with +] Diorite [Box] Felsic volcanics [Box with wavy line] Tuff, chlorite schist

Geological boundary... [Dashed line] Dip of rocks... 30° [Line with 30] Fault... [Wavy line]
 Diabase dyke... [Line with wavy line] Gossan (weathered iron rich zone)... [Thick black line]
 Sample location and number.... [Circle with dot] 2

Site No:	1	2	3	4	5	6	7	8	9
Hg in ppb:	48	19	20	43	34	67	94	26	23

Figure 7: Mercury and Copper distribution in High Lake.

were highest close to a possible site of mineralization.

At the pristine site located by Cameron and Durham (1974) levels for As in close proximity to mineralization were up to 394 ppm (Fig. 10).

Bear-Slave regional survey

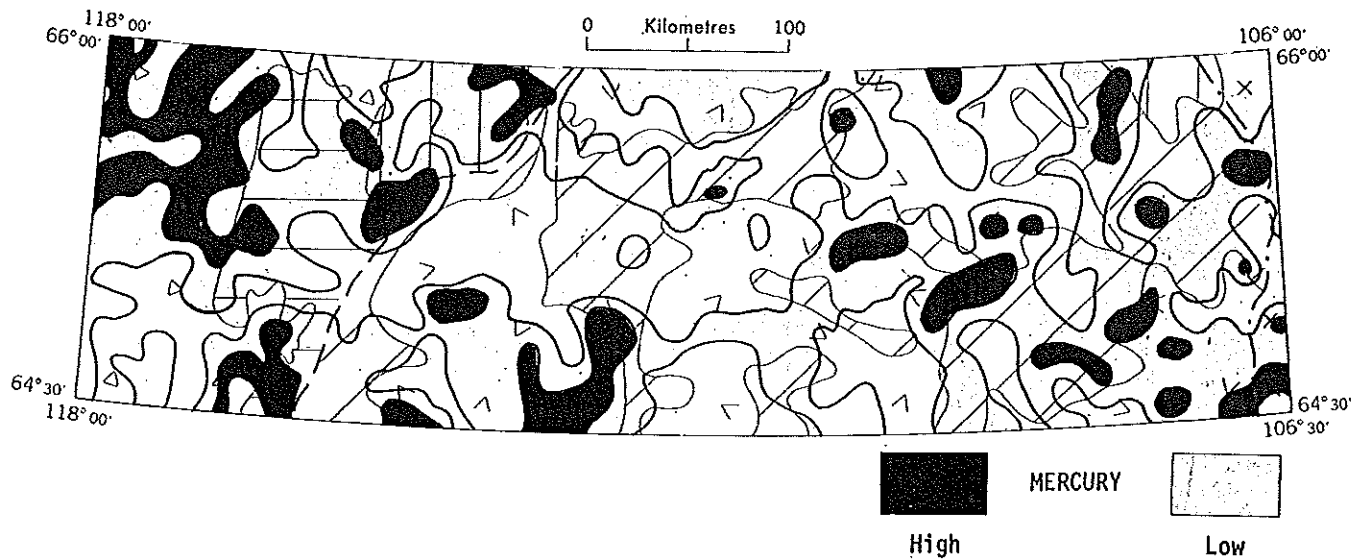
Abundance contours for Hg and As from sediments collected regionally are presented as superimpositions upon a geological base map of the study area (Figs. 8 and 9). Summary data on concentrations are presented in Table 7 for each of three sections (map sheets of the area. These equal area map sheets are numbered 1 to 3 from west to east. Sheet 1 is in the Bear Province, sheet 2 and 3 in the Slave.

Mercury distribution:

The regional distribution of mercury in lake sediments is displayed in Fig. 8. Generally the mercury contents of sediments derived from these granitic and volcanic rock types should be regarded as low. What highs do occur are to be found mainly in the north-west part of the area (See mean Hg, Table 8, Sheet 1) in what is known as the Great Bear Batholith - complex area of Proterozoic granitic and volcanic rocks but where there are relatively large areas of volcanic rocks which were deposited subaerially. These groups of elevated mercury levels (Fig. 8) are terminated to the east rather abruptly by a fault zone and to the south by a presently undefined geological feature. Mercury occurrences would appear to be genetically related to the distributions of lead, zinc, copper and perhaps uranium (Allan & Cameron, 1973), a situation which is not uncommon in ore geochemistry (Sears, 1970). There is an antipathetic relationship between mercury and arsenic (Figs. 8 and 9) in the region. The fact that mercury is most abundant in the Proterozoic rocks is interesting. As has already been noted, it is considered by some writers (Cameron and Jonasson, 1971; Jonasson and Sangster, 1974) that a definite mercury thumbprint exists in certain Proterozoic rocks and ores of the Canadian Shield which is quite characteristic of them. Such a feature is generally missing from the more ancient Archean rocks, although there are some notable exceptions in other parts of the world's shields, for example, in Rhodesia (Robertson, 1972).

Some mercury highs occur to the east of the Bear Province overlap some copper-lead anomalous areas. These are considered to be prospective targets for the discovery of base metal mineralization. The presence of increased mercury, lead and zinc may well reflect such concealed mineralization. The central part of the study area is one of low metal tenor.

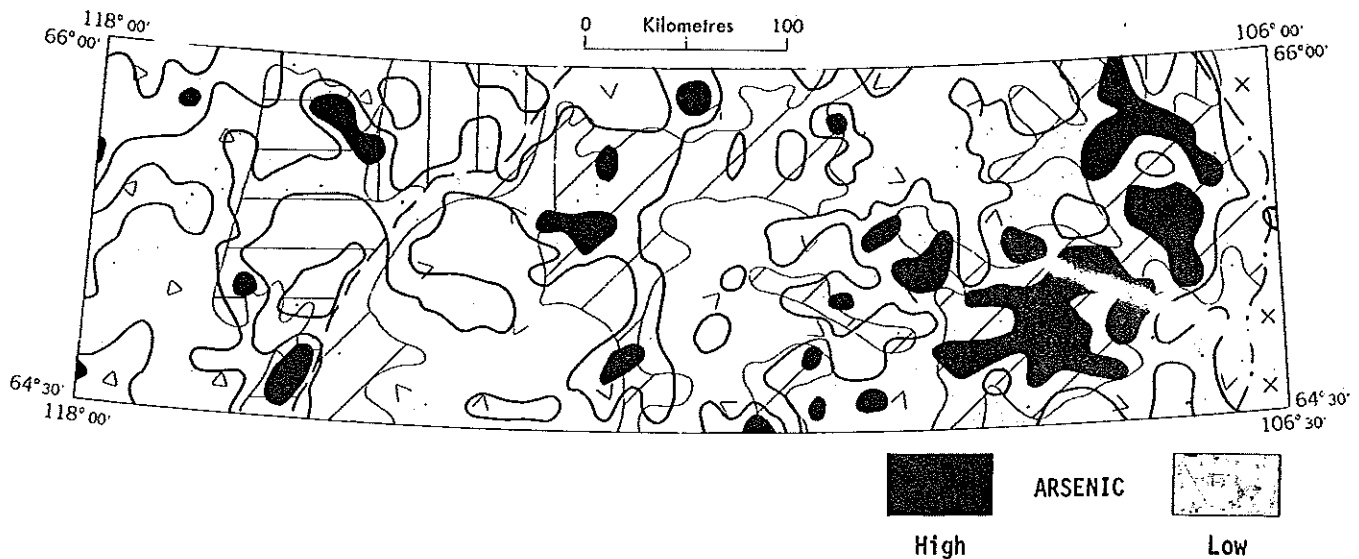
In the eastern part of survey area (Archean) high mercury values appear to be related to volcanic rocks, some of which have not been recognised unambiguously during earlier geological mapping. During Archean volcanism, solutions containing a variety of heavy metals poured into the seas surrounding volcanic centres, causing the precipitation of iron sulphides and carbonates, enriching those materials plus more normal sedimentary strata in heavy metals. The sediments, around these acid volcanic centres may often be enriched in mercury. An example of such volcanic exhalation sediments are the widespread pyrite-gold occurrences above acid volcanic rocks in the south east of the survey area. This zone is enriched in mercury and also in arsenic. In other parts of Sheet 3 the high mercury contents are more likely related to zinc mineralization of exhalative origin.



