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#### Abstract

Lakes comprise a complex system of interplay between various physical, chemical and biological factors. The distribution of heat and suspended and dissolved substances, including gases, as well as compositional variation within the sediment, are factors which can affect the dispersion of trace elements in the waters, and the accumulation or depletion of trace elements in the sediments of lakes.

A knowledge of the processes by which a metal is mobilized, transported, precipitated, and possibly remobilized, is of prime concern in order to comprehend possible controls on the metal. The principal mechanisms affecting base metal transport, accumulation and fixation into bottom deposits are thought to involve: scavenging of metals by organic matter; sorption and coprecipitation by hydrous oxides; sorption by clay minerals; chemical processes involving hydrolytic reactions; and variations in the gross physical-chemical nature of the sediments.

The range of possible physicochemical-limnological conditions within the lacustrine environment emphasizes the complexity of this regime. Variations in these conditions can affect the nature of metal response in lake bottom materials, with respect to mineralization, in different geographic — climatic and geological environments.

In recent years considerable attention has been focused on investigating the role of lake sediment geochemistry as a guide to mineralization, mostly within the Shield regions of the northern hemisphere. These regions can contain extensive glacial overburden and, being of low relief, are characterized by indefinite and disorganized drainage systems. Investigations have therefore been initiated because conventional geochemical exploration techniques have found limited application in many of these areas of the Shield.

In Canada studies of the relationships between lake sediment geochemistry and various types of mineralization have been performed by government agencies, the mining industry and university groups. Features which have contributed to the effectiveness of lake sediment geochemistry for reconnaissance mineral exploration within Shield areas include: the great abundance of lakes; centre-lake bottom sediments constituting a homogeneous sample medium for trace metal accumulation; the amenability of this procedure to rapid helicopter sampling techniques thus allowing large areas to be covered rapidly and relatively cheaply.

The effectiveness of lake sediment geochemistry for regional reconnaissance has been established in the northern permafrost regions of the Canadian Shield. However, the problems appear to be somewhat more complex in regions of the southern Shield, south of the zone of discontinuous permafrost, where, although some success has been achieved, only limited work has been done. The problems here include increased biologic activity; widely varying limnological environments; and an apparently less intense rate of weathering compared to northern Shield regions. Over the Shield as a whole it is clear that the effectiveness of the method varies with the element and type of deposit sought and with local terrain and overburden conditions. Because of all these considerations much research is required on a number of fundamental aspects, for example: on the rates of weathering of various types of mineralization in different regions of the Shield, on the transport and accumulation of metals within organic-rich environments, and on the physical and chemical processes which operate during and after glacial activity.

The techniques of lake sediment geochemistry are currently at a stage where they are being refined and evaluated and are being tested in different regions. The main application of lake sediment geochemistry for mineral exploration has been within the Canadian Shield and adjoining areas. The problems that originally led to its application in these regions are present in other regions. In North America these include parts of the Cordillera and Appalachians, and abroad the Scandinavian Shield.

#### Résumé

Les lacs sont le siège de tout un système complexe de réactions entre différents facteurs physiques, chimiques et biologiques. La distribution de la chaleur, les substances dissoutes et en suspension, y compris les gaz, ainsi que les différences de composition entre divers types de sédiments, sont autant de facteurs qui peuvent affecter la dispersion des éléments en trace que peut contenir l'eau et l'accumulation ou l'épuisement de ces éléments dans les sédiments lacustres.

Pour bien comprendre comment on peut contrôler la teneur d'une eau en un métal donné, il est essentiel de bien connaître les processus par lesquels ce métal est mobilisé, transporté, précipité et peut-être remobilisé. On pense que les principaux mécanismes affectant le transport, l'accumulation et la fixation d'un métal de base dans les sédiments de fond sont intervenir: l'extraction des métaux par la matière organique; l'adsorption et la coprécipitation par les oxydes hydratés; l'adsorption par les minéraux argileux; des processus chimiques mettant en jeu l'hydrolyse; les variations dans la nature physico-chimique des sédiments.

La gamme des conditions limniques et physico-chimiques possibles en milieu lacustre augmente la complexité de ce régime. Les variations de ces conditions peuvent affecter le comportement du métal se trouvant dans les sédiments de fond, en ce qui concerne la minéralisation, selon le contexte géographique-climatique et le contexte géologique.

Ces dernières années, l'attention des chercheurs s'est concentrée sur le rôle que la géochimie des sédiments lacustres peut jouer dans la découverte de minéralisation, en particulier dans les boucliers de l'hémisphère nord. Ces régions peuvent présenter de grandes étendues de couverture glaciaire, et avoir un relief peu accusé; elles sont caractérisées par des réseaux hydrographiques peu structurés, aux frontières mal définies. Des recherches ont donc été entreprises car les techniques classiques de la prospection géochimique s'appliquent mal dans de nombreuses régions du Bouclier.

Au Canada, plusieurs organismes du gouvernement, l'industrie minière, et certaines universités ont fait des études sur les relations existant entre la géochimie des sédiments lacustres et les différents types de minéralisation. Plusieurs facteurs contribuent à faire de la géochimie des sédiments lacustres appliquée à la prospection minérale de reconnaissance dans les régions du Bouclier un outil efficace, entre autres: la grande abondance des lacs; le fait que les sédiments au centre d'un lac constituent un exemple de milieu homogène pour l'accumulation de métaux en traces; cette méthode se prête aux techniques d'échantillonnage rapide par hélicoptère qui permettent de couvrir rapidement et économiquement de grandes étendues.

L'efficacité de la géochimie des sédiments lacustres appliquée à la reconnaissance régionale des zones de pergélisol de la partie nord du Bouclier canadien a été démontrée. Mais, les problèmes semblent être un peu plus complexes dans les régions sud du Bouclier, au sud de la zone de pergélisol discontinu, où, malgré quelques résultats intéressants, très peu de travaux ont été effectués. Dans ces régions, on rencontre en effet des difficultés: l'activité biologique est plus intense, le contexte limnologique varie beaucoup plus et l'érosion est moins active que dans le nord du Bouclier. Il est bien évident que l'efficacité de cette méthode appliquée au Bouclier varie avec l'élément et le type de gisements recherchés, avec le type de terrain rencontré et avec les conditions de la couverture. Compte tenu de toutes ces considérations, on doit alors faire beaucoup de recherches sur un grand nombre d'aspects fondamentaux, comme par exemple: le taux d'altération des différents types de minéralisation dans les différentes régions du Bouclier, le transport et l'accumulation des métaux dans les milieux riches en matière organique et les processus physiques et chimiques entrant en jeu pendant et après l'activité glaciaire.

Les techniques de la géochimie des sédiments lacustres en sont actuellement au stade de la mise au point et de la réévaluation; elles sont aussi mises à l'essai dans différentes régions. La principale application de la géochimie des sédiments lacustres pour l'exploration minière se fait dans le Bouclier canadien et les régions avoisinantes. On trouve ailleurs les problèmes qui nous ont amenés à appliquer ces Techniques dans ces régions. En Amérique du Nord, il s'agit d'une partie de la Cordillère et des Appalaches; à l'étranger c'est le cas du Bouclier scandinave.

## INTRODUCTION

The adoption of lake sediment and water geochemistry for mineral exploration by geologists and geochemists, is still in a relatively juvenile stage compared to the intensive study of the physical, chemical and biologic nature of lakes by limnologists. Over the past 100 years limnologists have accumulated a vast amount of information on lakes. However, relatively little work has been done on trace element cycles in the lacustrine environment. Only recently, because of environmental concern over pollution, and, to a certain extent, because of the application of lake sediment geochemistry to mineral exploration, has any concentrated attention been focused on the study of trace metals in the lacustrine environment.

It has only been since the late 1960s or early 1970s that any concerted effort has been made in investigating the role of lake sediment geochemistry as an indicator of mineralization. The majority of studies have taken place within the Precambrian Shield regions of the northern hemisphere. This is primarily because more conventional geochemical exploration techniques have found limited

application in Shield areas with extensive glacial overburden and low relief commonly characterized by indefinite and disorganized drainage systems.

Many geologists and geochemists, while they may utilize lake sediment geochemistry as part of an exploration program, are largely unaware of the characteristics and physicochemistry of the lacustrine environment. An attempt has therefore been made to review and summarize the relevant limnologic and chemical literature in order to outline the physical, chemical and biological processes operative on metal distributions in the lacustrine environment, and their importance to the interpretation of lake sediment chemical data. The final part of the paper reviews the application of lake sediment geochemistry to mineral exploration including a discussion of sampling equipment, logistics, costs and selected case histories.

## THE LAKE WATER – LAKE SEDIMENT ENVIRONMENT

Since lake sediment and water compositions are affected by the physicochemical processes active in the lake regime, these processes will be reviewed briefly. This will

allow an understanding of the factors to be considered when interpreting lake sediment and water geochemical data for use in mineral exploration. It is virtually impossible to discuss the geochemistry of lake sediments as a subject completely divorced from lake waters. Therefore, lake waters will be discussed, as required, to elucidate various aspects of the geochemistry of lake sediments. More detailed information on limnology, the scientific study of lakes, is available in texts by Hutchinson (1957, 1967), Ruttner (1963), Frey (1963), Kuznetsov (1970), and with particular reference to the application of lake water and sediment geochemistry to mineral exploration, by Levinson (1974).

### Origin and Morphometry of Lakes

Inland lakes cover a relatively small portion of the earth's land surface – only about 1.8 per cent or 2.5 million km<sup>2</sup>. The number of lakes in several countries such as Sweden, central Finland, Canada and the central northeastern United States of America, particularly within the recently glaciated Precambrian Shield regions of these countries, is very large and hence the dimensions of most lakes are relatively small. In the Canadian Shield most lakes are small, less than 10 hectares (1 hectare = 2.471 acres = 10 000 m<sup>2</sup>), and relatively shallow, usually less than 9 m deep (Cleugh and Hauser, 1971).

Lakes may be formed by a variety of processes. Almost all lakes within the Precambrian Shield regions of Sweden, Finland and Canada occupy depressions that are of glacial and/or tectonic origin. Lake basins formed by glacial action predominate in these Shield regions, as well as in the Canadian Cordillera and Appalachian regions. Lake basins formed by glacial action can be placed into four major categories: (1) those formed in cirques and mountain valleys as a result of mountain glaciation; (2) those occupying glacial rock basins formed by scour action on peneplains or in shallow valleys, due to continental glaciation. The position of the lakes in (1) and (2) is a function of variation in lithology and/or the existence of joints, faults and shatter belts; (3) those developed in glacial or postglacial sediments such as in kettles, subglacial channels, or irregularities in ground moraine; (4) those dammed by surficial materials including ice, moraine, etc. Of these four, most lakes in Shield regions can be placed in category (2).

Lake waters originate as any one or combination of stream waters, groundwaters, surface runoff, rain and snow. Lake basins are ephemeral, geologically, and grow ever shallower with time, through erosion of the enclosing rim and through sedimentation: thus the lifespan of a lake is limited.

### The Physicochemical Nature of Lakes

Lakes comprise a complex system involving interplay between various physical, chemical and biological factors. The complex natural processes active in the lake environment are presented in graphical form in Figure 20.1. The distribution of heat and suspended and dissolved substances, including gases absorbed from the atmosphere, as well as compositional variation within the sediment, are factors which can affect the dispersion of trace elements in the waters, and the accumulation or depletion of trace elements in the sediments of lakes. Limnological environments may be classified in terms of water column temperature, oxygen, and dissolved and suspended matter profiles as illustrated in Figure 20.2.

### Thermal Properties of Lakes

Deeper lakes in temperate regions are generally subject to gradual heating of the waters in the spring and summer resulting in a characteristic form of thermal stratification (Fig. 20.2) consisting of: (1) the **epilimnion**, an upper region of

generally uniformly warm, circulating and fairly turbulent water; (2) the **hypolimnion**, a bottom layer of cold and relatively undisturbed water separated from the epilimnion by (3) the **metalimnion**, an intermediate region in which the temperature gradient, the **thermocline**, is steepest. The distribution of heat in lakes depends largely on the mixing effect of wind and, to a lesser extent, on convection currents. The metalimnion, which acts as a barrier between the epilimnion and hypolimnion, indicates the limit of mixing from the surface.

Not all lakes display this classic type of thermal stratification and there are many different forms of stratification brought about by the form, size, depth, and location of the lake basin, volume of through-flow, and effects of climate.

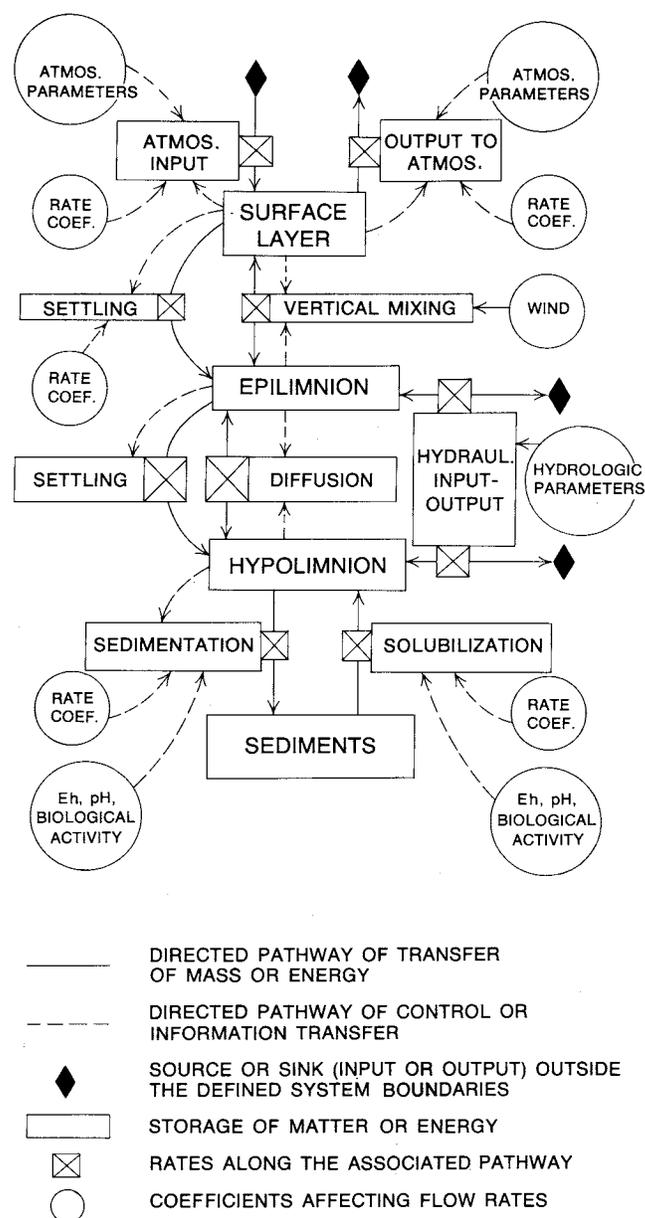


Figure 20.1. Graphical representation of the complex natural processes operative in the lacustrine environment (from Sain and Neufeld, 1975).

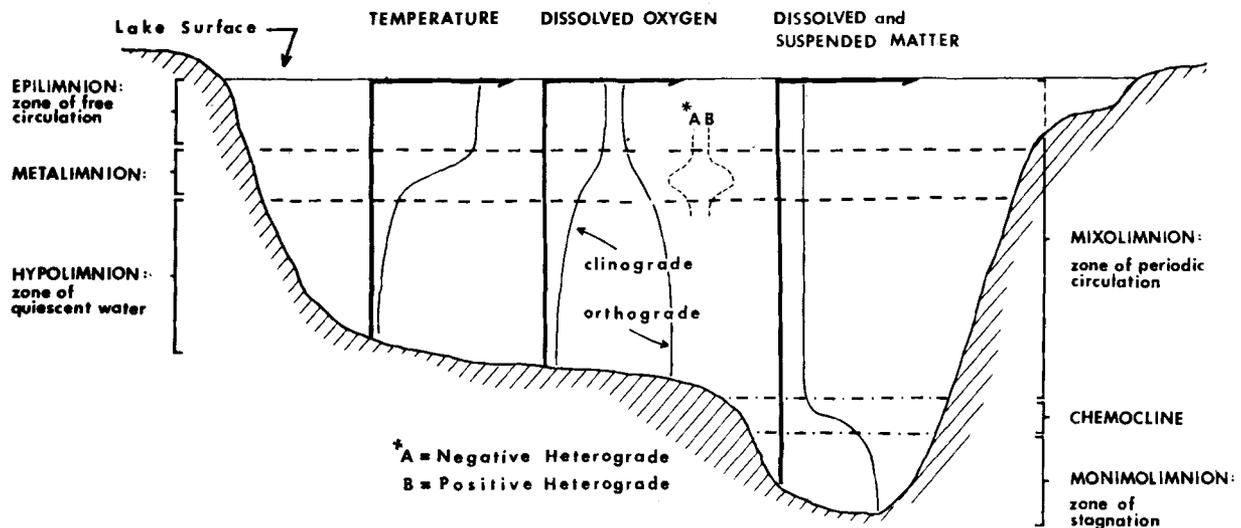


Figure 20.2. Stratification within lake environments (from Nichol et al., 1975).

Lakes may be further classified into thermal types on the basis of the number of periods of circulation per year (mixing of surface to bottom waters due to temperature and as a result, density uniformity). The types of interest are: (1) **monimictic**, water circulation once a year; (2) **dimictic**, freely circulating twice a year, spring and fall, inversely stratified in winter, directly in summer. A type of dimictic lake, termed **meromictic**, is one in which water circulation does not extend to the base of the water column. The water mass that does not take part in the mixing is termed the **monimolimnion** and the expression **chemocline** has been applied to the boundary zone that separates the bottom waters stabilized by dissolved or suspended substances, from the overlying less dense waters; (3) **polymictic**, as applied to shallow northern temperate lakes (Schindler, 1971), display stratification by heating during the day with complete mixing occurring during the cooler evenings; (4) **unstratified**, display uniform temperature distribution and can go through freely circulating periods at which time the circulation is complete to the bottom.

Mainly dimictic, although some polymictic and unstratified lakes, were reported in the Canadian Shield of northwestern Ontario (Conroy, 1971; Schindler, 1971; and Coker and Nichol, 1975). While deep lakes examined within the northern region of the Canadian Shield displayed well marked temperature stratification and were classified primarily as dimictic, most shallow lakes were unstratified (Brewer, 1958; Jackson and Nichol, 1975; Klassen et al., 1975; and Shilts et al., 1976). In northern Saskatchewan (Arnold, 1970) and in southern Ontario (Jonasson, 1976; Coker and Jonasson, 1977a, b) the lakes studied displayed temperature profiles having approximately constant temperature or decreasing temperature with depth, generally characteristic of unstratified and dimictic lakes respectively. Variations in the thermal stratification and the resulting nature of the circulation of lake waters can play a definite role in determining the distribution of suspended and dissolved substances, including gases, within the lake water column. The distribution of heat, more than any other single parameter, governs the chemical nature of the water column with the thermocline, when present, restricting the exchange of materials between sediment/hypolimnion and the epilimnion, and hence influencing whether trace metals remain in solution and disperse in the waters or precipitate and accumulate in the sediments of the lakes.

#### Dissolved Gases

Of the gases present dissolved in lake waters, oxygen, carbon dioxide and hydrogen sulphide, along with their various gaseous compounds and dissociated ionic forms, are perhaps most important in determining the movement and fixation of trace elements in lakes.

At times of lake water circulation, the gases in the lake waters can become entirely in equilibrium with those in the atmosphere. This equilibrium will, however, depend on the atmospheric pressure (and therefore on the altitude), lake water temperature, the completeness of mixing, the length of the circulation period, and complexed species formed. In most cases an equilibrium between the gases in the water and air is reached and the whole lake is then replenished with atmospheric gases from top to bottom. These gases then can become enriched or depleted within the lake water column after the period of circulation.

Lakes can be classified on the basis of biological productivity related to the dissolved oxygen content and nutrient supply. Lakes with a rich biota can supply more oxidizable organic debris to the lake bottom and thereby deplete oxygen concentration in bottom waters. In temperate regions, lakes are classified into two groups: (1) **eutrophic**, mature lakes with considerable organic matter and nutrients which can result in a high plankton population. The oxygen distribution in such lakes is generally **clinograde**, displaying decreases in oxygen content in the metalimnion and hypolimnion in a manner almost parallel to the temperature curve (Fig. 20.2); (2) **oligotrophic**, youthful lakes with high oxygen and low nutrient content. These lakes display an **orthograde**, oxygen distribution, one in which the oxygen content remains almost uniform in the whole water column (Fig. 20.2).

Oxygen stratification may be found in all gradations between the extremes of oligotrophic and eutrophic lakes. In some lakes, very striking maxima in oxygen concentrations can develop in the metalimnion, during stratification, as a result of photosynthesis; this type of distribution is termed **positive heterograde** (B, Fig. 20.2). Many cases are also known of marked minima, **negative heterograde**, (A, Fig. 20.2) caused by accumulation of oxidizable materials.

Studies of relatively deep lakes, greater than 10 m, in the Canadian Shield of northern Saskatchewan indicated the presence of both oligotrophic and eutrophic lakes (Arnold, 1970). In the Shield lakes of northwestern Ontario shallow

(less than 4 m), unstratified or polymictic lakes are oligotrophic being nearly saturated with oxygen all summer and having uniform oxygen content with depth, (Schindler, 1971). Lakes from 5 to 12 m had bottom waters that became anaerobic, or nearly so, by late summer. Lakes greater than 12 m showed a definite oxygen depletion in their bottom waters and good oxygen stratification displaying decreasing oxygen content with depth. These deep lakes were classified as eutrophic. Similar observations were made in other Shield lakes of northwestern Ontario (Conroy, 1971; Coker and Nichol, 1975). In the northern regions of the Canadian Shield, near Yellowknife, lakes were classified as eutrophic or oligotrophic and in certain cases oxygen maxima occur in the metalimnion (Jackson and Nichol, 1975); in the Kaminak Lake area the lakes are oligotrophic with the highest oxygen levels occurring either in the metalimnion or hypolimnion (Klassen et al., 1975; Shilts et al., 1976). In the Nechako Plateau of the Canadian Cordillera, Hoffman and Fletcher (1976) identified two contrasting limnological environments: (1) large (> 3 km in length) oligotrophic lakes and; (2) smaller lakes, associated with swampy areas of low relief, classified as eutrophic or **dystrophic** (brown-water lakes with very low lime content and a very high humus content, often characterized by a severe poverty of nutrients (Ruttner, 1963).

The carbon dioxide profile, including bicarbonate, is often roughly the inverse of the oxygen distribution during the summer period of stratification (Hutchinson, 1957). This is due to the close association of the carbon cycle with the dissolved oxygen content of the lake waters. In the water column high biological activity can result in decreases in the carbon dioxide content and increases in the oxygen content, even to supersaturation levels, due to photosynthesis in the upper **trophogenic** layer (region of photosynthetic production) (Ruttner, 1963). Respiration and oxidation processes, primarily the bacterial oxidation of organic matter, in the lower **tropholytic** region (region of breakdown), can cause enrichment in carbon dioxide (or its salts) and depletion in oxygen. Also, one of the main products of the oxidation of organic matter is the sulphate ion, which under anaerobic conditions is generally reduced to sulphide species,  $H_2S$ ,  $HS^-$ , and  $S^{2-}$  (Hutchinson, 1957; Garrels, 1960; Kuznetsov, 1970 and 1975).

The presence of oxygen, carbon dioxide and/or hydrogen sulphide, along with their various gaseous compounds and dissociated ionic forms, determine whether aerobic oxidizing or anaerobic reducing conditions exist through the water column. The nature of the electrochemical conditions of the water column determines whether dissolved trace elements remain in solution, or are precipitated and accumulated in the underlying sediment, and whether selected trace elements are retained within the surface sediments, or released through dissolution or desorption back into the overlying water.

## pH

The usual pH range for open lakes is between 4 and 9, with lakes in regions of acid rocks displaying pH values below 7 and lakes over calcareous rocks exhibiting values well over 8 (Hutchinson, 1957; Baas Becking et al., 1960). In most lakes which have near neutral pH, the pH is regulated by the carbon dioxide – bicarbonate – carbonate system (Hutchinson, 1957; Garrels and Christ, 1965). In general, oligotrophic waters tend to have slightly acid pH, whereas eutrophic waters tend to be more alkaline. In most cases the pH of the waters tends to be about 7 and oligotrophic cannot be distinguished from eutrophic on the basis of pH. The form of the pH profile tends to follow that of temperature, with the surface waters having higher pH values than the deeper waters. The lower pH in the deeper waters can be attributed to the release of carbon dioxide from respiration reactions and/or the bacterial

oxidation of organic matter and the subsequent hydrolysis to  $H_2CO_3$ . Also, the pH of the surface waters will be increased as carbon dioxide is consumed during photosynthesis. In a number of geochemical studies of Canadian Shield lakes, pH values were recorded ranging from 3.0 to 8.7 with extremely acid pH values being associated with lakes adjacent to oxidizing sulphide mineralization and alkaline pH values being associated with lakes in areas of carbonate lithologies (Arnold, 1970; Conroy, 1971; Schindler, 1971; Allan et al., 1973a; Closs, 1975; Coker and Nichol, 1975; Jackson and Nichol, 1975; Klassen et al., 1975; Jonasson, 1976; Meineke et al., 1976; Shilts et al., 1976; Cameron, 1977; Cameron and Ballantyne, 1977; Coker and Jonasson, 1977a, b; Maurice, 1977a, b).

## Dissolved and Suspended Solids

In normal fresh water the total content of dissolved solids consists of only a few salts: the carbonates (including bicarbonates), sulphates and chlorides of the alkali (Na, K) and alkaline-earth (Ca, Mg) elements, silicic acid, and small amounts of nitrogen and phosphorus compounds (Hutchinson, 1957; Ruttner, 1963; Kuznetsov, 1970). Compounds of iron and manganese can also reach significant concentrations in waters under suitable anaerobic conditions (Juday et al., 1938; Mortimer 1941, 1942, and 1971; Hutchinson, 1957; Livingston, 1963; Ruttner, 1963; Mackereth, 1965; Arnold, 1970, and Kuznetsov, 1970). In addition, there are minute concentrations of trace elements in solution, generally at the parts per billion (ppb) level, together with various mineral colloids and suspensions (Riley, 1939; Turekian and Kleinkopf, 1956; Hutchinson, 1957; Ruttner, 1963; Gorham and Swaine, 1965; Allan and Hornbrook 1970; Arnold, 1970; Kuznetsov, 1970; Dyck et al., 1971; Hornbrook and Jonasson, 1971; Allan et al., 1973a,b; Cameron, 1977; Coker and Jonasson, 1977a,b; Maurice, 1977a,b).

Water conductivity may be regarded as a measure of the ionic material present in the water. There is generally a direct relationship between conductivity, bicarbonate alkalinity and the pH of lake waters (Coker, 1974) and consequently, as has been demonstrated by many surveys in the Canadian Shield, surface lake waters with high conductivities will occur in carbonate-enriched terrain, whereas lower conductivities will occur in granitic terrains (Armstrong and Schindler, 1971; Conroy, 1971; Closs, 1975; Coker and Nichol, 1975; Jackson and Nichol, 1975; Klassen et al., 1975; Semkin, 1975; Dean and Gorham, 1976; Shilts et al., 1976; Cameron and Ballantyne, 1977; Coker and Jonasson, 1977a,b). Cameron (1977) noted a trend of increasing conductivity and acidity and decreasing alkalinity and pH in the surface waters of lakes in positions varying from remote to adjacent to actively oxidizing sulphide mineralization (see Fig. 20.6).

Organic substances occur in solution in both suspended and dissolved forms within natural waters. Concentrations of dissolved organic matter in natural waters, expressed as the amount of carbon per unit volume of water, are commonly in the range 0.1 to 10 mg/L (Stumm and Morgan, 1970). Organic substances that occur in solution frequently exceed by several fold those in particulate form (Birge and Juday, 1934; Kuznetsov, 1970). Suspended organic matter consists mainly of: (1) living, and the remains of dead and decayed plankton, bacteria and algae; (2) vegetation and animal-derived detritus from the littoral zone of the lake, from around the edge of the lake, and that brought in by wind, drainage and precipitation. Dissolved organic matter, including colloidal organic substances, is composed primarily of: (1) intermediate decomposition products such as amino acids, fatty acids, alcohols, hydrocarbons, proteins, etc.; (2) substances resistant to further degradation – a group broadly named "aquatic humus" (Swain, 1958; Kuznetsov, 1970). Humic matter is

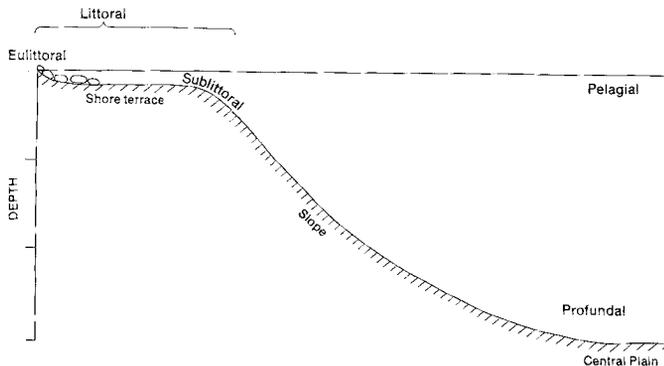


Figure 20.3. Lake habitat subdivisions (after Ruttner, 1963).

derived, in part, by leaching and/or eroding of soils and swamps (**allochthonous** origin – material formed outside the lake) and, in part, from the cellular constituents and exudates of indigenous aquatic organisms (**autochthonous** origin – material formed within the lake) (Hutchinson, 1957; Bordovsky, 1965; Flaig, 1971; Nissenbaum and Kaplan, 1972). It is concentrations of humic substances which give the brown to yellow colour characteristic of the waters of many lakes in Shield areas. The structure of humus, as it is known, is very complex and still in dispute. The following classification of humic substances is now generally accepted: (1) humins, (2) fulvic acid, (3) humic acid (Flaig, 1971).

#### Lake Sediments – Major Composition

The composition of lake bottom deposits (sediments) depends on: lake morphology, biota types and abundances, drainage, glacial history of the area including type of glacial deposit, and geographical (climatic) and geological location. According to composition these deposits are partly inorganic, partly organic; according to origin they are either **autochthonous**, having been formed in the lake itself by life processes or physical-chemical processes separating them from the water, or **allochthonous**, having been introduced from outside the lake by inflowing water, falling dust, precipitation, etc. (Hutchinson, 1957; Ruttner, 1963).