For key to geology see Figure 3.

High - greater than 20 ppb. Low - greater than 10 ppb.

Figure 8. Mercury in ppb in Lake Sediments: Bear-Slave Survey Area.



For key to geology see Figure 3.

High - greater than 5 ppm. Low - greater than 2 ppm.

Figure 9. Arsenic in ppm in Lake Sediments: Bear-Slave Survey Area.

TABLE 7

Mercury and Arsenic Concentrations in Lake
Sediments from the Bear-Slave Study Area.

AREA	STATISTIC	Hg (ppb)	As (ppm)
Sheet 1: by area	arith. mean	16.8	2.0
80% Proterozoic Bear Province:	std. dev.	18.2	1.68
20% Archean Slave Province:	log. mean	1.106	0.179
1241 samples	std. dev.	0.297	0.350
	geom. mean	12.8	1.5
	minimum value	1	0.1
	maximum value	210	26
Sheet 2: by area	arith. mean	12.0	2.4
90% Archean Slave Province:	std. dev.	14.6	2.23
10% Proterozoic Bear Province:	log. mean	0.988	0.254
1294 samples	std. dev.	0.262	0.355
	geom. mean	9.7	1.8
	minimum value	1	0.1
	maximum value	438	35
Sheet 3: by area	arith. mean	13.5	3.8
90% Archean Slave Province:	std. dev.	13.5	4.52
10% Proterozoic Churchill Province:	log. mean	1.049	0.353
1349 samples	std. dev.	0.253	0.472
	geom. mean	11.2	2.3
	minimum value	0	0.1
	maximum value	308	58

Some interesting figures are available for some ore zone sulphides collected from the Hackett River (Fig. 2) zinc-lead occurrence. Two sphalerites (ZnS) contained 14.4 ppm and 27.8 ppm Hg respectively; 50 ppm and 400 ppm As respectively. One sample of pyrite ore contained in excess of 2% As (Jonasson and Sangster, 1974). Thus the types of base metal sulphides, (Cu, Zn and Pb), which are shown to occur in ores in the Archean part of the study area can be regarded as being relatively enriched in both arsenic and mercury and should generate measurable secondary dispersion haloes of these metals into lake sediments. This is indeed the case.

Arsenic distribution:

Arsenic has been mentioned previously with regard to its relationships with mercury and gold in Archean volcanic-sedimentary rocks of the study area. Arsenic levels (Fig. 9) in the west (Proterozoic) of the area are approximately one-half of those measured in the gold-bearing regions to the east. Possible sources of arsenic (as sulphides and arsenides) may be confined to rare occurrences of vein-type silver mineralization such as are found just west of the limits of the study area near Terra Mine (Table 4) (Fig. 2).

The summary data of Table 7 show a steady increase in the mean arsenic content of sediments sampled from west to east. None of the arsenic means are particularly high. It seems likely from the distribution patterns of individual high samples that arsenic occurrence will be confined primarily to areas of disseminated sulphides, or of vein sulphide zones; and furthermore that the degree of surficial migration of arsenic from its sources is much more limited in extent relative to mercury. Arsenic is somewhat unique amongst metals and metalloids in that it rarely occurs in quantity in the absence of sulphide minerals. Details of this aspect and other relevant geochemistry of arsenic with respect to its occurrence and environmental migration characteristics have been outlined by Boyle and Jonasson, (1973), and need not be reiterated here.

Further to the south in the Yellowknife area of the Slave Province (Fig. 2) economic accumulations of gold are mined. These deposits (Boyle, 1961) contain native gold in close association with arsenopyrite in quartz veins and shears. Smaller occurrences of similar materials are widespread throughout the volcanic rocks of the Yellowknife region. In 1972, a lake sediment survey of areas surrounding Yellowknife city to the north and west was sponsored by the Department of Indian Affairs and Northern Development (Nickerson, 1972). Arsenic was amongst a series of elements sought in the sediments because of its specific genetic relationship to gold mineralization which occurs in these areas. It is enlightening to compare values reported for arsenic in the vicinity of the city of Yellowknife and its gold ore roasting plants, with those found in similar geological terrains, viz., volcanics, at the extremities of the survey area (3200 sq. km.).

It seems clear that arsenic levels which reach 300 ppm close to Yellowknife contain a significant contribution from industrial contamination. However, more typical elevated arsenic levels are in the range 15 to 60 ppm. Inspection of Nickerson's data reveals that baseline levels are probably in the range 4 to 40 ppm and that these are the typical arsenic values which would be characteristic of lakes in close proximity to gold mineralization, non-economic or otherwise. Such values are observed near Prosperous Lake some 25 km to the northeast of Yellowknife (Fig. 2).

Similar data have been reported for lakes in the volcanic terrain farther to the north near Indian Lake both by Nickerson (1972) and herein; although background levels may be nearer the low end of the range, as quoted above, than is the Yellowknife area.

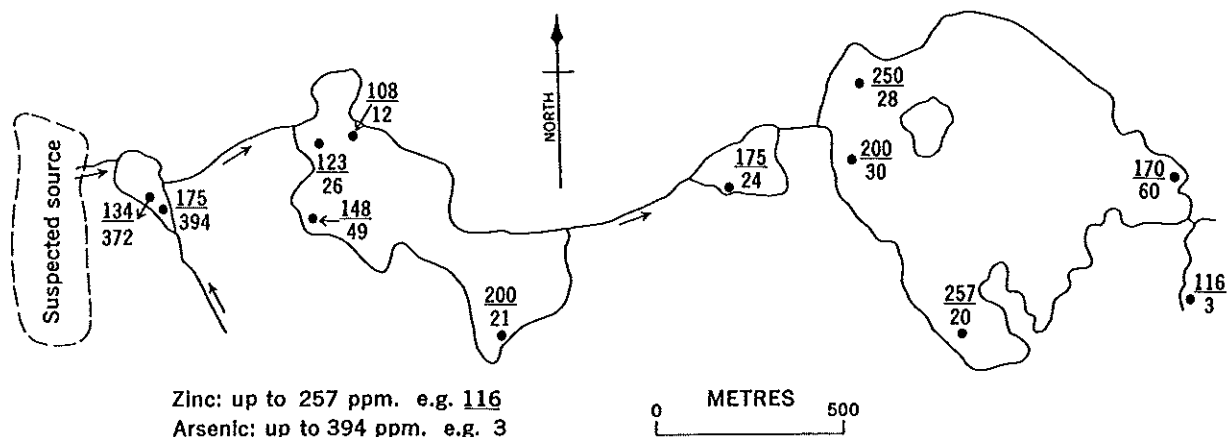


Figure 10. Migration of Arsenic through a lake system, in the tundra terrain of the Slave Structural Province.

A fine example of the extent and degree of arsenic dispersion in the Slave Province (south of Hackett River) is presented in Fig. 10. This pattern became manifest during follow-up studies (Cameron and Durham, 1974) of a suspected base metal mineralization location detected in the earlier regional survey of the Slave Province (Allan, *et al*, 1973). It can be seen that drainage sediments from the mineralized zone (west to east) carries arsenic in steadily decreasing amounts through three small lakes over a distance of 5 km. The point of note is that in each lake the values hold reasonably constant for all sample sites. The first, near the source, averages about 380 ppm, the second averages about 30 ppm and the third averages about 22 ppm. By comparison, the more mobile zinc remains fairly constant across the whole profile, with perhaps the highest values in the main sink area to the west. Mercury might be expected to behave similarly in being leached from the source and accumulated some distance from its source. The highest mercury value recorded in this northeastern part of the Slave Province was 775 ppm. This sediment came from a lake in the High Lake area (Fig. 2).