The inorganic allochthonous particles introduced into a lake undergo sorting according to their size and density. In the vicinity of effluents, and within the littoral zones (Fig. 20.3) of many lakes (due to sorting by wave action and periglacial processes), materials derived from the glacial and postglacial sediments of the drainage basin are deposited and reworked into zones of coarser and finer materials. The finer portions are distributed more uniformly throughout the lake, settling out over the entire lake bottom and contributing substantially to the inorganic component of sediments in the deepest and/or central (profundal – see Fig. 20.3) portion of the lake basin. Where present (in quantity, generally south of the treeline (see Fig. 20.11)) the organic component of allochthonous sediments contains a considerable amount of humic matter, derived from the leaching of the organic layer of soils and swamps, coarser organic detritus from vegetation around the edge of the lake, and to a lesser extent animal materials, such as hair, exudates, chitinous parts of insects, etc. The contribution of airborne dust can be considerable, particularly in the spring when plants are in bloom and lake surface waters are commonly covered with a yellow film of pollen and spores, which eventually are incorporated into the sediment.

Autochthonous sediments consist primarily of two types: (1) precipitates that form external to living processes, as a result of physical-chemical changes (i.e.: the precipitation of compounds of Fe, Mn, Ca, Si etc.); (2) plant

and animal remains from the lake community along with their inorganic and organic integuments and supporting materials. After being worked over by bottom animals and bacteria, in an environment at least periodically supplied with oxygen, the organic and inorganic materials in the lake centre (profundal) basin forms a very characteristic, finely divided sediment of grey, greyish brown to brown-black colour and at times of elastic consistency, called **gyttja** (Ruttner, 1963).

Lake sediments, particularly from areas within the Canadian Shield, have been grouped into three distinct classes each of which has broad chemical, physical and mineralogical characteristics that are relatively uniform (Jonasson, 1976): (1) **organic gels** (gyttja) are materials commonly found in the deeper waters (profundal basin) of organic-rich lakes and are abundant in most parts of the Canadian Shield where there is a deciduous-coniferous forest cover. Almost completely organic in composition, they have a strong odour ( $H_2S$ ), indicative of reducing conditions, and are thixotropic. As their coherence often is very low the gels may disperse freely into the lake waters if the sediment-water interface is disturbed. Their origin probably lies in the sedimentation of fine, dispersed particles of vegetation debris (pollen, spores etc.), and of coagulating colloids of dissolved organic matter (organic acids such as humates, fulvates, etc.). Relatively little coarse organic debris or mull is present in these samples or organic gels which occur in the central and/or deepest parts of a lake. These gels dry to a hard, dark, lustreless, homogeneous cake which is difficult to break and does so conchoidally; (2) **organic sediments** are widespread throughout most lakes of the Shield especially in shallow waters either near shores or near inflows. They are also the most abundant material in swamps and marshes, and may be regarded as mixtures of organic gels, organic debris, and inorganic sediments (mainly silts and clays but also some sands, gravels and boulders may be present); (3) **inorganic sediments** implies various combinations of boulders, gravel, sand, silt, marl and clay with inorganic oxides and hydroxides (precipitates and colloids) with virtually no organic matter, and with little or no regard paid to mode of deposition or derivation of materials. Inorganic sediments commonly occur throughout lake basins in areas of the Shield which have few or no trees and in shallow waters in most lakes, especially at the shores of a lake, and near inflows and outflows. They may originate from the winnowing action of waves on shoreline sediments and soils, or may occur as silty deposits in deeper waters.

Although the classification of Jonasson (1976) probably applies to lake sediments from most areas of the southern Canadian and Fennoscandian Precambrian Shields, as well as to the Canadian Appalachia, a limited number of detailed compositional studies of lake sediments from these areas, as summarized in Table 20.1, have produced additional data on the nature of the major composition of lake bottom deposits.

Studies carried out on the compositional nature of lake sediments from lakes in the northern Canadian Shield, characterized by open woodland and/or tundra landscape, illustrate some distinct differences, and yet similarities, to the composition of sediments from lakes in the south of the Shield below the treeline. In the tundra of the Coppermine River area, District of Mackenzie, nearly all nearshore lake bottom samples were composed of inorganic clastic material (boulders to silts) with only a few being organic (sludges or algal gels) or clayey (Allan, 1971).

Near Yellowknife, District of Mackenzie, an area of predominantly open woodland, nearshore sediment composition varied from sand to silt to clay to decomposed and relatively undecomposed organic material (Jackson, 1975). Towards lake centres the sediment became more homogeneous in composition consisting either of clay, silt-sized particles or organic-rich ooze. In nineteen lakes examined in detail the organic content of sediments, as determined by L.O.I. ( $450^{\circ}C$ ), varied from <1% to 85%.

Table 20.1

Compositional nature of lake sediments from the southern part of the Canadian and the Fennoscandian Precambrian Shields

Area	Organic content	Composition
Lac La Ronge – Flin Flon area Saskatchewan, Canada. (Arnold, 1970)	L.O.I. (700°C): 2 to 58%	Silicate fraction: quartz, garnet, minor Ferromagnesian minerals. Feldspars in nearshore sediments. Clay mineral: illite. Heavy mineral separate: hematite, magnetite and pyrite.
East-central Saskatchewan, Canada. (Lehto et al., 1977)		Sand, silt and clay sized mineral matter Organic fraction: algae, plant fibre, diatoms and the remains of fish and small crustaceans.
Northwestern Ontario, Canada. (Brunskill et al., 1971)	L.O.I. (900°C): 18 to 62%. Organic carbon: 8 to 34%. L.O.I.: C ratio is 2.7 (low organics) to 2.3 (high organics)	Major minerals: quartz, plagioclase, potassium feldspar, illite, chlorite and kaolinite. Organic matter, water, Si and Al are main components of sediments
Red Lake – Uchi Lake area, north-western Ontario, Canada. (Timperley and Allan, 1974)	L.O.I. (450 to 550°C): 5 to 50%.	Sediments in the deep part of large lakes: maximum L.O.I. of 40%, grey-green ooze; organics are humic colloids and algal remains; composed of quartz feldspar, minor clays and micas coated with organics, free-floating organics, skeletal remains of plankton, pollen and spores. Sediments in shallow lakes and areas of impeded drainage: L.O.I. could exceed 60%; organic matter derived from shoreline and aquatic vegetation. Ferromanganese nodules noted.
Northwestern Ontario, Canada. (Coker and Nichol, 1975)	L.O.I. (450°C): 14 to 61%. L.O.I. : C ratio is 2.4	Lakeshore sediments: silt, fine sand and coarser materials. Lake-centre sediments: silt, clay and organics. Silt, clay and organics are most abundant and homogeneous in lake centre (profundal) sediments. Primary minerals: quartz, plagioclase, potash feldspars, amphiboles, micas and rock fragments. Secondary minerals: illite, kaolinite, chlorite with trace vermiculite, layered clays, and montmorillonite.
Minnesota, U.S.A. (Dean and Gorham, 1976)	L.O.I. (550°C) of profundal sediments: 6 to 60%. Mean L.O.I.: C ratio is 2.1.	Mean carbonate content (L.O.I. (1000°C-550°C)) for profundal sediments is 16% with lakes in carbonate lithologies averaging 26%. Carbonate minerals are calcite, dolomite and aragonite. Clastic component of profundal sediments contain little sand-sized material consisting mainly of approximately equal amounts of silt and clay-sized material. Primary minerals: quartz, plagioclase and orthoclase. Secondary minerals: illite, kaolinite and chlorite.
Minnesota, U.S.A. (Meinke et al., 1976).	L.O.I. (800°C): 16 to 85%	Sediments of small lakes: exhibit H <sub>2</sub> S odour, contain fibric-organic, fine-grained organic and clastic material. Large lakes: nearshore sediments composed of sand and/or gravel with depth. Medium lakes: organic-rich gelatinous sediment.
Southwestern Finland. (Koljonen and Carlson, 1975)	L.O.I. (550°C): 6 to 80%	Quartz, plagioclase and potassium feldspar identified in all samples.
Eastern Finland. (Bjorklund et al., 1976)	L.O.I. (550°C): 0 to 98%	Organic gels.
(L.O.I. = loss-on-ignition)		

Numerous lakes occupy depressions on the perennially frozen glaciated tundra in the Kaminak Lake area, District of Keewatin. The shallow margins of these lakes are characterized by periglacial features such as polygonal patterns, frost-heaved boulders, and mudboils (Shilts and Dean, 1975). Digitate, cobble-covered ribs and boulder-filled troughs, composed of till and thought to be the subaqueous equivalents of mudboils, commonly form a crenulate pattern in shallow shelves adjacent to till-covered shores. Sediments of zones away from the lake margins are generally soft, loosely consolidated grey to olive-grey silts and, locally, yellowish brown silty clays which sometimes grade into an underlying firm, grey, coarse sand-silt (Klassen et al., 1975). These sediments are composed predominantly of quartz and feldspar fragments. Organic matter in the sediments, as determined by L.O.I. (450°C) varies from <1% to 27% averaging 6%. The upper silt material varies from structurally uniform to finely laminated. A stiff to watery, gel-like sediment that flocculates rather than dispersing in the lake water is thought to represent true modern lake sediment in the area (Shilts et al., 1976). This gel is either absent or very thin, rarely exceeding 1m, over large parts of many lake basins. The surface of the sediment is generally a reddish orange colour, and black or orange (manganese/iron precipitates) horizontal bands are commonly observed through the sediment (Klassen et al., 1975; Shilts et al., 1976). Also, in some lakes a significant thickness of massive to laminated, grey to pink silty clay, interpreted as marine sediment, was found to underlie the gel and overlie a unit interpreted as till (Shilts et al., 1976).

Two distinct types of sediment, nearshore and centre-lake, were found in lakes in the tundra landscape of the Agricola Lake area, District of Mackenzie (Cameron, 1977). Nearshore sediments show patterned features and are heterogeneous mixtures of material from cobble to clay size. The second type, centre-lake, was described by Williams (1975) as consisting of two varieties: (1) having a reddish uppermost layer overlying soupy brownish material; and (2) consisting of bright reddish surface material overlying brownish material over bluish grey sediment.

In general the stratigraphy of lake bottom materials from northern and southern Canadian Shield lakes is very similar. The upper strata of freshwater lake sediments comprises relatively modern organic-bearing materials. This sediment is thickest and contains the greatest amount of organic material in lakes of the southern Shield and is relatively thin and areally restricted, where present at all, in lakes of the northern Shield. This is largely because lakes of the south have been sites of accumulation through a longer period of time and have also had higher organic productivity both within the lake itself and within the associated drainage basin. Inorganic components of these modern organic sediments, which are generally minor, are derived from glacial and/or postglacial sediments within the associated drainage basin. In nearshore areas, where the modern organic sediments may be largely absent, the inorganic materials are washed glacial or postglacial sediments. Underlying the modern lake sediments can be deposits of glacial-lacustrine and/or marine sediments in areas that have been covered by glacial lakes and/or subjected to marine invasion. In areas that have not been postglacially submerged, modern organic material generally directly overlies till, the next lowest stratigraphic unit. In some cases the modern organic material may lie directly over bedrock and/or paleosol material or these materials may constitute the lake bottom itself. The thickness and types of bottom deposits in any individual lake can vary both horizontally and vertically and any of the stratigraphic units can form the lake bottom depending on the sedimentation history of the lake. Mineral exploration surveys which collect material from lake centres in the southern parts of the Canadian Shield and, in limited cases in

the northern Shield, are most likely collecting the organic lake sediment facies. In contrast, surveys collecting material from the mineral sediment found around the margins of Shield lakes are not necessarily collecting modern lake sediment but are generally obtaining glacial, glacial-lacustrine or marine sediments, or slumped soils which have been subjected to some reworking, including wave action and, in addition, in the north of the Shield, to various periglacial processes.

#### FACTORS AFFECTING TRACE METAL DISPERSION AND ACCUMULATION IN THE LAKE ENVIRONMENT

A knowledge of the processes by which a metal is mobilized, transported, precipitated, and possibly remobilized, is of prime concern in order to comprehend possible controls on that metal's dispersion, accumulation, and fixation into lake bottom materials. Certain of these processes, operative within the lacustrine environment, and the nature of lake bottom deposits, have been previously described.

The principal mechanisms affecting trace metal transport, accumulation, and fixation into bottom deposits are thought to involve: (1) scavenging of metals by algal and plankton blooms and other organic matter, both particulate and dissolved; (2) sorption and coprecipitation by hydrous iron and manganese oxides; (3) sorption by clay minerals; (4) chemical processes involving hydrolytic reactions and both complexed and dissolved ions, for example sulphide, carbonate, hydroxide; and (5) variations in the gross physical-chemical nature of the sediments. Interactions between these various mechanisms commonly occur. One model for metal transport and accumulation in lakes within the forested portion of the Canadian Shield is presented in Figure 20.4 (Timperley and Allan, 1974).

#### *Aquatic Biota*

Trace metal scavenging by algal and plankton blooms and other suspended and dissolved organic particles followed by deposition and incorporation of the metal-bearing materials into the lake bottom deposits has been documented (Kuznetsov, 1970; Morris, 1971; Andelman, 1973; Gibbs, 1973; Knauer and Martin, 1973; Leland et al., 1973; de Groot and Allersma, 1975; Trollope and Evans, 1976). Excretory products of plankton are also a source of many trace elements (Boothe and Knauer, 1972). After death or moulting of plankton settling occurs. The efficiency of metal transport to the sediment depends in part on the rate of decay during settling of the dead organism, test, moulted exoskeleton, or excretory product.

Bacterial activity in the surficial sediments causes further decay at the sediment-water interface and, after burial, may result in increases in trace element concentrations in the sediments (Leland et al., 1973). Trace metals may accumulate in the upper 5 to 20 cm of lake sediment by biological and geochemical mechanisms as well as recent cultural loading (Mortimer, 1942 and 1971; Gorham and Swaine, 1965; Mackereth, 1966; Cline and Upchurch, 1973). Upward migration of heavy metals may occur because of dewatering due to compaction and unidirectional ion migration, but, to a much greater extent, migration appears to be due to a bacterial mechanism (Cline and Upchurch, 1973). Bacteria can also cause a drop in Eh and pH; which will cause release of the complexed metals. The heavy metals may then be transported upward either on bubble interfaces, in a gaseous complex or as soluble organic complexes. When the metal reaches the biologically active surficial sediment, which is generally oxidizing in nature (Mortimer, 1942 and 1971; Gorham, 1958), it is immobilized as a new organic complex or an inorganic precipitate. Therefore, heavy metals have a tendency to remain at the sediment-water interface.

If the surficial sediments are reducing in nature, and in fact the overlying waters are also, the heavy metals may in fact be mobilized into the waters.

Aquatic flora and fauna can concentrate many trace metals to levels much higher than those existing in the waters (Leland et al., 1973; Trollope and Evans, 1976). Concentration factors depend upon the physicochemical interactions of each metal with other environmental parameters and organisms, as well as the nutritional requirements of individual species. In lakes having aquatic flora and fauna as a significant source of organic matter, such as many lakes of the southern Canadian Shield as opposed to those of the north, or in which waters are highly productive and sedimentation is rapid, the influence of organisms on trace element distribution may be significant.

### Organic Matter

Organic matter probably plays an important role in the complexing of heavy metals in lake waters and sediments. Within surficial waters metal-organic interaction is generally accepted to involve chelation of trace elements with humic matter (Bowen, 1966; Saxby, 1969). Of the organic species involved, humic acids, fulvic acids and humins are most abundant. These substances are probably also important in pore waters and interstitial waters of sediments representing as they do end members of humic matter degradation. Micro-organisms are, in part, responsible for the decomposition of the higher weight organic acids to produce smaller, more soluble fragments (Kuznetsov, 1975). Micro-organisms are also important in mobilizing certain metals from the sediments by means of very specific biochemical interactions (Wood, 1974 and 1975; Wong et al., 1975; Chau et al., 1976).