These aspects of migration behavior of different elements are important factors in enabling regional dispersion patterns to be detected and sampled reliably. The use of elements like arsenic becomes more important in follow-up stages of geochemical prospecting. The magnitude of arsenic values indicated represent the natural levels which can occur in remote areas of the Shield, and which are entirely due to processes of geochemical dispersion.

Superior and Southern Structural Province

The Superior Structural Province is of dominantly Archean age (>2.5 b.y.). Bedrock can, at the simplest level, be divided into two types. Firstly, the major part of the province is underlain by rocks of granitic type of either plutonic or metamorphic origin. Secondly, scattered through this matrix of granites are individual "greenstone" belts, consisting of volcanic and sedimentary rocks and their metamorphic equivalents. Mineralization is usually associated with these greenstone belts where most of the major base metal mining operations of the southern Canadian Shield are located. All three study sites in the Superior can be thought of as belts

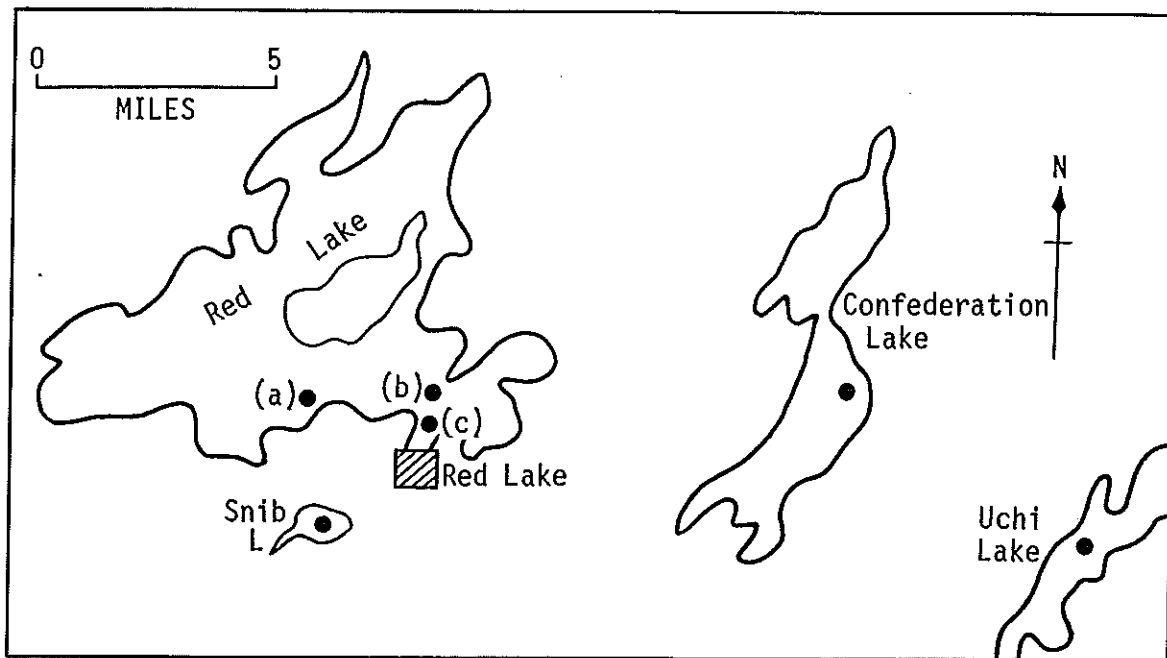


Figure 11. Lake sediment core sample sites: Red Lake-Uchi Lake area.

of volcanic-sedimentary rocks; although only the Red Lake area truly fits the greenstone belt definition. Brief descriptions of the geology and mineralization in the three areas are given in Table 1. The geology of Red Lake is described in detail by Horwood (1945). The other two areas are somewhat unusual. The origin of the Sudbury irruptive and nickel-copper ores is still debatable, although the geology is well documented (Guy-Bray, 1972). The irruptive itself is of Proterozoic age although the surrounding granites are Archean. The copper-gold areas at Chibougamau are associated with mafic and ultramafic intrusions of anorthositic character (Duquette, 1970).

Red Lake-Uchi Lake area

Sample locations of lake sediment cores are shown in Fig. 11. Cores were taken in Red Lake itself and from Confederation and Uchi lakes which lie some 90 km to the east. In the Red Lake area, only gold deposits have so far been exploited. However, a recently discovered zinc deposit is now being mined on the east shore of Confederation Lake.

Mercury levels (Table 8) are approximately twice as high as the average values found in the Bear-Slave survey area of the northern permafrosted Shield, about 40 ppb relative to 20 ppb. Contents of mercury in the Red Lake cores are very uniform to a depth of 45 cm. The higher values in the two surface samples from Snib Lake may be due to mining exploration activity in the vicinity of the lake.

The site in Confederation Lake is very close to the zinc mine noted above. The levels in the cores are characteristic of the general area and compare with those from Red Lake, 90 km to the west. Values in Uchi Lake are about three times as high as in the other lakes. Tailings from formerly producing gold mines may once have accumulated in this part of Uchi Lake and this could contribute to the higher mercury concentration of this core.

TABLE 8

Mercury (ppb) and Arsenic (ppm) Distributions in
Lake Sediment Cores from the Red Lake-Uchi Lake
area in the Superior Province of Archean age.

MERCURY						
Depth in Core (cm)	Name of Lake (Water Depth in Feet)					
	(15) Snib	(50) (a)	(50) Red Lake (b)	(40) (c)	(30) Confederation	(25) Uchi
0 - 5	122	45	49	38	38	143
5 - 10	86	47	45	38	38	120
10 - 15	56	60	33	45	42	117
15 - 20	53	60	47	-	45	92
20 - 25	60	60	45	-	47	-
25 - 30	63	63	53	-	-	-
30 - 35	51	56	63	-	-	-
35 - 40	-	51	-	-	-	-
40 - 45	-	65	-	-	-	-

ARSENIC						
Depth in Core (cm)	Name of Lake (Water Depth in Feet)					
	(15) Snib	(50) (a)	(50) Red Lake (b)	(40) (c)	(30) Confederation	(25) Uchi
0 - 5	18	2	5	3	2	3
5 - 10	6	1	4	4	1	2
10 - 15	4	1	5	4	1	2
15 - 20	1	2	1	-	1	3
20 - 25	1	1	1	-	<1	-
25 - 30	1	2	2	-	-	-
30 - 35	3	2	2	-	-	-
35 - 40	-	1	-	-	-	-
40 - 45	-	2	-	-	-	-

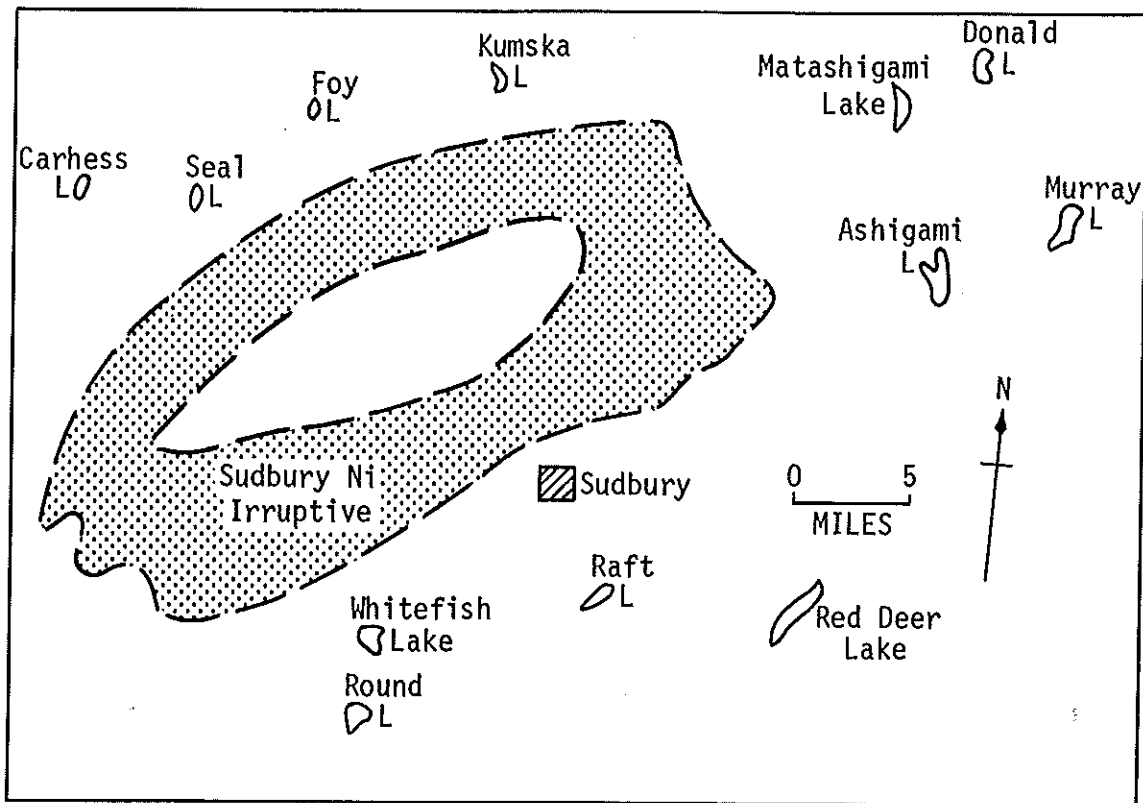


Figure 12. Lake sediment core sample sites: Sudbury Basin Area.

Arsenic concentrations (Table 8) in the Red Lake area are not particularly high, considering that this is one of the major gold mining areas of the Superior province. Arsenopyrite is a common accessory mineral in such gold mineralization (Boyle and Jonasson, 1973). However, the levels of 2 to 5 ppm compare more with those found, for example, in the Slave Province, e.g., Indin Lake, an area with known gold occurrences, rather than with the average values of about 2 ppm As found in the Proterozoic Bear Province, which is not known to be associated with gold deposits but rather with silver ores.

The higher value of 18 ppm As in the surface sample from Snib Lake, may be related to either sediment disturbance by winter drilling beneath the lake or to movement of tailings into the lake in very minor quantities. The levels of As in the core taken adjacent to the zinc deposit at Confederation Lake are low and uniform in comparison with the anomalies found in the western part of the Slave Province (Figs. 9 and 10) where similar massive sulphide occurrences are suspected to be the main source of this metal.

Sudbury Basin

Sample locations of lake sediment cores are shown in Fig. 12. All of the sites discussed here are outside the Sudbury Basin proper, i.e., the outer limit of the nickel-irruptive. Samples taken at 5-10 cm depths are probably beneath the surface materials affected by airborne pollution which has greatly increased nickel levels in soils in the area (Costescu and Hutchinson, 1972). Similarly, fallout of dust may well have contributed to the measured sediment values for mercury and arsenic. Hg levels are relatively uniform, often falling between 100 and 200 ppb mercury (Table 9).

TABLE 9

Mercury (ppb) and Arsenic (ppm) Distribution in Lake Sediment¹
Cores from the Sudbury Area in the Southern Province of Archean age.

MERCURY						
Sample Depth (cm)	Name of Lake (Depth of Water in Feet)					
	(30) Seal	(45) Raft	(30) Whitefish	(26) Carness	(80) Matashigami	(30) Foy
Surface Dredge	139	<u>181</u>	154	182	212	266
0 - 5	(60) ²	<u>104</u>	<u>98</u>	(131)	191	(239)
5 - 10	(60) ²	<u>157</u>	<u>76</u>	(131)	150	(239)
10 - 15	(60)	-	<u>73</u>	(85)	-	(194)
15 - 20	(60)	-	-	(85)	-	(194)
Sample Depth (cm)	(35) Murray	(30) Red Deer	(65) Round	(30) Ashigami	(56) Donald	(50) Kumska
Surface Dredge	182	<u>336</u>	<u>230</u>	121	221	243
0 - 5	(109)	<u>322</u>	(<u>187</u>)	(106)	(<u>163</u>)	(117)
5 - 10	(109)	<u>243</u>	(<u>187</u>)	(106)	(<u>163</u>)	(117)
10 - 15	(<u>76</u>)	196	(<u>144</u>)	<u>71</u>	(<u>78</u>)	(<u>78</u>)
15 - 20	(<u>76</u>)	169	(<u>144</u>)	-	(<u>78</u>)	(<u>78</u>)
ARSENIC						
Sample Depth (cm)	Name of Lake (Depth of Water in Feet)					
	(30) Seal	(45) Raft	(30) Whitefish	(26) Carness	(80) Matashigami	(30) Foy
Surface Dredge	6.5	<u>3.0</u>	1.4	12.0	2.3	14.0
0 - 5	(2.3)	<u>1.6</u>	<u>0.3</u>	(9.9)	1.6	(5.2)
5 - 10	(2.3)	<u>8.4</u> ³	<u>1.0</u>	(9.9)	43.0 ³	(5.2)
10 - 15	(56.0) ³	-	<u>0.3</u>	(3.3)	-	(40.0) ³
15 - 20	(56.0)	-	-	(3.3)	-	(40.0)
Sample Depth (cm)	(35) Murray	(30) Red Deer	(65) Round	(30) Ashigami	(56) Donald	(50) Kumska
Surface Dredge	2.0	<u>3.2</u>	2.4	5.1	2.4	16.0
0 - 5	(1.5)	(<u>6.5</u>)	(<u>1.8</u>)	(1.6)	(<u>2.0</u>)	(6.7)
5 - 10	(1.5)	<u>1.0</u>	(<u>1.8</u>)	(1.6)	(<u>2.0</u>)	(6.7)
10 - 15	(<u>1.0</u>)	1.0	(<u>8.5</u>) ³	(<u>0.3</u>)	(<u>0.3</u>)	(<u>2.9</u>)
15 - 20	(<u>1.0</u>)	1.0	(<u>8.5</u>)	-	(<u>0.3</u>)	(<u>2.9</u>)

¹ "Non-organic" samples are underlined, i.e., less than 5% Loss on Ignition.

² Same sample - 10 cm core.

³ These samples were reanalysed. The high values could not be repeated. This does not change the conclusion as to airborne particulate contamination of the sediment. Results for all samples reanalysed, were in the order of 2 ppm As.

However, these levels are 3 to 4 times higher than in the Red Lake area at the same depth in cores (Table 8); and considerably higher than the values detected regionally in both the Bear and Slave provinces (Fig. 8).

Mercury distribution with depth (Table 9) often shows a slight maximum in samples collected by surface dredge. The dredge device, an Eckman-Birge model, tends to scrape the organic iron-rich surface sediment, only a few centimetres thick, from the lake bottom. Accordingly these values are likely to be higher than the true core samples. In all but one core there is a decrease in mercury levels with depth. It is possible that part of this mercury has been added at many sites by atmospheric pollution of the lakes. However, at 10 to 15 cm depth concentrations appear to even out at about 60 to 80 ppb. As these horizons are well below the sediments which have accumulated since mining activity began, these values probably reflect the original natural concentrations characteristic of the area. As such they are still 1.5 to 2 times the levels recorded in the Archean Red Lake-Uchi Lake area. It is our contention that this area is naturally higher in Hg perhaps due in part to the presence of the volcanic irruptive and its associated Proterozoic age ores of nickel, copper and zinc. Some sphalerites collected from within the basin average 140 ppm Hg (Jonasson and Sangster, 1974) which is a quite high value but nevertheless, typical for zinc sulphides of Proterozoic age.