Humic and fulvic acids behave as negatively charged species in solution. Neutralization of this charge by interacting metal ions, metal oxide colloids, or adsorption onto clay particles can lead to flocculation of the colloids and subsequently, further coprecipitation of metals. Mechanisms by which metallic ions from natural waters are absorbed or complexed by such organic matter, have been extensively discussed (Krauskopf, 1955; Curtis, 1966; Schnitzer and Khan, 1972). The ability of solid humic matter to physically and chemically adsorb metals from aqueous solution has been documented (Rashid, 1974). Jackson and Jonasson (1977) suggested a probable order of binding strength for a number of metal ions onto humic or fulvic acids;  $UO_2^{++} > Hg^{++} > Cu^{++} > Pb^{++} = Ca^{++} > Zn^{++} > Ni^{++} > Co^{++}$ . The partitioning of trace elements in the organic phases of lake sediments from the Elliot Lake and Sturgeon Lake areas, Ontario was examined by Schaef (1975). Results indicated that Zn is preferentially concentrated in the fulvic component while, U, Cu and Pb are concentrated in the humic component.

Another function of organic matter in water-sediment interactions concerns the ability of soluble organic acids to chemically leach and even dissolve minerals, extracting a variety of elements including trace metals (Baker, 1973; Guy and Chakrabarti, 1976). Interactions between metal ions, minerals, organic sediments and water seem to be mutually destructive of all solid species. The ultimate result of the breakdown of a mineral or metal-sediment complex by organic acids must be to promote the remobilization of that metal ion until the adsorption, flocculation, polymerization, precipitation cycle takes it out of solution again.

Organic matter is also capable of acting as a reducing agent. In this way selected metal ions can be stabilized by complexation with certain organic acids or humic acid compounds (Rashid and Leonard, 1973; Theis and Singer, 1973).

From the studies that have been carried out to date it appears that metal-humic matter interactions are potentially important in the following geochemical processes: (1) leaching of metals from solid mineral phases; (2) dispersion within drainage basins as soluble or colloidal metal-organic species; and (3) concentration and fractionation of many elements within organic-rich sediments.

In the flat-lying, tree-covered terrain characteristic of the southern Canadian Shield and Fennoscandian Shield, and in the terrain of the Canadian Appalachians, the incidence of organic matter is high and metal-organic interactions are predominant. Streams and other waters which supply lakes are commonly fed by waters from swamps, marshes and muskeg. The dissolution residence time of waters within organic trash ensures considerable quantities of humic materials are present. Silts and clays are often coated with organic matter. By contrast, lakes in Shield areas above the treeline and from the alpine Cordilleran regions are fed by waters derived mainly from snow melt which contains very little dissolved organic material. Absorption of metals directly into clays, rock flour, and hydrous metal oxides and dissolution of mineral particles are the predominant water-sediment interactions.

### Hydrous Metal Oxides

The geochemical cycles of iron and manganese in the exogenic environment have been extensively reviewed in the literature, notably by Mortimer (1941, 1942 and 1971), Hutchinson (1957), Krauskopf (1957, 1967), Hem (1964), Gorham and Swain (1965), Mackereth (1966), Jenne (1968), and Stumm and Morgan (1970). There are also a large number of publications that describe the occurrence, composition and origins of freshwater ferromanganese deposits in European and North American lakes (viz.; Kindler 1932, 1935 and 1936; Twenhofel and McKelvey, 1941; Lundgeer, 1953; Beals, 1966; Delfino and Lee, 1968; Rossman and Callender, 1968, 1969; Harriss and Troup, 1969; Troup, 1969; Arnold, 1970; Cronan and Thomas, 1970, 1972; Dean, 1970; Edgington and Callender, 1970; Schoettle and Friedman, 1971; Damiani et al., 1973; Sozanski, 1974; Timperley and Allan, 1974; Coker and Nichol, 1975; Cook and Felix, 1975; Jackson and Nichol, 1975; Klassen et al., 1975; Koljonen and Carlson, 1975; Robbins and Callender, 1975).

Under oxidizing conditions, hydrous oxides of iron and manganese are excellent scavengers of trace elements; however, under reducing conditions they are made soluble and may result in increases in concentrations of cations and anions in overlying waters (Mortimer, 1941, 1942 and 1971; Hutchinson, 1957). Upon their release from rocks and overburden as divalent ions, iron and manganese respond similarly to changing Eh-pH conditions, but iron is oxidized and precipitated at lower Eh-pH fields than manganese, activities being equal. Much of the iron and manganese may be transported colloiddally in water as oxide hydrosols, likely stabilized by interactions with organic matter (Hem, 1971). Incoming runoff can bring iron and manganese into the lake as: (1) oxide coatings on mineral grains; (2) in solution and organic complexes; (3) adsorbed on solids; and (4) incorporated in organic solids. The proportion of the metals arriving in solution and in colloidal form, as complexes and in organic solids, will be high in the swampy creeks (rich in humic content and generally low in pH) that characterize much of the carbonate-poor forested Shield regions of the northern hemisphere. In the better aerated, sometimes rapid influents of the barren northern Canadian Shield and alpine Canadian Cordilleran regions oxide-coated particles and hydrous oxide complexes can attain predominance. On entering the lake most of the streamborne particles will

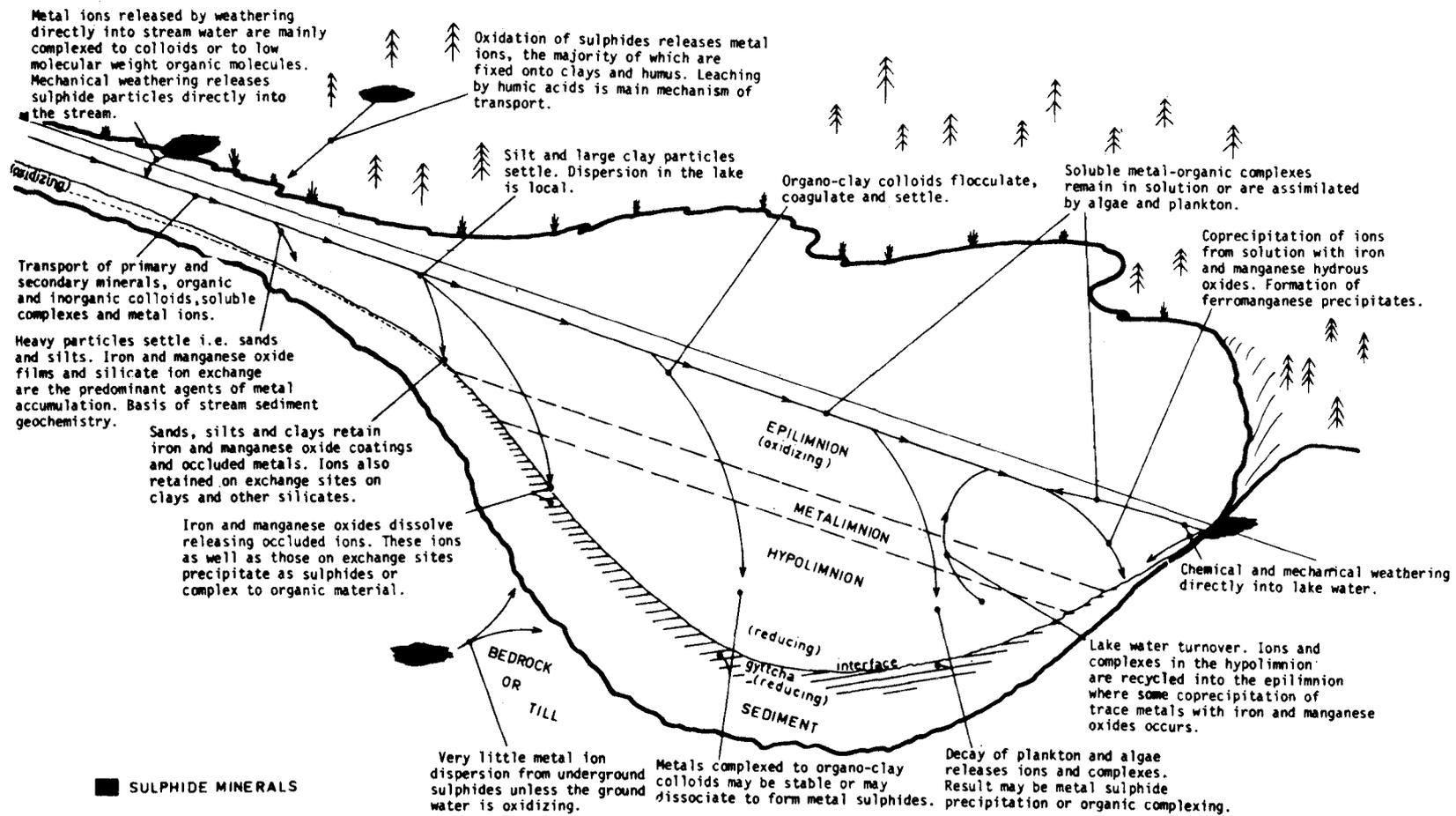


Figure 20.4. One model for mineral weathering, metal transport and metal accumulation within lakes of the forested portion of the Canadian Shield (from Timperley and Allan, 1974).

settle onto the bottom. When manganese and iron are brought into a lake basin which has oxidizing conditions, they will be oxidized and eventually precipitated, along with any trace elements they have absorbed, and incorporated into the sediment. In the forested areas of the Shield, the lake centre (profundal) sediments are generally characterized by a microzone of oxidizing sediment, at the sediment-water interface, overlying highly reducing organic-rich material (gyttja) (Mortimer, 1942 and 1971; Gorham, 1958). Littoral zone material is generally in an oxidizing environment. In the barren northern parts of the Shield the littoral and profundal sediments are generally oxidizing in nature, although under winter ice cover reducing conditions could result and are perhaps one explanation for the cyclic oxide banding (Klassen et al., 1975) noted in some sediments. If the sediments are reducing in nature, as is the general case in most profundal sediments in lakes from forested areas of the Shield, chemical dissolution of the hydrous oxides of manganese and iron can occur via two mechanisms: (1) the formation of iron or manganese complexes with organic acids (Baker, 1973); and (2) reduction of the hydrous oxides to more soluble species (Hem, 1960; Theis and Singer, 1973). Once this occurs the metals can then migrate laterally and up through interporous spaces in the sediments, along potential gradients, until oxidizing conditions are encountered and they are reprecipitated as crusts or nodular to discoid concretions in or atop the oxidized surface profundal or littoral zone sediments (Rossman and Callender, 1968). Other proposed models of concretion formation usually combine diagenetic and hydrogenous sources of iron and manganese (Troup, 1969; Terasmae, 1971; Cronan and Thomas, 1972). The effect of biota as direct oxidizers of iron and manganese has been widely asserted (Kindle, 1935; Troup, 1969; Kuznetsov, 1975), although some writers are skeptical about the role of microorganisms in the overall precipitation of the oxides (Krauskopf, 1957; Stumm and Morgan, 1970). If during the process of summer oxygen stratification, anaerobic conditions develop in the hypolimnion and the surface profundal sediments become reducing, manganic oxides and complexes in the sediments could be reduced and mobilized into the overlying lake waters. If oxygen becomes sufficiently depleted, the bottom water conditions will eventually lead to the reduction of ferric iron which would facilitate its migration from the sediments into the overlying waters as well. This phenomenon also affects the trace elements that are coprecipitated with the iron and manganese. However, as the conditions in the bottom waters become reducing in nature, the formation of carbon dioxide and hydrogen sulphide (or their salts) in appreciable quantities is facilitated. These can result in further solution of the trace elements as bicarbonates or polysulphides or reprecipitation of the trace elements as carbonates or sulphides. When a lake reaches the eutrophic stage all its sediments and most of its waters are reducing, thereby preventing the formation of higher oxides.

The scavenging effect of both iron and manganese hydroxide precipitates on trace metals in the lacustrine environment and the resulting false anomalies (Hawkes and Webb, 1962; Levinson, 1974) in lake sediments has been noted in the course of several exploration-oriented lake sediment studies (e.g. Arnold, 1970; Davenport et al., 1975a,b; Timperley and Allan, 1974; Coker and Nichol, 1975 and 1976; Jackson and Nichol, 1975; Hoffman and Fletcher, 1976; Hornbrook and Garrett, 1976; Cameron, 1977). Horizontal bands of precipitated iron and manganese are distinctive features of profundal sediments from lakes in the Kaminak Lake area, District of Keewatin although the trace metal content of the surface zones of the precipitate do not differ from those of the underlying sediment (Klassen et al., 1975). Various statistical methods have been employed to compensate for such false trace metal (mainly Zn, Co and Ni) anomalies, caused as a result of coprecipitation with iron and

manganese. These include ratioing (Coker and Nichol, 1975 and 1976; Jackson and Nichol, 1975) although this method was objected to by Clarke (1976) who like Spilsbury and Fletcher (1974), Davenport et al. (1975b) and Hornbrook and Garrett (1976) preferred to employ regression analysis. In general, the percentage of lakes in which iron and manganese concentrations are high enough to result in falsely anomalous trace metal occurrences is low. Such lakes can be readily identified by the abnormally high levels of iron and manganese present in their profundal sediments. Also, as has been suggested by Coker and Nichol (1975) and others, sampling below the surficial oxidizing layer of sediment into the reducing sediment, which is generally achieved by most sampling devices in use today, will avoid many of the problems of dealing with the more chemically-active surficial sediment.

Iron and manganese oxides are certainly important species in organic systems but their role as direct absorbers of metal ions is overshadowed by competition from the more reactive humic materials and organo-clays or obscured by coatings of organic matter. Moreover, these oxides are unstable in certain organic rich sediments, particularly if reducing. In lakes found in the barren tundra of Canada and in the Canadian Cordilleran regions, the role of organic matter in water-sediment interactions can be relatively unimportant compared with the influences of hydrous iron and manganese oxides.

### Clay Minerals

The relative importance of clay minerals in the transport and accumulation of trace metals within the lacustrine environment is poorly understood. The charge characteristics of clays, which impart their ion-exchange properties, originate from isomorphous replacements and the broken edges of crystal surfaces (Leland et al., 1973). The basic principles governing the selectivity characteristics of clays for different cations are valence, hydrated ionic radius, electronegativity, and the free energy of formation. Ionic potential (charge/radius) is a useful parameter for predicting the affinities of clays for different cations. The order of difficulty in displacement of cations is approximately (Mitchell, 1964):  $\text{Cu}^{++} > \text{Pb}^{++} > \text{Ni}^{++} > \text{Co}^{++} > \text{Zn}^{++} > \text{Ba}^{++} > \text{Rb}^{+} > \text{Sr}^{++} > \text{Ca}^{++} > \text{Mg}^{++} > \text{Na}^{+} > \text{Li}^{+}$  but relative positions in such a series vary with concentration in solution and the nature of the substrate. Complexing agents seem to alter the affinity of clay minerals for different cations. Several complexing agents are present in lacustrine environments but how they may affect the exchange properties of clay minerals or retention of heavy metals is not well known.

Examination of the inorganic clay-sized fraction of some profundal sediments from lakes in the southern Canadian Shield revealed that the true clay minerals present, mainly illite, chlorite and kaolinite, generally constitute less than half of the clay-size fraction. Quartz, plagioclase and potassium feldspar were the main minerals present. In the overall composition of certain profundal sediments true clay minerals were a very minor component (Arnold, 1970; Brunskill et al., 1971; Timperley and Allan, 1974; Coker and Nichol, 1975; and Dean and Gorham, 1976). The cation exchange capacity of illite, chlorite and kaolinite is relatively low for clays and very low relative to humic matter which undoubtedly coats the clay minerals in many instances.