Arsenic concentrations are not particularly high in comparison with levels in the wilderness areas of the Bear and Slave Provinces and are certainly considerably less than those encountered in the Yellowknife area (Nickerson, 1972). Levels are normally around 2 to 4 ppm (Table 9). There were, however, occasional very high concentrations at depths of 10-15 cm, e.g., in Round, Seal, Foy and Matashigami Lakes. The source of this arsenic is uncertain and may be due to fallout of smelter derived airborne particulates which have settled into gel-like, organic sediments. Reanalysis of these high samples gave values of about 2 ppm. Thus the "rare airborne particle" may produce these random high concentrations.

Chibougamau area

Sample locations of lake sediment cores are shown in Fig. 13. The cores were collected from several lakes distant from the copper and gold mining activity which is largely concentrated around Lac Doré, and which was also sampled. Two cores also came from Mistassini Lake which lies outside the Archean volcanics of Chibougamau and within an extensive basin of Proterozoic sedimentary rocks including black shales.

Mercury concentrations (Table 10) show that there is a generally uniform distribution with depths in sites (Cachisca and Lemieux) in Archean granite areas remote from mining activity. There may be a tendency for mercury levels to be lower in the intermediate core depths - 10-20 cm at Lac Lemieux, however, this variation is not consistent. Even at these granitic bedrock sites, mercury levels are around 40 to 60 ppb - similar to the levels at Red Lake-Uchi Lake and approaching the levels found at 10 and 15 cm depth in the Sudbury cores. Because of the wide separation of these three study areas, it appears that mercury levels in the greenstone belts of the Superior Province are in general 2 to 3 times those found in either the Bear or Slave Structural Provinces of the Shield. Such variations must be considered meaningful when assessing higher levels encountered in the Superior Province in terms of man's industrial and mining activities.

Levels are higher at Lacs Bourbeau and Caché which are closer to mining operations in the Chibougamau area. Bourbeau appears to lie in a mercury-rich environment as levels are fairly consistent with depth. Lac Caché has higher mercury levels in the surfact 10 cm, which may well be related to the fact that this is the location of two seaplane bases. Levels below 10 cm at Caché are within the 40 to 60 ppb range (Table 10). Lac Doré is surrounded by mining activity. The levels in the cores at the two sites sampled strongly indicate a lack of mercury addition to the lake, at least at the locations sampled, by mining operations. Some recent work by McLatchy and Jonasson, (1974) has clearly established that there is very little mercury present in the copper ores of this region - in fact less than 1 ppm on the average. It is not unexpected then that little mercury reaches Lac Doré as a result of mining activity. In general, the higher mercury concentrations at Chibougamau fit the Red Lake-Uchi Lake Sudbury pattern.

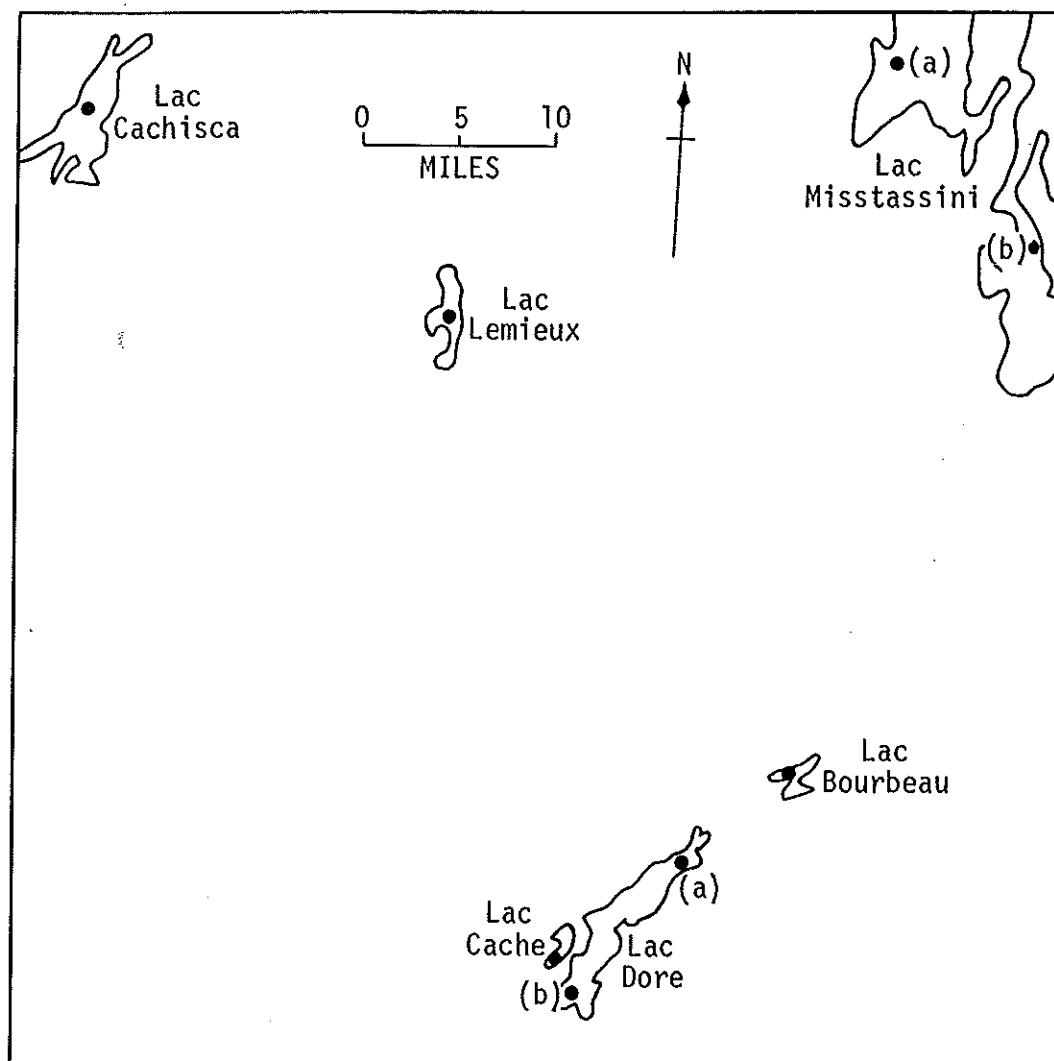


Figure 13. Lake sediment core sample sites: Chibougamau Area.

TABLE 10

Mercury (ppb) and Arsenic (ppm) Distribution in
Lake Sediment Cores from the Chibougamau Area
in the Superior Province of Archean age.

MERCURY								
Depth in Core (cm)	Name of Lake (Depth of Water in Feet)							
	(20) Cachisca	(12) Lemieux	(40) Bourbeau	(20) Cache	(60) Mistassini (a)	(35) (b)	(25) Dore (a)	(20) (b)
0 - 5	49	71	220 ¹	194 ¹	43	112	78	73 ¹
5 - 10	27	68	168 ¹	344 ¹	49	109	94	87
10 - 15	35	54	128 ¹	81	49	100	75	81
15 - 20	32	49	156 ¹	49	27	107	80 ¹	73 ¹
20 - 25	35	62	140 ¹	63	32	107	71 ¹	-
25 - 30	43	64	-	66	32	-	87	-
30 - 35	35	71	-	-	27	-	-	-
35 - 40	46	-	-	-				
40 - 45	37	-	-	-				
45 - 50	43	-	-	-				
ARSENIC								
Depth in Core (cm)	Name of Lake (Depth of Water in Feet)							
	(20) Cachisca	(12) Lemieux	(40) Bourbeau	(20) Cache	(60) Mistassini	(35) (b)	(25) Dore (a)	(20) (b)
0 - 5	1	<1	2	3	<1	1	<1	<1
5 - 10	<1	<1	1	2	<1	1	<1	<1
10 - 15	<1	<1	1	2	<1	3	<1	<1
15 - 20	<1	<1	1	2	<1	<1	<1	<1
20 - 25	<1	<1	1	2	<1	<1	<1	-
25 - 30	<1	<1	-	-	<1	-	<1	-
30 - 35	<1	<1	-	-	<1	-	-	-
35 - 40	<1	-	-	-				
40 - 45	<1	-	-	-				
45 - 50	<1	-	-	-				

¹Average of two determinations.

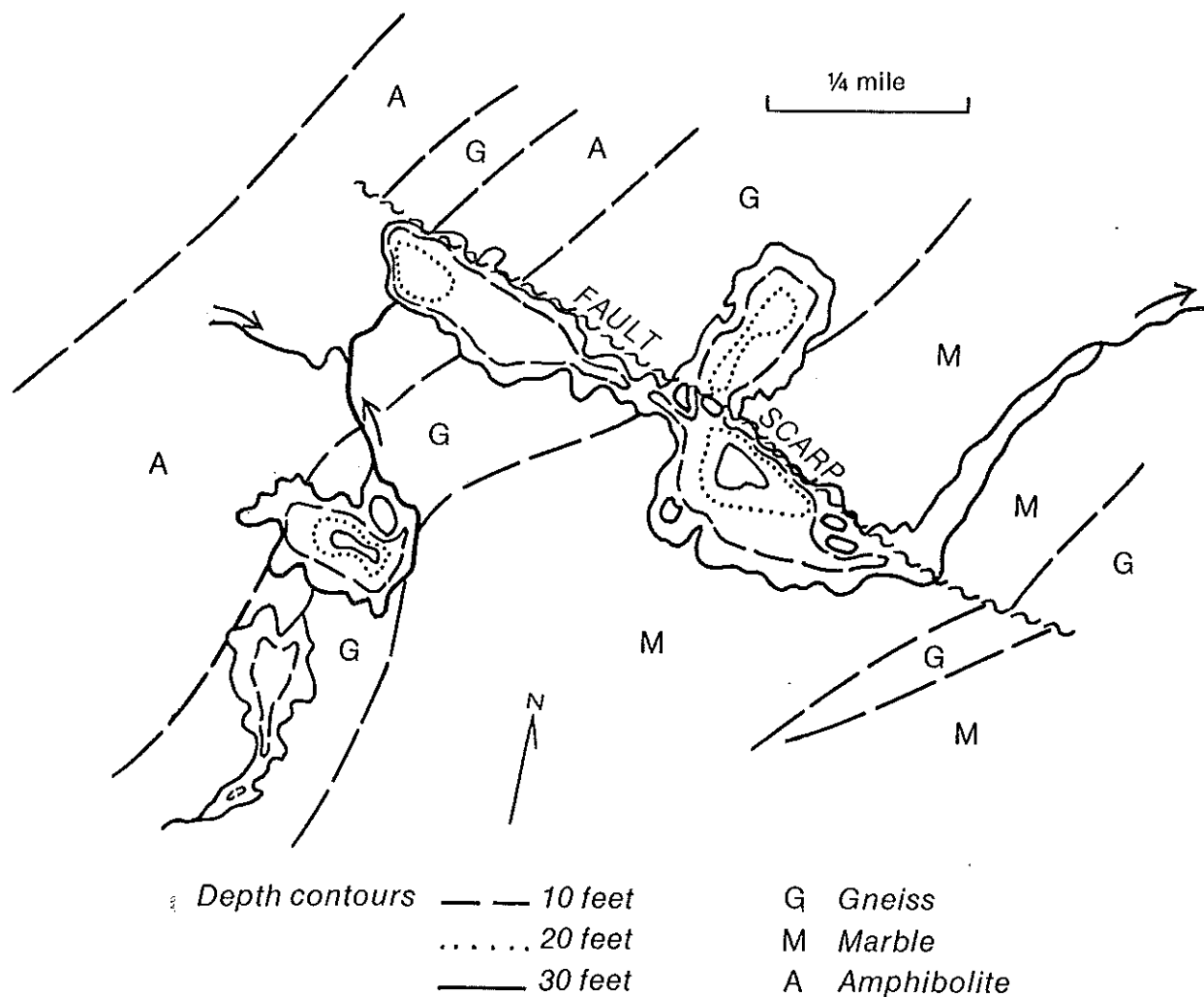


Figure 14. Geology and Lake Depth Contours, Perch Lake and Lavant Long Lake, Lanark Co., Ontario. [geology after Peach (1957) and Nikols (1972)].

Arsenic (Table 10) at Chibougamau shows a disappointing uniformity in terms of the use of the metal as a pathfinder for copper and gold deposits. The background lakes, Cachisca and Lemieux, show uniformly low As levels of less than 1 ppm with depth; levels which are similar to those observed in most of the granite areas of the Bear and Slave Provinces (Fig. 9). Lac Caché, located in the Chibougamau anorthosite has the highest As level in the area. Also underlain by the anorthosite, is Lac Doré. However, whereas there are no mines on the banks of Lac Cache, Lac Doré is surrounded by several operating mines. However, arsenic levels in sediments from Doré are lower than in Caché sediments. Also, levels at the inflow end of Doré (Table 10,a) are similar to those at the lake outflow (Table 10,b).

Grenville Structural Province

Lanark County

The local geology of the basin in which Lavant Long Lake, Perch Lake and the marsh to the south of Perch Lake lie is presented in Fig. 14. The