Although clay minerals can be important in retention and transport of trace elements, most prominently in the Canadian Cordillera, and barren tundra portions of the Canadian Shield, their relative role must be evaluated with caution. Most recent literature emphasizes the importance of organic matter and hydrous oxides in the transport of heavy metals; particularly in the forested Shield regions of the northern hemisphere.

Table 20.2

The main forms of trace metal ions found in aquatic systems for pH's from 5 to 9.5 and various main constituent concentrations (from Morel et al., 1973).

Species Accounting for more than 90%	Species Accounting for a few per cent
Fe Fe(OH) <sub>2</sub> <sup>+</sup> , FePO <sub>4</sub> (s), Fe(OH) <sub>3</sub> (s) FeCO <sub>3</sub> (s), FeS(s), FeSiO <sub>3</sub> (s)	
Mn Mn <sup>++</sup> , MnCO <sub>3</sub> (s), MnO <sub>2</sub> (s) MnS(s)	MnHCO <sub>3</sub> <sup>+</sup> , MnSO <sub>4</sub> , MnCl <sup>+</sup>
Cu Cu <sup>++</sup> , Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub> CuCO <sub>3</sub> , Cu(OH) <sub>2</sub> (s) CuS(s)	CuSO <sub>4</sub>
Ba Ba <sup>++</sup> , BaSO <sub>4</sub> (s)	
Cd Cd <sup>++</sup> , CdCO <sub>3</sub> (s), Cd(OH) <sub>2</sub> (s) CdS(s)	CdSO <sub>4</sub> , CdCl <sup>+</sup>
Zn Zn <sup>++</sup> , ZnCO <sub>3</sub> (s), ZnSiO <sub>3</sub> (s) ZnS(s)	ZnSO <sub>4</sub> , ZnCl <sup>+</sup>
Ni Ni <sup>++</sup> , Ni(OH) <sub>2</sub> (s) NiS(s)	NiSO <sub>4</sub>
Hg HgCl <sub>2</sub> , Hg(OH) <sub>2</sub> (s) HgS(s), Hg(liq), HgS <sub>2</sub> <sup>2-</sup> , Hg(SH) <sub>2</sub>	
Pb Pb <sup>++</sup> , PbCO <sub>3</sub> (s), PbO <sub>2</sub> (s) PbS(s)	PbSO <sub>4</sub> , PbCl <sup>+</sup>
Co Co <sup>++</sup> , CoCO <sub>3</sub> (s), Co(OH) <sub>3</sub> (s) CoS(s)	CoSO <sub>4</sub> , CoCl <sup>+</sup>
Ag Ag <sup>+</sup> , AgCl Ag <sub>2</sub> S(s)	
Al Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (s), Al(OH) <sub>3</sub> (s)	AlF <sup>+2</sup> , AlF <sub>2</sub> <sup>+</sup>
The species of each metal are listed in the order they are found with increasing pH. ((s) solid precipitate)	

### Solubility Chemistry

The ability of a trace metal ion to remain in solution in an aqueous system is limited by the stability of the compounds it forms by reactions with the other components in solution (i.e.: carbonate, chloride, sulphate and hydroxide, etc.). The Eh-pH conditions of the water are the main controlling factors as has been discussed at length by Baas Becking et al. (1960), Garrels and Christ (1965), Krauskopf (1967) and others.

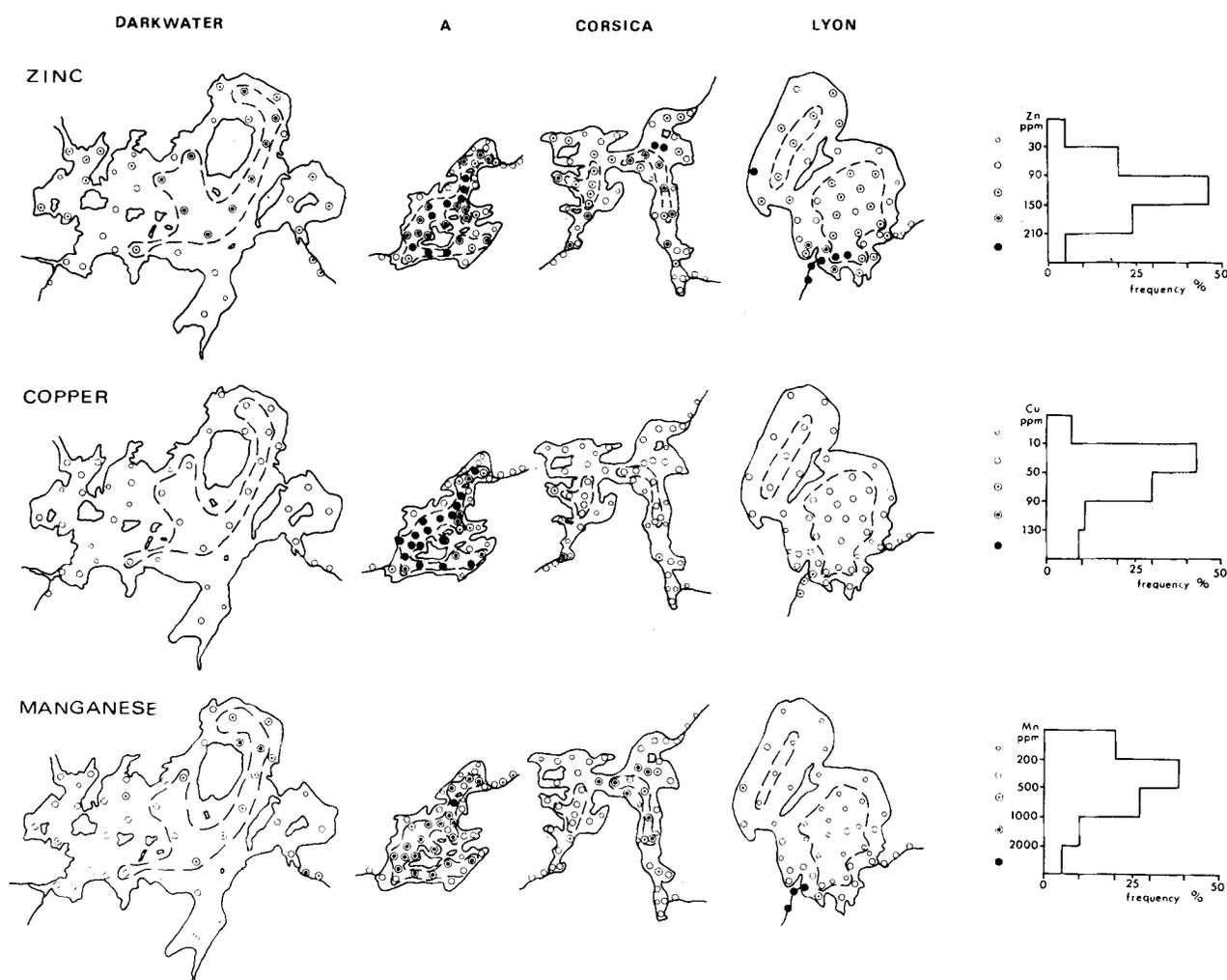
Morel et al. (1973) listed the main forms of trace metal ions found in aquatic systems for pH ranging from 5 to 9.5 and various main constituent concentrations (Table 20.2). The species are listed in the order in which they are found with increasing pH. The general pattern is well known: the free ions tend to predominate at low pH, the carbonate and then the oxide, hydroxide or even silicate solids precipitate at higher pH. Because the complexing or precipitating ligands are usually in large excess of the trace metals, they mediate few important interactions (competition) among those metals.

As has been previously discussed, organic ligands can play a major role in natural waters by complexing trace metal ions and also by mediating interactions among trace metal ions. However, the relative stability of soluble metal humates or fulvates in competition with other complexing ions such as carbonate, sulphide and hydroxide is not well known. The adsorption influences induced by the presence of solid substrates are also little known. In one experimental laboratory study the presence of humic acid strongly inhibited trace metal complexation and precipitation by the

inorganic ligand (carbonate, sulphide or hydroxide) (Rashid and Leonard, 1973). Hydroxide appeared most effective in causing trace metal precipitation, in competition with soluble metal humate formation, followed by sulphide and then carbonate. However, at the lower final pH of the hydroxide reactions, H<sup>+</sup> ions can interfere in the precipitation reactions.

One of the main products of the oxidation of organic matter is the sulphate ion which in reducing environments is reduced chemically or bacterially to sulphide species, H<sub>2</sub>S, HS and S<sup>2-</sup> (Hutchinson, 1957; Garrels, 1960; Kuznetsov, 1970 and 1975). Within the bottom reducing muds of lakes, metals may be partitioned to varying degrees between inorganic sulphides and organic complexing agents. Timperley and Allan (1974) attempted to determine the forms of binding of Cu, Fe and Zn in organic-rich reducing muds. One of the main conclusions drawn was that Cu was held mainly by sulphide precipitation, whereas organic complexing was more important for Zn and Fe. In another study carried out by Jackson (1977) almost the reverse conclusions were drawn. The degree of affinity of trace metals for sulphide, relative to degree of affinity for organic matter, correlated strongly with the standard entropy of the metal sulphides, decreasing in the order Hg > Cd > Cu > Fe > Zn (Jackson, 1977). Thus, the stability of the metal sulphides tends to control the partitioning of metals between sulphide and organic matter. Sulphide appears much more effective than organic matter in preventing remobilization of Zn, Cd and Fe from the mud. The behaviour of Cu suggested strong affinity for organic chelating agents.

The role of the carbon dioxide-bicarbonate-carbonate cycle in the dispersion and accumulation of trace metals in the lacustrine environment can be significant. Both iron and manganese and most trace metals, including Cu, Zn, Ni, Co and Pb are immobile under oxidizing alkaline (high pH) conditions and mobile under reducing acid (low pH) conditions (Baas Becking et al., 1960; Hawkes and Webb, 1962; Garrels and Christ, 1965; Krauskopf, 1967; Andrews-Jones, 1968). In the Sturgeon Lake area of northwestern Ontario the dispersion of Zn from a massive sulphide source into the centre of adjacent Lyon Lake was restricted when the relatively neutral (pH ~ 7) waters of the inflowing stream encountered the relatively alkaline (pH ~ 8) lake waters (Fig. 20.5) (Coker and Nichol, 1975). The effect of increasing alkalinity on restricting trace metal dispersion in the Agricola Lake area of the barren northern Shield was noted by Cameron and Ballantyne (1975) and Cameron (1977) (Fig. 20.6). The influence of bicarbonate ion on uranium solubility has long been recognized (Bowie et al., 1971) and was postulated as a potential influence effecting the lack of correspondence between anomalous levels of U in water and sediment from the same lake (Cameron and Hornbrook, 1976; Coker and Jonasson, 1977a,b; Maurice, 1977a,b). Maurice (1977a) stated that at low alkalinities the lake sediments are in most cases more useful than the lake waters in indicating uranium dispersion in the Baffin Island study area and the converse applies for high alkalinities. Jackson (1975) designed a laboratory study over pH ranges from 4 to 9 in order to simulate interactions in the system dissolved metal ion-clay-dissolved natural organic acids. He found the behaviour of Ni was strongly controlled by interference reactions with carbonate and hydroxide and also that Pb and Fe favoured organic complexing, Cu dispersion was by sorption to organic-rich sediments, and that his experimental scheme was inadequate for Zn.



**Figure 20.5.** The distribution of Zn, Cu and Mn in four lakes, Sturgeon Lake area, Ontario (after Coker and Nichol, 1975).

### Lake Sediment Physicochemistry

The physicochemical characteristics of lake bottom deposits play a major role in determining the distribution of trace metals within an individual lake. One of the most influential variables is the organic carbon content of the bottom deposits. Deep-water, generally centre-lake (profundal) sediments from lakes in the southern Canadian Shield generally have very homogeneous organic contents as shown in Figure 20.7 for lakes in northwestern Ontario (Coker and Nichol, 1975). Jonasson (1976) found this same feature in lakes examined in detail in the Grenville geological province of Ontario. A similar, although not so clear cut relationship, due to factors discussed previously was found in lakes of the northern Canadian Shield (Jackson and Nichol, 1975; Klassen et al., 1975). Most trace metals tend to be enriched in the organic sediments, a factor which is most probably due to the nature and strength of metal-organic binding and perhaps increased ion-exchange capacity of organic sediments over inorganic types. As a result, the highest and most uniform concentrations of trace metals generally occur in the deep central areas (profundal basins) of each lake where the sediments generally have the highest and most homogeneous organic contents (Coker and Nichol, 1975; Jonasson, 1976). This feature is illustrated diagrammatically (Figs. 20.5 and 20.8) and arithmetically (Tables 20.3 and 20.4), as indicated by the generally smaller coefficients of variation for trace

metals in lake-centre sediments compared to lakeshore materials (Coker and Nichol, 1975; Jonasson, 1976). The presence of organic carbon in relatively highly variable quantities in shoreline (littoral) materials strongly influences the levels of trace metals found.

However, each lake is an entity as its sediments have individual characteristic amounts of organics which can vary considerably from lake to lake within a large survey area. This particular phenomenon has been examined by Garrett and Hornbrook (1976), for Zn, from some 3850 lake-centre sediment samples collected from northern Saskatchewan (Fig. 20.9). The Zn content of the centre-lake bottom sediments was found to rise linearly with increasing organic content, as measured by L.O.I. at 500°C, only at low levels (0 to 12% L.O.I.). At these low levels the Zn distribution patterns will therefore be partly controlled by the amount of organic material present and may not truly reflect the chemistry of the drainage basin. Where there is an excess adsorption capacity in the sediments (L.O.I. > 12%), the Zn distribution patterns should reflect the chemistry of the drainage basin. The observed decrease in Zn values with very high organic contents (> 50% L.O.I.) may be reflecting a dilution factor introduced by the ever increasing load of organic material to a system which is not receiving more Zn. Preliminary studies of the relationship of Zn and U with both Fe and Mn and of U with L.O.I. revealed a similar general

Table 20.3  
 Arithmetic mean, range and coefficient of variation of Zn, Cu and Mn  
 in sediments from four lakes, Sturgeon Lake area, Ontario  
 (from Coker and Nichol, 1975)

Lake Population		Lyon		A		Corsica		Darkwater	
		C	S	C	S	C	S	C	S
Zinc	$\bar{x}$	79	58	115	51	84	29	106	44
	R	53-435	12-92	68-220	17-111	65-110	16-41	90-137	21-120
	V	114	31	35	49	11	24	12	60
Copper	$\bar{x}$	14	11	85	21	26	8	23	10
	R	10-17	<4-18	56-121	<4-60	24-28	4-12	21-25	4-37
	V	12	38	20	77	7	27	6	91
Manganese	$\bar{x}$	94	151	712	283	492	216	410	326
	R	70-203	66-292	125-1465	115-877	190-1199	127-426	221-675	187-432
	V	38	40	45	64	74	35	38	26
	n	18	25	24	16	10	17	10	13

Population: C = Lake-centre sediments. (profundal)  
 S = Lake-shore sediments. (littoral)  
 $\bar{x}$  = Arithmetic mean (quoted in ppm).  
 R = Highest and lowest value (quoted in ppm).  
 V = Coefficient of variation ((Standard deviation/ $\bar{x}$ ) X 100).  
 n = Number of samples.