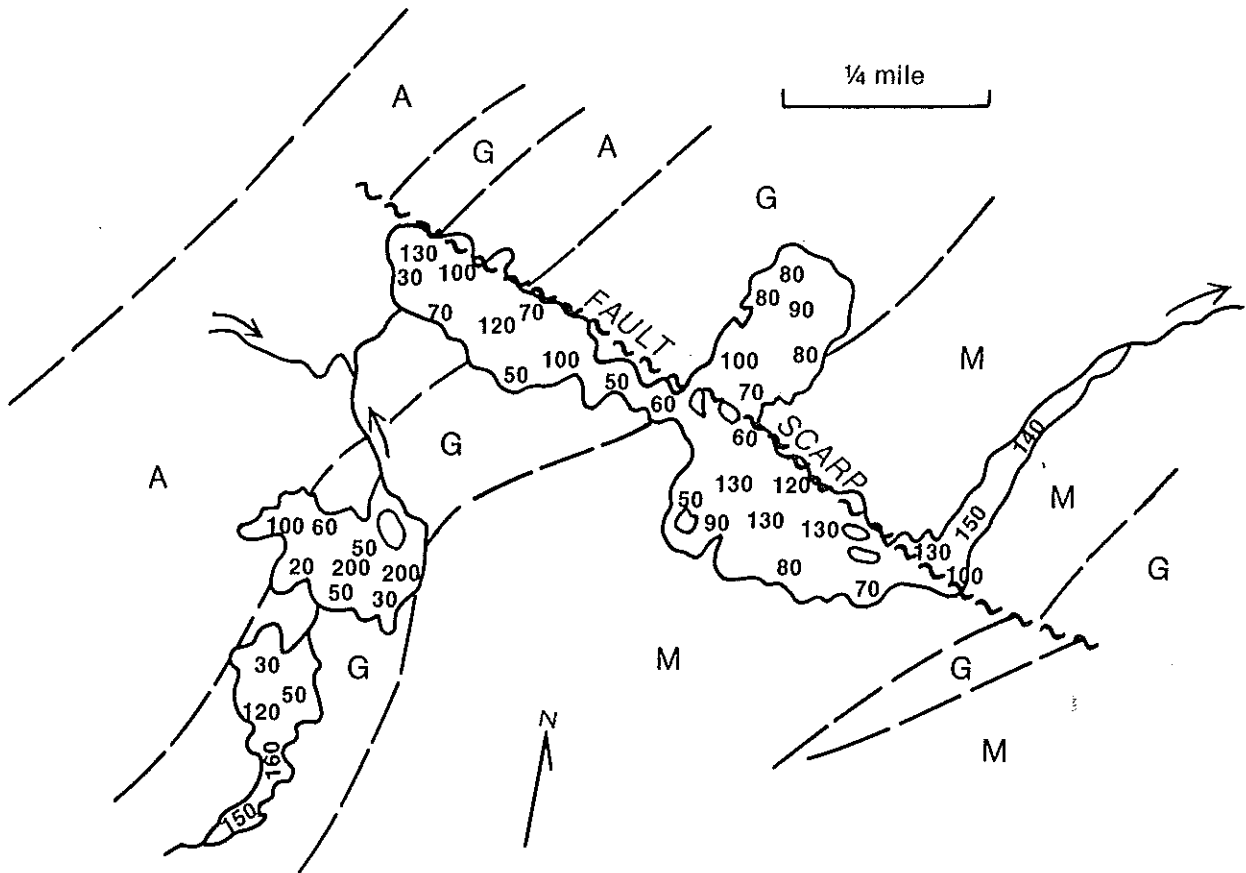


Figure 15. Mercury content (ppb) in organic lake sediments.

same figure also displays depth contours for the lake systems. Known sulphide mineralization, which is usually very minor and disseminated in character, is confined to the interlayered marbles (M), dolomites and skarns at the east end of Lavant Long Lake. Traces of Hg, Cu, Zn, As and Sb bearing sulphides are common. The west end of Lavant Lake is largely enclosed by banded granitic gneiss (G) and schists along with some patches of amphibolites (A) and pegmatites, all of which show traces of Ni, Co, U and Zn held mainly in magnetite. The Perch Lake system lies completely within gneiss except for the extreme eastern edge of Perch which cuts marbles. Lavant Long Lake is structurally controlled by a fault of Cretaceous age (Long Lake fault) recently described by Nikols, (1972). It may well be that the presence of discrete mercury mineralization in nearby Proterozoic rocks can be related to these more recent tectonic events which formed the Ottawa Valley Rift system. However, it is considered by others (R.V. Kirkham: personal communication) that the copper mineralization which dominates the mercury occurrence is syngenetic with the Proterozoic host rocks.

The deepest parts of Lavant Long Lake lie in the main water body at the foot of a high cliff (fault scarp) in the form of a trench some 16 metres deep. The lake system is largely fed by snow-melt waters so there is only a very small flow through them to the Clyde River in late summer. Lavant Long Lake is spring-fed in the deep trench but there is no obvious ground water flow into Perch Lake or its marsh. These observations were made by scuba-equipped divers.

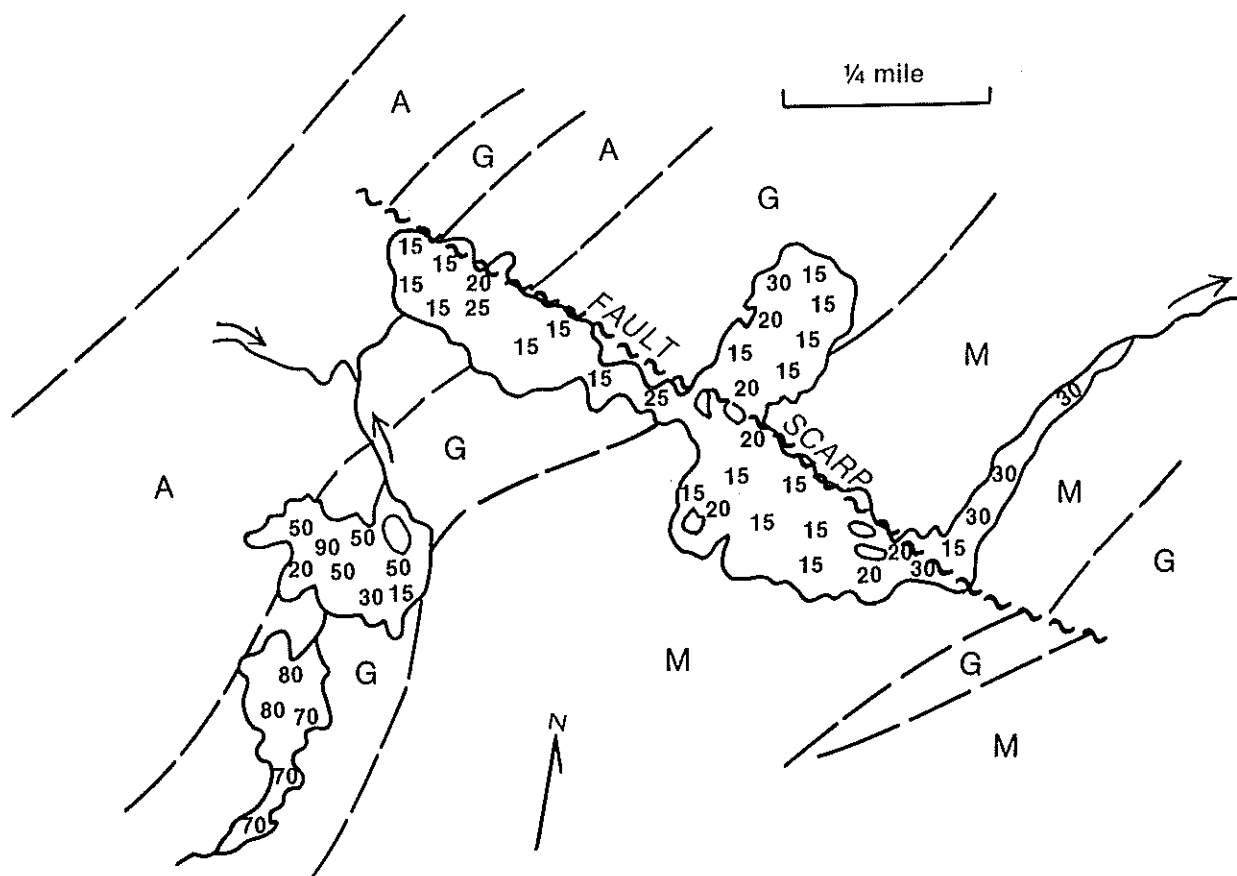


Figure 16. Mercury content (pg/ml) surface waters.

The lake sediments, collected by the same means from depths in the bottom materials of around 20 to 50 cm, were almost completely of the gyttja type - total carbon content was usually between 30 and 40% by weight; sulphur content was usually 1.5 to 2.0% by weight. Physically, they were commonly greenish or grey in colour and smelling of hydrogen sulphide, of minimal consistency and coherence and could be best described as thixotropic gels (Timperley *et al*, 1973). Near-shore samples attained a more mull-like character than the deep water samples indicating that transport of fine materials was mainly to the centres of the lakes.

It can be seen from Fig. 15 that mercury contents in organic sediments, expressed in ppb (ng/g), were generally higher in the deeper zones of the lakes. Highest values were found in the vicinity of the spring-fed trench which may imply some mercury input from groundwaters. Fig. 16 shows a similar distribution pattern for mercury in water samples. In the late summer the lakes are very clear and there is little water movement. Each sample point represents both surface waters and bottom waters which in most instances yielded virtually identical mercury contents.

The second main feature of the mercury data is that there is geological control over the measured values. In Lavant Long Lake the highest values are to be found in the east end of the lake particularly near the outflow arm, where Grenville marble dominates the terrain. It is in these rocks that traces of sulphides are found. Analyses of rock along the shore-line shows the presence of Hg, Cu, Zn, Pb and a number of other metals characteristic of the sulphides known to occur in the area. Mercury appears

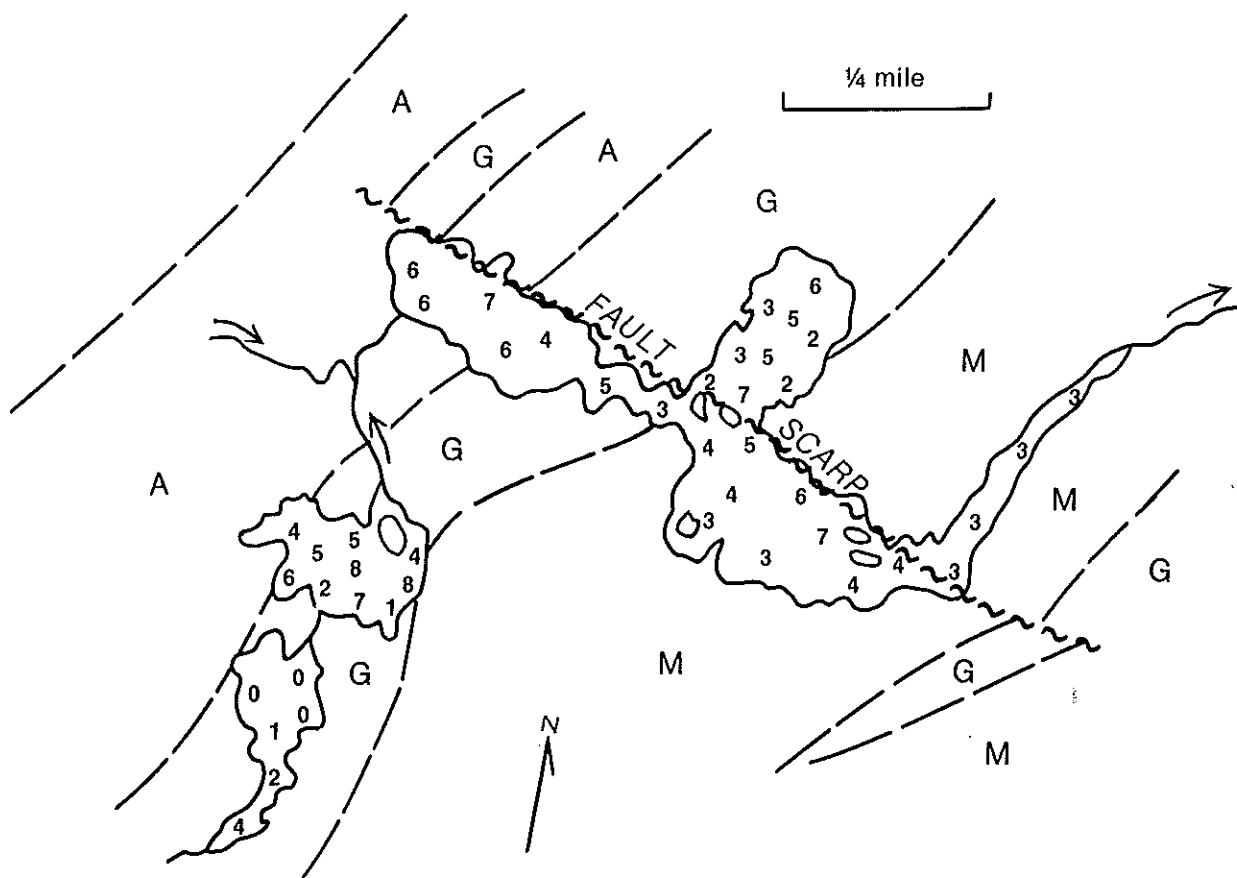


Figure 17. Arsenic content (ppm) in organic lake sediments.

to be a very mobile element in that its distribution across the lake in both waters and sediments is quite even, although the subtle differences noted above are readily discernible. It is worth noting that the distribution of uranium and nickel in both sediments and water dominantly favours the zones of both lakes in which gneissic rocks prevail.

The mercury distribution in Perch system is interesting in that there seem to be a significant input of the element from the headwater. Further work on the streams will have to be done to track down the sources.

The mercury concentrations in the organic-rich sediments of Lavant Long Lake are of the order of 100 ppb. This concentration is far higher than those found regionally in the Bear-Slave Survey area. Alternatively they are in the range of the values found at Red Lake, Sudbury and Chibougamau. However, mineralization is much less extensive at the Lanark County location. The sediments taken as cores at Red Lake, Sudbury and Chibougamau were in many cases, at least at the 10 to 15 cm level, inorganic silts (see underlined values in Table 9). At Sudbury, concentration of mercury in the silty cores at 10 to 15 cm are 73, 76, 144, 71, 78 ppb respectively. It is likely that these values are true levels and not influenced by environmental-organic considerations. In Lavant Long Lake, inorganic, silty, shoreline sediments have concentration of mercury of about 20 ppb, some 5 times less than the organic sediments at the same sites. From this, it appears likely that inorganic silty sediments taken by coring are more representative of the

absolute trace metal levels due to geology and mineralogy, than are the organic gels. With the gels geological effects are still visible through the amplified mercury levels within one lake, but the degree of amplification between silts and organics in not predictable from lake to lake from a knowledge of environmental factors.

Fig. 17 presents the arsenic distribution in both lakes. Once again the highest arsenic levels are to be found in the deeper sediments which are aggregates of the finest organic colloids and gels. The distribution of arsenic generally favours the gneissic zones of the Lake basins - an observation which is borne out by analyses of some soils and rocks along the shorelines. In both cases the amounts of arsenic and mercury found in the sediments are generally 4 to 5 times higher than measured in the host rocks, soils or on-shore sands. It is clear that some accumulation mechanism of these metals by the organic sediments is operative in such a way that the finer materials scavenge the larger proportion of them.

From the view-point of regional sampling of these lakes, it is clear that selecting a single sample at random from the lake bottom will yield a value for mercury or arsenic which is fairly characteristic of that lake. The same observation is true of other metals which are mobile in solution or on fine colloidal particles. In this way the *regional* chemical characteristics of a lake's drainage basin can be assessed reasonably well by taking a single sample from the deeper parts of the lake. This observation applies particularly to the sampling of organic sediments or oozes.

CONCLUSIONS

The Geological Survey of Canada has over the past three years acquired many thousands of sediments from fresh water lakes located in all areas of the Canadian Shield. This effort has been largely aimed at the development of detailed and reconnaissance techniques for locating mineralized areas, and thereby new ore deposits. Two of the elements often used as pathfinders to the presence of a wide variety of ores are mercury and arsenic. This fact itself indicates that there will be areas which will have *naturally occurring* anomalous metal levels in lakes simply because of the presence of mineralization. High levels may also be related to the age of certain rock types and thereby to the average metal content of any part of the ancient crust.

In the Shield, segments of the ancient crust which have been formed at specific time periods under recognisably diverse geological conditions are referred to as structural provinces. Accordingly, certain provinces may have an inherently higher level of one or other of these and other elements, relative to another large discrete area. These elevated levels may extend for thousands of square kilometres.

Thus, *two geological factors, mineralization and crustal evolution, can affect the natural levels of elements*, including potentially toxic ones such as mercury and arsenic, at specific locations. The work presented here establishes the validity of these hypotheses in that naturally occurring higher levels of both mercury and arsenic have been related to both the presence of metal ore deposits and regional variations on a grand scale

between large blocks of the crust of different geological history. *The influences of environmental effects* such as organic content of sediments and restrictions on drainage from source rocks imposed by vegetation ground cover *must also be considered* with regard to their impact on measured mercury and arsenic levels in sediments from all areas of the Shield. The data presented herein also constitute a background data bank for the levels of these metals in widely separated areas of the Canadian Shield. Such a data bank will permit any future industrial input of the same metals to be easily assessed relative to the measured geochemical and biogeochemical baselines.

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