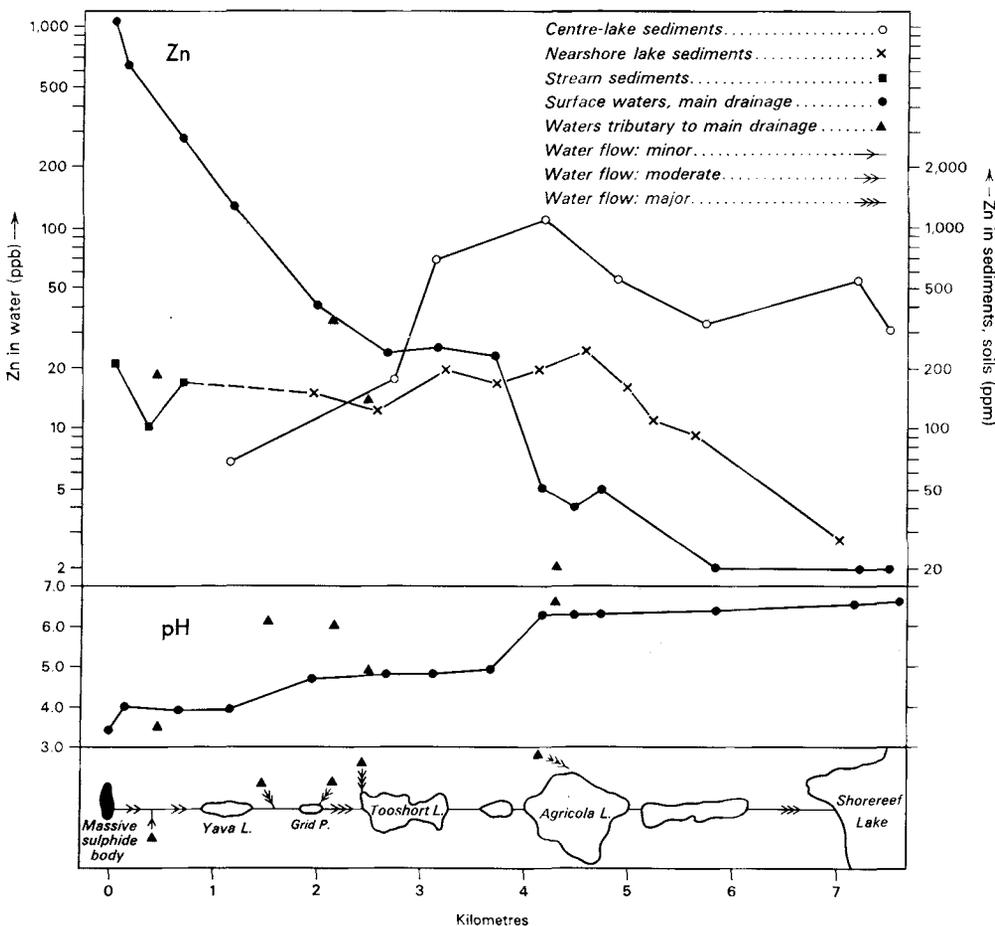
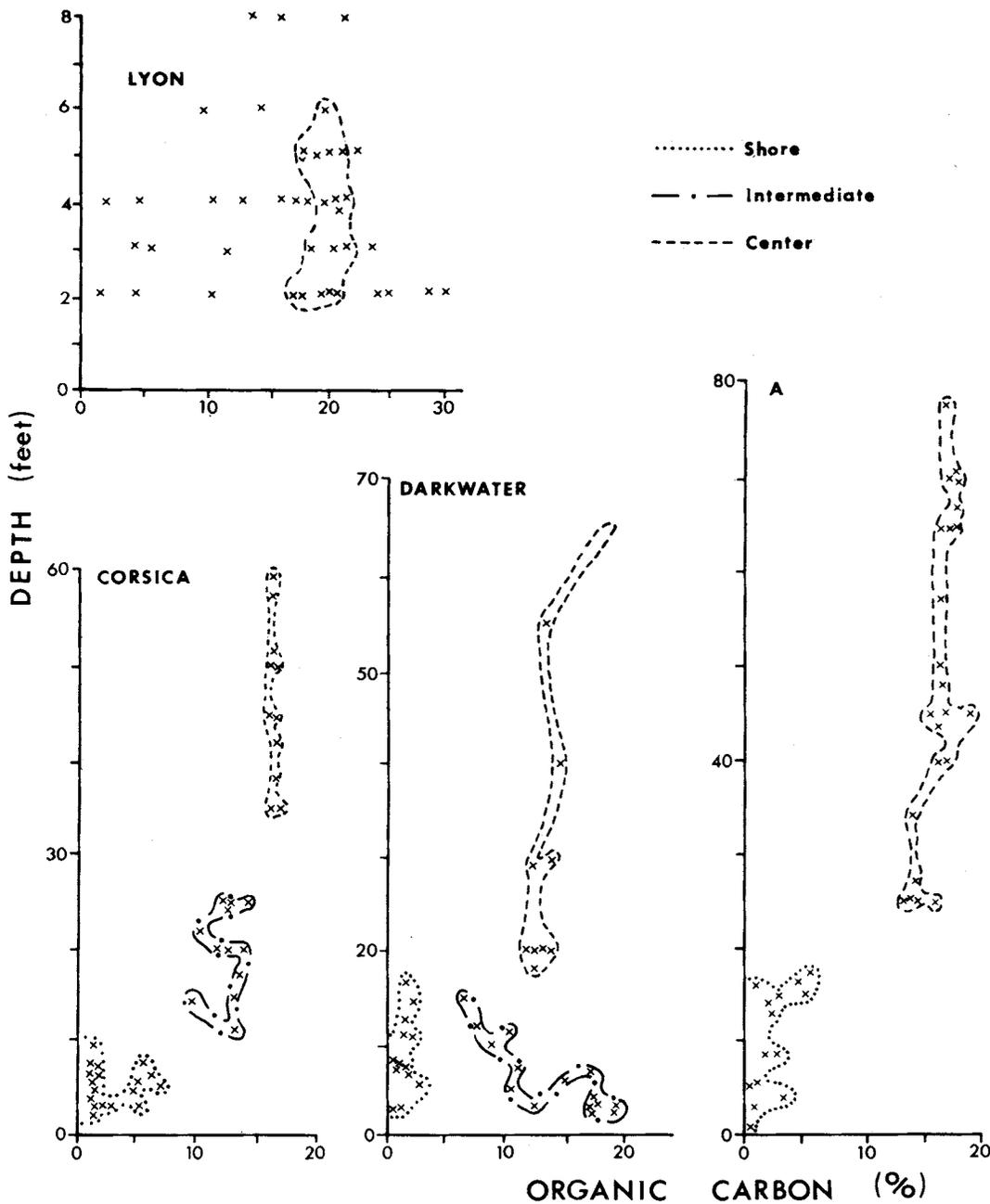


Figure 20.6.  
 Distribution of Zn in lake and stream sediments and waters, Agricola Lake system, District of Mackenzie (after Cameron, 1977).



**Figure 20.7.**  
Relation between organic carbon content of sediments and water depth within four lakes, Sturgeon Lake area, Ontario (from Coker and Nichol, 1975).

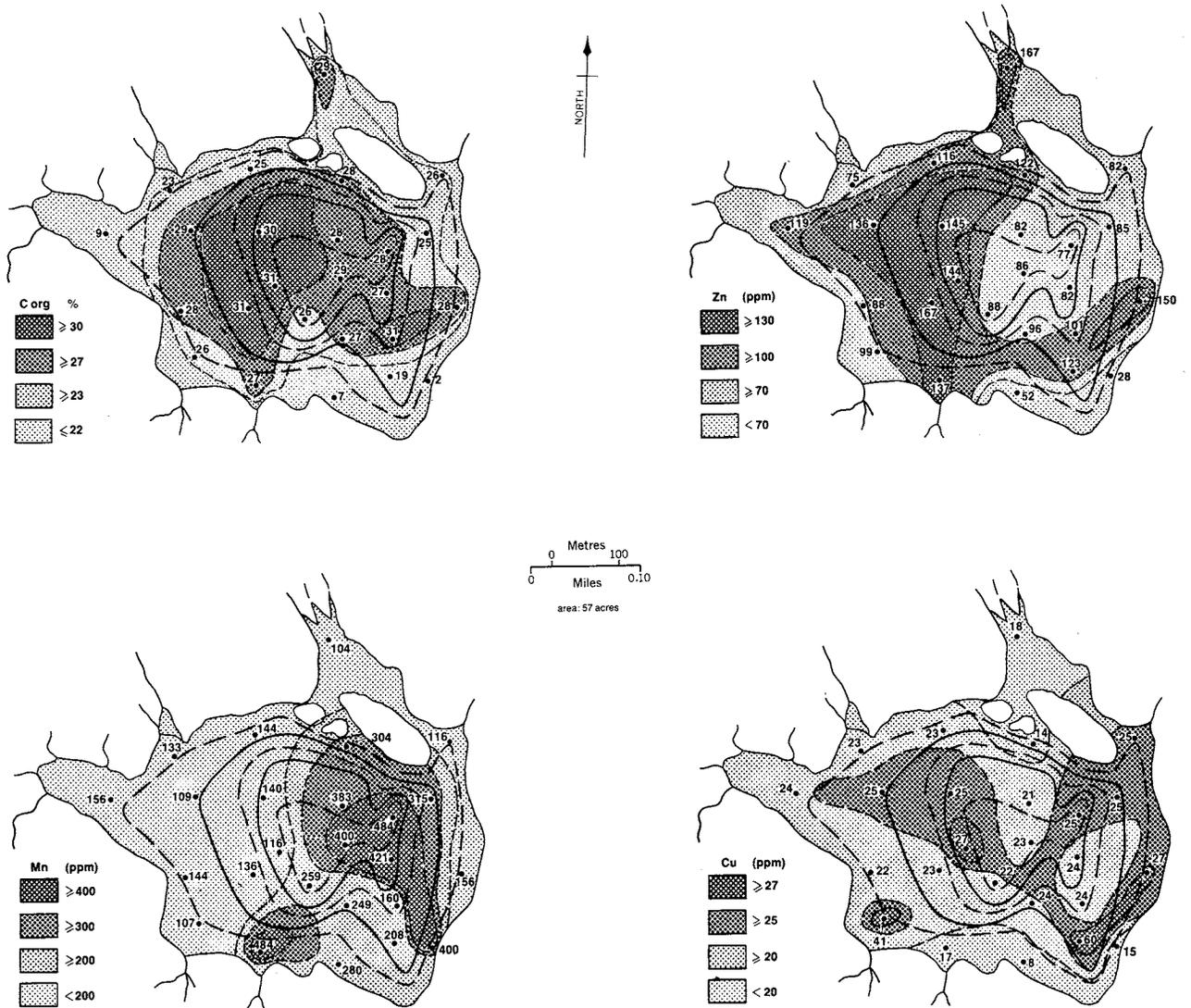
behaviour to that of Zn with L.O.I. for the lake-centre sediments samples from northern Saskatchewan (Garrett and Hornbrook, 1976).

The relationship between the Zn and organic contents of 275 reconnaissance lake-centre sediments from the Sturgeon Lake area in northwestern Ontario was similar to that found in sediments from northern Saskatchewan (Coker and Nichol, 1976). However, the use of ignited Zn data (analysis based on a fixed weight of ash residue) was thought to constitute a more homogeneous data set, which is relatively independent of the amount of organic matter, over a larger range of data than for unignited Zn data (analysis of a fixed weight of dried sample).

Bjorklund et al. (1976) also used analysis of ignited organic-rich lake sediments to examine the distribution of U in lake sediments from Karelia, Finland. In addition they

examined the distribution of U in material lost-on-ignition from organic-rich sediments (i.e. approximately the organic part) and also the U contents expressed as relative deviation from a polynomial function, approximated through the medians of uranium contents constructed from a graph of U in ignited sediment versus L.O.I. The significance of the various interpretational methods has not been thoroughly studied to date.

The relationship between the U and organic contents of sediments from several individual lakes in northern Saskatchewan was examined by Lehto et al. (1977). A roughly linear relationship exists for each lake and the slope of the U versus organic curve was unique for any given lake and was felt to be a function of the local geological-geochemical-limnological environment. Similar relationships for Cu and Zn versus organic matter, iron and manganese were shown for



**Figure 20.8.** Organic carbon, Zn, Mn and Cu distribution in organic sediments of Perch Lake, Ontario (after Jonasson, 1976).

Table 20.4

Geochemical comparisons of silty shoreline (littoral) and organic deep water (profundal) sediment samples from Perch Lake, Ontario (after Jonasson, 1976).

Element	Shoreline Silts		Organic gels		Organic enrichment factor $\frac{X_o}{X_s} = R$
	$X_s$	$C_v\%$	$X_o$	$C_v\%$	
Zn (ppm)	44	52	106	33	2.41
Cu (ppm)	5.5	83	24	40	4.36
Mn (ppm)	103	60	236	54	2.29
C org (%)	8.4	132	24.7	31	2.94

$X_s$  = arithmetic mean for shoreline silts. (littoral)  
 $X_o$  = arithmetic mean for organic gels. (profundal)  
 $C_v\%$  = coefficient of variation.

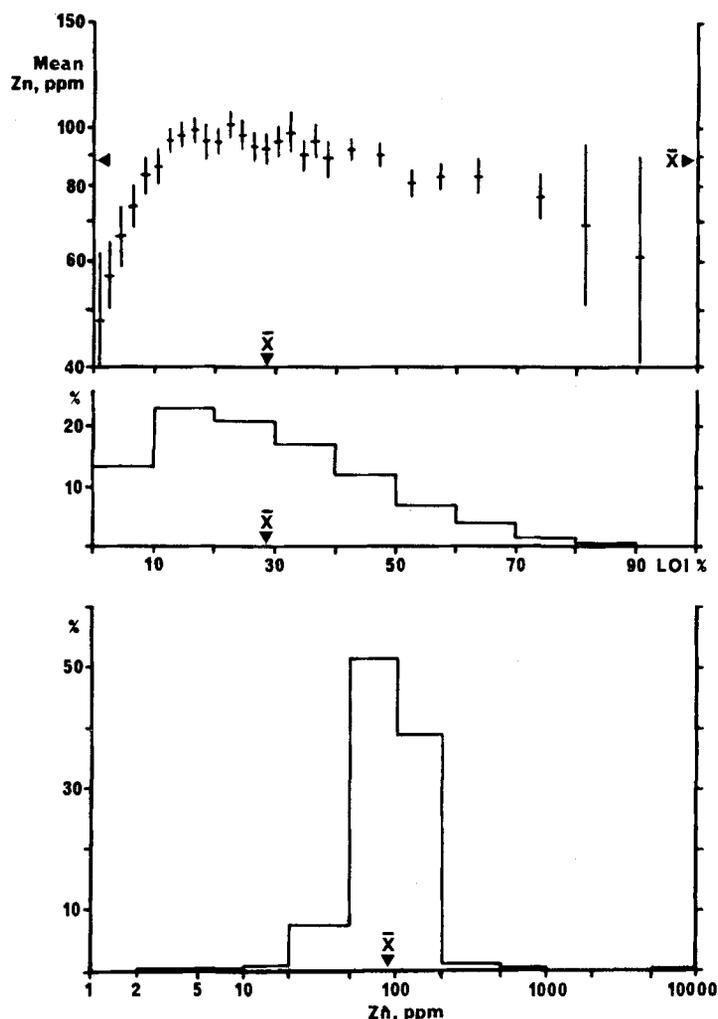


Figure 20.9. Graphic display of the relationship between Zn and L.O.I., and histograms for Zn and L.O.I. from 3844 centre-lake bottom sediments, east-central Saskatchewan (from Garrett and Hornbrook, 1976).

selected single lakes from the Kaminak Lake area, District of Keewatin, Yellowknife area, District of Mackenzie, and Sturgeon Lake area, Ontario (Nichol et al., 1975). Lehto et al. (1977) stated that by sampling organic-rich sediments from lake centres the chemical data obtained would tend to plot on the outer ends of the metal versus organic matter curve for each individual lake which, when examined together would give the curved distribution as found by Garrett and Hornbrook (1976) in Figure 20.9. They further suggest that since the trace metals appear to be associated with the organic fraction of lake sediments the metal values should be normalized for varied dilution by recalculating to 100% organic matter (essentially similar to calculating metal values on a loss-on-ignition basis).

Another method of determining lake sediment data, as suggested by Parslow (1977), involves employing a constant volume of sample rather than a constant weight.

In general, regardless of the method of analyzing the sediments (although use of ignited or constant volume data have not received much application to date), it appears that a homogeneous and ubiquitous sample medium which does not exhibit severe matrix problems can be found in organic-rich lake-centre sediments with L.O.I.'s generally ranging between a lower limit of 10 to 20% and an upper limit of 50 to 70%.

## LAKE SEDIMENTS AND MINERAL EXPLORATION

The range of physicochemical-limnological conditions present within the lacustrine environment, as previously outlined, should emphasize the complexity of this regime. Variations in these conditions can effect the nature of metal transport, and accumulation in lake bottom materials, with respect to mineralization in different geographic – climatic and geological environments.

Within the last decade universities, government agencies, and the mineral exploration industry have carried out research studies and orientation, regional reconnaissance and follow-up lake sediment surveys in the search for various types of mineralization. The majority of these surveys have taken place within the Canadian Precambrian Shield and to a lesser extent within the Cordilleran and Appalachian regions of Canada. In addition, some lake sediment surveys have taken place in the Precambrian Shield, Cordilleran and Appalachian regions of the United States of America and the Precambrian Shield of Fennoscandia.

### Sampling Equipment, Logistics and Cost

A wide variety of sampling devices have been used by geochemists to collect lake sediments. One type of lake sediment sampler currently in wide use in North America, by both government and industry, is the 1976 model Geological Survey of Canada sampler (Fig. 20.10), or some device similar to it. This sampler has successively evolved, with extensive modifications, from a sampler developed by the Geological Survey of Canada and the Newfoundland Department of Mines and Energy in the early 1970s (Hornbrook et al., 1975a; Hornbrook and Garrett, 1976). The sampler now features a nose design similar to a previously developed Finnish lake sediment sampler (Bjorklund et al., 1976). The nose section of the 1976 model sampler (Fig. 20.10) has a stainless-steel butterfly valve inset, which prevents loss of sample material by automatically closing, below the collected sample, upon retrieval of the sampler. This sampler was not designed to collect lake bottom materials with a large coarse clastic component or coarse organic debris component, as these types of sample compositions are not desired. It was designed to achieve rapid sampling of organic sediments from profundal lake basins.

Many other types of lake bottom samplers have been, and still are used. The bucket-type Ekman Birge-bottom dredge, which closes by means of a messenger sent down from surface, works well and collects large quantities of material in organic muds and gels, but is inefficient in coarse clastic materials or coarse organic debris (Closs, 1975; Coker and Nichol, 1975). The clam-type Petite Ponar grab sampler (Klassen et al., 1975), and the Kel Scientific Instruments mud snapper (Hoffman and Fletcher, 1976), both of which are triggered shut on impact, are efficient in clastic materials but not in organic muds or gels. These clam- and bucket-type samplers are generally not as amenable to rapid sample collection from the float of a helicopter as are the pipe-like devices similar to the 1976 model Geological Survey of Canada sampler. The Phleger corer has been used to collect lake sediment cores (Closs, 1975) as have other specially designed sediment corers (Coker, 1974; Meineke et al., 1976), all of which employ plastic core barrel liners. Nearshore lake bottom materials have been collected by hand or with extension posthole augers (Allan et al., 1973b) and with a home-made tube device with a one-way valve (Dyck, 1974). A combination of home-made extension augers, telephone-spoon shovel, and sample tubes, driven by a portable overburden drill, were used by Hornbrook and Gleeson (1972) to collect lake bottom materials through winter ice cover. Collection of lake sediment grab samples and core sections has also been carried out by scuba divers (Jonasson, 1976; R.A. Klassen, pers. comm.).

Table 20.5

A summary of lake sediment surveys carried out in the Canadian Cordillera, Shield and Appalachians.

Location Number and Location	Geology	Mineralization	Glacial Sediments	Density, Area, Site Location	Size Fraction, Elements	Survey Type	Reference Number
1 Central, British Columbia Nechako Plateau	volcanics and intrusives	Mo	ground moraine and fluvio-glacial deposits	>1/24 km <sup>2</sup> 16,000 km <sup>2</sup> centre-lake	-80 mesh Cu, Mo, Pb, Zn, Ni, Mn, L.O.I., Sr, Ba, Cr, Co, Ga, Ag, V, Ti, Bi, Zn, Sb	A-1	35
2 Central Interior British Columbia	volcanics and intrusives	Mo	ground moraine	1/10 km <sup>2</sup> centre-lake	Mo	B-1	50
3 South-central British Columbia	volcanics and intrusives	Cu	ground moraine and fluvio-glacial deposits	various nearshore	-80 mesh Cu, Fe, Mn, Zn, K	B-1	34
CANADIAN SHIELD, NORTHERN (north of latitude 60°00'N)							
4 Coppermine River Area NWT	Proterozoic basalts and sediments	Cu	ground moraine minor glacio-marine sediments	1/26 km <sup>2</sup> 3400 km <sup>2</sup> nearshore	-80 mesh Cu, Zn	A-2	2
5 Bear Province NWT	Archean and Proterozoic volcanics, sediments and granites	U	ground moraine	1/26 km <sup>2</sup> nearshore	-250 mesh U, Si, Al, Fe, Mg, Ca, Ti, Mn, Ba, Na, K, Zn, Cu, Pb, Ni, Co, Ag, As, Hg	A-1	12
6 High Lake area, N. Slave Province NWT	volcanics	Cu, Zn	ground moraine	1/26 km <sup>2</sup> 700 km <sup>2</sup> nearshore	-250 mesh Zn, Cu, Pb, Ni, Co, Ag, Si, Al, Fe, Mg, Ca, Ti, Mn, Ba	B-1	3
7 Hackett River, E. Slave Province NWT	volcanics	Zn, Pb, Ag, Cu	ground moraine	1/26 km <sup>2</sup> 700 km <sup>2</sup> nearshore	-250 mesh Zn, Cu, Pb, Ni, Co, Ag, Si, Al, Fe, Mg, Cu, Ti, Mn, Ba	B-1	3
8 Agricola Lake, E. Slave Province NWT	metavolcanics metasediments	Zn, Cu, Pb, Ag, Au, As, Cd, Hg	ground moraine	various nearshore centre-lake	-250 mesh Zn, Cu, Pb, Ni, Co, Ag, Fe, Mn, Hg, As	B-1	11
9 Bear Slave Provinces NWT	Archean and Proterozoic volcanics and sediments	Cu, Zn, Au, U	ground moraine	1/26 km <sup>2</sup> 93 000 km <sup>2</sup> nearshore	-250 mesh Zn, Ag, Mn, Li, U, As, Sb, Cu, Pb, Sn, V, Mo, Cr, Co, Ni, Be, La, Y, Zr, Sr, Ba, Ti, Ca, Mg, Fe, K	A-1	4
10 Yellowknife NWT	Archean metavolcanics, metasediments and granites	Cu, Pb, Zn, Ag, Au	ground moraine glaciolacustrine deposits	* centre-lake	-80 mesh Cu, Zn, Pb, As, Ag, Mn, L.O.I., Co, Ni, Fe	B-1	42
11 Yellowknife NWT	Archean volcanics, sediments	Cu, Pb, Zn, Ag, Au	ground moraine and glacio-lacustrine deposits	1/26 km <sup>2</sup> 2600 km <sup>2</sup> nearshore	-250 mesh Cu, Pb, Zn, Ag, Co, Ni, Fe, Mn	A-1	52
12 East Arm, Great Slave Lake, NWT	Archean volcanics, sediments and granites	Cu, Pb, Zn, Ag	ground moraine glaciolacustrine sediments	1/2.6 km <sup>2</sup> 260 km <sup>2</sup> centre-lake	-80 mesh Cu, Zn, Pb, As, Ag, Mn, L.O.I., Co, Ni, Fe	A-1	42
13 Nonacho Lake, NWT	sediments volcanics granites	U, Cu	ground moraine glaciolacustrine	1/1 km <sup>2</sup> 1400 km <sup>2</sup> centre-lake	-80 mesh U, Zn, Cu, Pb, Ni, Co, Ag, Mn, As, Mo, Fe, Hg, L.O.I.	B-2	46 48

Table 20.5 (cont'd)

Location Number and Location	Geology	Mineralization	Glacial Sediments	Density, Area, Site Location	Size Fraction, Elements	Survey Type	Reference Number
14 Kaminak Lake, NWT	Archean meta-volcanics, metasediments and intrusives	Cu, Zn, Ni	ground moraine glaciomarine	* centre-lake	-80 mesh Cu, Zn, Pb, Ag, Fe, Mn, Co, Ni	B-1	44
15 Baffin Island, NWT	Proterozoic granite, migmatite and quartzfeldspar gneiss	U	ground moraine and glaciomarine permafrost	1/3 km <sup>2</sup> 323 km <sup>2</sup> 1/13 km <sup>2</sup> 3800 km <sup>2</sup> centre-lake	-200 mesh U, Fe, Mn, Cu, Pb, Zn, Ni, Mo, Ag, V, Cr, Be, La, Y, Sr, Ba, Co, Ti	B-1	47
16 Cape Smith – Wakeham Bay, N. Quebec	serpentinized ultramafic sills	Ni, Cu	ground moraine permafrost	65 km <sup>2</sup> nearshore	-80 mesh Ni, Cu	B-1	1
CANADIAN SHIELD, SOUTHERN (south of latitude 60°00'N)							
17 Beaverlodge, Saskatchewan	metasediments granites meta-volcanics and sediments	U, Cu, Co, Ni, Pb, Zn, V, Hg, Pt, Au	ground moraine glaciolacustrine sediments	1/0.6 km <sup>2</sup> 77 km <sup>2</sup> nearshore	-60 mesh Ra, U, Zn, Cu, Pb, Ni, Fe, Mn, organic content	B-1	29
18 Rabbit Lake, N. Saskatchewan	Proterozoic Athabasca sandstone metasedimentary rocks	U	ground moraine	>1/13 km <sup>2</sup> 1300 km <sup>2</sup> centre-lake	-80 mesh U, Zn, Cu, Pb, Ni, Co, Ag, Mn, Fe, Mo, L.O.I.	B-1	13
19 N. Saskatchewan	Athabasca sandstone	U	ground moraine glaciolacustrine sediments	1/6 km <sup>2</sup> 6000 km <sup>2</sup> centre-lake	U, Cu, Pb, Zn, Ni, Co, Fe, Mn	B-1	53
20 Key Lake, N. Saskatchewan	Athabasca sandstone Archean metasediments	U, Ni	ground moraine	>1/1 km <sup>2</sup>	U, Ni, Cu, Pb, Zn	B-1	53 55
21 Mudjatik Lake, Saskatchewan	mafic granulites, felsic gneiss	U	ground moraine	3600 km <sup>2</sup> nearshore centre-lake	-60 mesh Hg, Co, Ni, Cu, Pb, Zn, U, Mo	B-1	33
22 Stanley area, Saskatchewan	volcanics sediments intrusives	Cu, Au	ground moraine glaciolacustrine sediments	440 km <sup>2</sup> nearshore	Cu, Zn, Ni, Pb, Mo, U, Co, Fe, Mg, Mn, Na, Hg	B-1	32
23 Southeast Saskatchewan	Archean volcanics sediments and intrusives	Cu, Ni, Au, U	ground moraine glaciolacustrine sediments	>1/1 km <sup>2</sup>	U, Cu, As, Zn	B-2	45
24 La Ronge, Saskatchewan	volcanics sediments granites	Cu, Zn, Au, Ag	ground moraine glaciolacustrine deposits	* centre-lake	Cu, Zn, Ni, Fe, Mn, Co	B-1	7

\* one or more lakes sampled in detail from a variety of site locations for various lake bottom materials.

Survey Type A Regional 1 Reconnaissance survey  
2 Detail survey

B Research 1 Orientation survey  
2 Follow-up survey

Location Number refers to site number on location map, Figure 20.11

Reference Number refers to source in the bibliography

Table 20.5 (cont'd)

Location Number and Location	Geology	Mineralization	Glacial Sediments	Density, Area, Site Location	Size Fraction, Elements	Survey Type	Reference Number
25 East-central Saskatchewan	Archean volcanics sediments intrusives	Cu, Ni, Au	ground moraine glaciolacustrine sediments	1/13 km <sup>2</sup> 52 000 km <sup>2</sup> centre-lake	-80 mesh Zn, Cu, Pb, Co, Ni, Ag, Fe, Mn, Hg, As, Mo, U, L.O.I.	A-1	39 40 41
26 N.W. Manitoba	Archean granites Aphedian sedi- ments intrusives	U	ground moraine glacio-fluvial deposits	1/1 km <sup>2</sup> 900 km <sup>2</sup> centre-lake	-80 mesh Zn, Cu, Pb, Ni, Co, Ag, Mn, As, Mo, Fe, Hg, L.O.I., U, F	B-2	16
27 Fox Lake Manitoba	Archean volcanics sediments and intrusives	Cu, Zn	ground moraine glaciolacustrine sediments	*	Cu	B-1	9 14
28 Saskatchewan west of Flin Flon, Manitoba	volcanics sediments granites	Cu, Zn, Au, Ag	ground moraine glaciolacustrine	*	Cu, Zn, Ni, Fe, Mn, Co	B-1	7
29 Wintering Lake, Manitoba	Archean volcanics sediments intrusives	Cu, Ni	glaciolacustrine deposits	*	Cu, Ni	B-1	8
30 Red Lake- Uchi Lake, Ontario	volcanics sediments	Au	ground moraine glaciolacustrine deposits and outwash	*	Cu, Zn, Mn, Fe, H <sub>2</sub> S, HS <sup>-</sup> , S <sup>2-</sup> , L.O.I.	B-1	56
31 Northwestern Ontario	Archean volcanics sediments and intrusives		ground moraine	*		B-1	10
32 Upper Manitou Lake, N.W. Ontario	volcanic sedimentary and intrusive rocks	Cu, Zn, Ag, Ni	ground moraine glaciolacustrine deposits	* centre-lake	-80 mesh Zn, Ni, Mn, Cu, Pb, Ag, Fe, Co, L.O.I.	B-1	17 18
33 Sturgeon Lake, N.W. Ontario	volcanic sedimentary and intrusive rocks	Cu, Zn, Ag, Ni	ground moraine glaciolacustrine deposits	* centre-lake	-80 mesh Zn, Ni, Mn, Cu, Pb, Ag, Fe, Co, L.O.I.	B-1	17 18
34 Shebandowan Lake, N.W. Ontario	volcanic, sedimentary and intrusive rocks	Cu, Zn, Ag, Ni	ground moraine glaciolacustrine deposits	* centre-lake	-80 mesh Zn, Ni, Mn, Cu, Pb, Ag, Fe, Co, L.O.I.	B-1	17 18
35 Manitouwadge Lake, N.W. Ontario	volcanic sedimentary and intrusive rocks	Cu, Zn, Ag, Ni	ground moraine glaciolacustrine deposits	* centre-lake	-80 mesh Zn, Ni, Mn, Cu, Pb, Ag, Fe, Co, L.O.I.	B-1	17 18
36 Elliot Lake, Ontario	Aphebian sediments	U	ground moraine glaciolacustrine deposits	* centre-lake	-80 mesh U, Sc, Y, Pb, Fe, Mn, As, Ag, Cu, Ni, Zn, Zr, L.O.I.	B-1	15
37 Sudbury, Ontario	ultramafic irruptive metasediments and volcanics	Ni, Cu, Pb, Zn	ground moraine glaciolacustrine deposits	* nearshore	-200 mesh Ni, Cu, Zn, Pb, Ag, Cd, Fe, Mn, As, Hg, Sb, Mo, L.O.I.	B-1	6
38 Timmins- Val d'Or area, Ontario and Quebec	volcanics sediments intrusives	Cu, Zn, Au	ground moraine glaciolacustrine sediments	1/8 km <sup>2</sup> 34 000 km <sup>2</sup> various	-230 mesh Cu, Pb, Zn, Ni, Mn, As, Ag, Mo	A-1	30 31 36 37

Table 20.5 (cont'd)

Location Number and Location	Geology	Mineralization	Glacial Sediments	Density, Area, Site Location	Size Fraction, Elements	Survey Type	Reference Number
39 Renfrew area, Ontario	Proterozoic granites gneisses and carbonate rocks	U, Mo, Pb, Zn	ground moraine	1/4.6 km <sup>2</sup> 1150 km <sup>2</sup> centre-lake	-80 mesh Cu, Zn, Fe, Mn, Co, Ni, Mo, U, L.O.I.	B-1	19 20
40 Lanark area, Ontario	Grenville terrain, marbles, etc.	Hg, Ag	ground moraine	* various	Zn, Pb, Cu, Fe, Mn, Hg, As, Ni, Mo, U, C, CO <sub>3</sub> , S, L.O.I.	B-1	5 43
41 Chibougamou, Quebec	volcanics basic intrusives granites	Cu, Au, Ag	ground moraine glaciolacustrine sediments	*	-80 mesh cxHM	B-1	6 54
42 Kaipokok area, Labrador	Proterozoic volcanics and sediments	U, Cu	ground moraine	* nearshore	-80 mesh U, Cu, C	B-1	51
APPALACHIA							
43 Bathurst, New Brunswick	Paleozoic sediments and volcanics	Pb, Zn, Cu	ground moraine	*	-80 mesh cxHM	B-1	54
44 Daniel's Harbour, Newfoundland	Lower Paleozoic carbonates	Zn, Pb	ground moraine glaciomarine deposits	1/5.2 km <sup>2</sup> 900 km <sup>2</sup> centre-lake	-80 mesh Zn, Cu, Pb, Co, Ni, Ag, Mn, Fe, L.O.I.	B-1	38
45 Western Newfoundland	Lower Paleozoic carbonates	Zn, Pb	ground moraine glaciomarine deposits	1/3.1 km <sup>2</sup> 7800 km <sup>2</sup> centre-lake	-80 mesh Pb, Zn, Mn, Fe U, L.O.I.	A-1	21 24
46 Burlington Peninsula, Newfoundland	volcanics sediments granite gneiss	Cu, Au, Ag	ground moraine	1/2.7 km <sup>2</sup> 1300 km <sup>2</sup> centre-lake	-80 mesh Cu, Pb, Zn, Co, Ni, Ag, Mn, Fe, L.O.I., As, Mo, F, U	A-2	22 25 27
47 New Bay Pond area, Newfoundland	volcanics	Cu, Zn, As	ground moraine	1/2.3 km <sup>2</sup> 250 km <sup>2</sup> centre-lake	Cu, Zn, Pb, Co, Ni, Ag, Mn, Fe, Hg, L.O.I.	B-1	38
48 Southwestern Newfoundland	Carboniferous sediments		ground moraine glaciomarine deposits	1/5.3 km <sup>2</sup> 1800 km <sup>2</sup> centre-lake	Cu, Pb, Zn, Ba Sr, U, Mn, Fe L.O.I.	A-2	49
49 Burrin Peninsula, Newfoundland	volcanics sediments granites	F	ground moraine	1/3 km <sup>2</sup> 3900 km <sup>2</sup> centre-lake	U, F, L.O.I.	A-2	26
50 Avalon Peninsula, Newfoundland	sediments volcanics granites		ground moraine	1/3.8 km <sup>2</sup> 4800 km <sup>2</sup> centre-lake	Cu, Pb, Zn, Co, Ni, Mo, Ag, As, F, Mn, Fe, U, L.O.I.	A-2	23 25

\* one or more lakes sampled in detail from a variety of site locations for various lake bottom materials.

Survey Type A Regional 1 Reconnaissance survey  
2 Detail survey

B Research 1 Orientation survey  
2 Follow-up survey

Location Number refers to site number on location map, Figure 20.11  
Reference Number refers to source in the bibliography

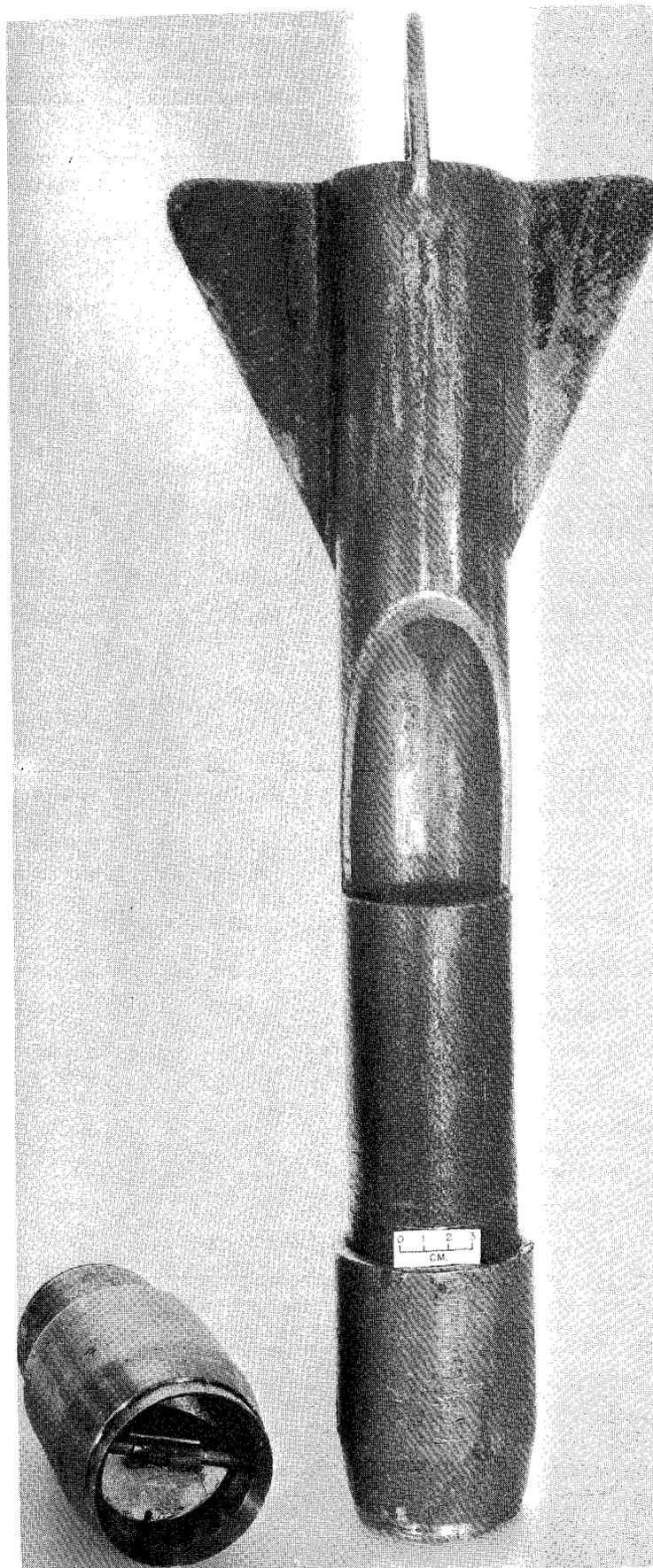
It is important, as Coker and Nichol (1975) and others have pointed out, that the top 5 cm, to as much as 20 cm, of the sediment at the defined sediment-water interface be discarded because it is subject to complex redox reactions as described by Mortimer (1942 and 1971). If the discard is not automatic as in the case of the 1976 model sampler then it should be done prior to bagging the sample.

Water sampling is often an integral part of a lake sediment survey. Water samples have been collected by Closs (1975) at various depths using, for example, a Hydro Products Van Dorn water sampler. Water sampling is amenable to automation in helicopter supported surveys. Cameron and Durham (1975) and Durham and Cameron (1975) have described a helicopter-mounted automated water-collecting system with pumps, tubes, reservoirs and instruments for measuring pH, conductivity and temperature with an onboard digital readout system. To avoid surface contaminants surface water samples should be collected below (i.e.: arms length at least) the water-air interface. Water samples collected below the surface epilimnion in the hypolimnion can be subject to widely varied physicochemical (i.e.: oxygen, temperature, pH, Eh) conditions from one lake to another as previously discussed.

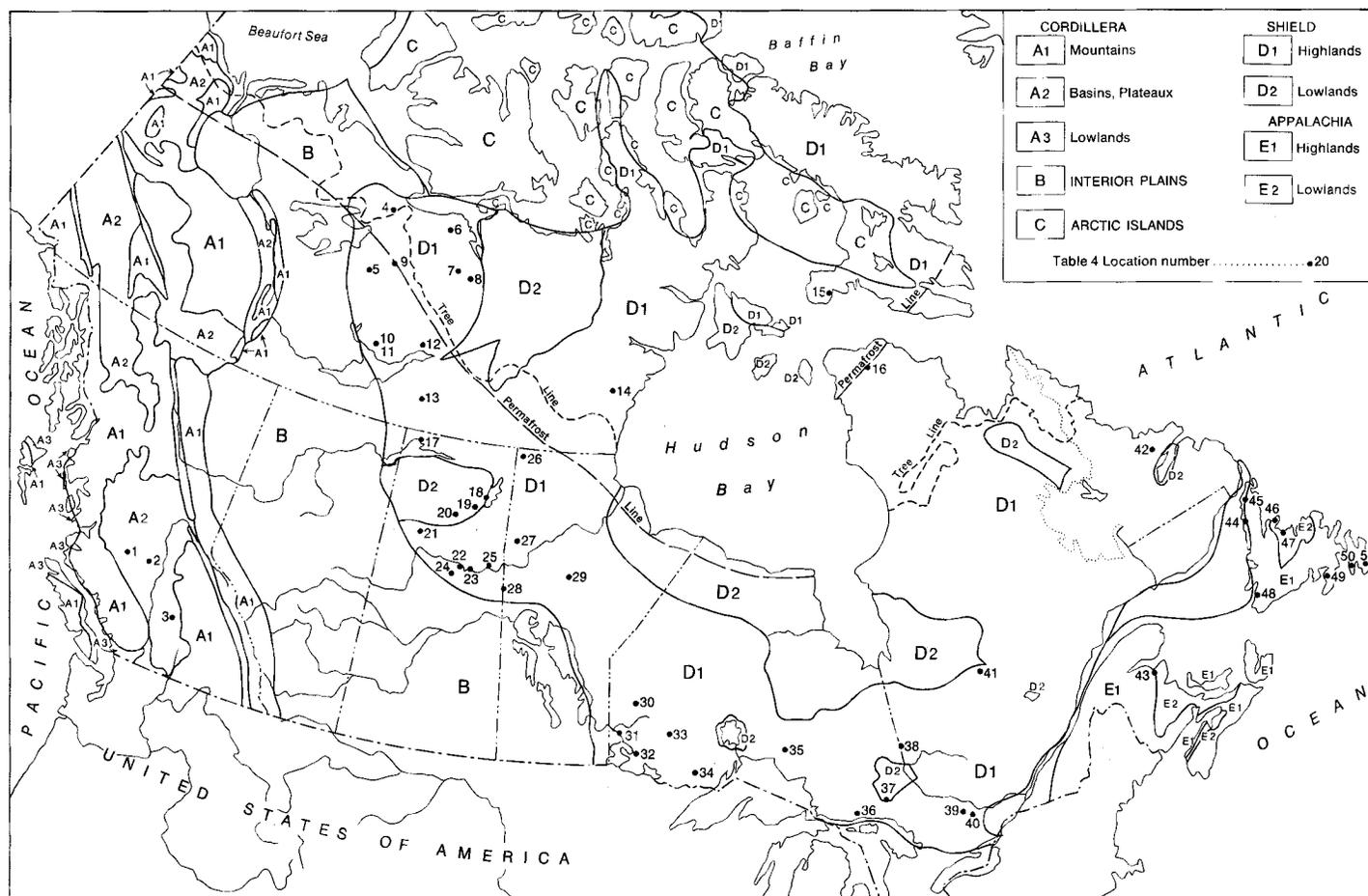
Lake sediment sample-site densities have ranged from detailed sampling of all available bodies of water (i.e.: Coker and Jonasson, 1977a,b) some lakes more than once or in detail (i.e.: Jonasson, 1976), up to wide interval reconnaissance survey densities of one sample per 13 km<sup>2</sup> (i.e.: Hornbrook and Garrett, 1976) and as great as one sample per 90 km<sup>2</sup> as used by Barringer Research Limited in an area of northern Ontario – Manitoba in the late 1960s (Bradshaw, pers. comm.) (see Table 20.5).

The sample density employed should be a function of the type and objectives of the survey modified by a knowledge of the mobility and characteristic geochemical dispersion of the elements related to the intended target (see Table 20.5). Distributions of mobile elements are defined by wide-interval reconnaissance surveys and of relatively immobile elements by detailed surveys. The routine Geological Survey of Canada Uranium Reconnaissance Program (U.R.P.) sampling density of one site per 13 km<sup>2</sup> satisfactorily defines the regional distribution of a mobile element like uranium. The effectiveness of this density in the Great Bear Lake area, District of Mackenzie, was tested and confirmed for uranium distribution by an extensive and independent resampling program in 1975 (Hornbrook, 1977). However, in Newfoundland, where base metal targets had priority, reconnaissance surveys for the less mobile elements (Cu, Pb, Zn, Co, Ni) had to be carried out at a greater sample density (one site per 2.7 km<sup>2</sup> to one site per 5.3 km<sup>2</sup>) to satisfactorily define element distribution (Davenport and Butler, 1975; McArthur et al., 1975). Most detailed or follow-up lake sediment surveys are carried out at densities equal to or greater than one site per 1 km<sup>2</sup>.

Theoretically, in a given geochemical survey, the density chosen would be the ideal one to satisfactorily define the least mobile element desired. In practice, the design of most multi-element surveys incorporates some compromise where the density is better than required for highly mobile elements but frequently not entirely sufficient to satisfactorily define the least mobile element. This primarily occurs because of the increasing costs of detailed high-density sampling over a given area relative to wide-interval sampling coverage. If the sampling density used in a given area is not sufficient for the key elements, as should be determined by orientation studies, then such a survey is a wasted effort because the area cannot be confidently excluded from further exploration for these elements.



**Figure 20.10.** The 1976 model Geological Survey of Canada lake sediment sampler.



**Figure 20.11.** Lake Sediment Investigations in the Canadian Cordillera, Shield, and Appalachia (Numbers on map refer to Table 20.5).

Most lake sediment and/or water surveys are helicopter-supported usually by a Hughes 500C or a Bell Jet Ranger 206B type of turbine-powered rotary-wing aircraft because of their speed and manoeuvrability. Frequently, as in the case of all U.R.P. geochemical surveys, a winching device and external working platform are installed on the helicopter fuselage and one of the floats respectively, to facilitate and increase the efficiency of sediment sampling operations.

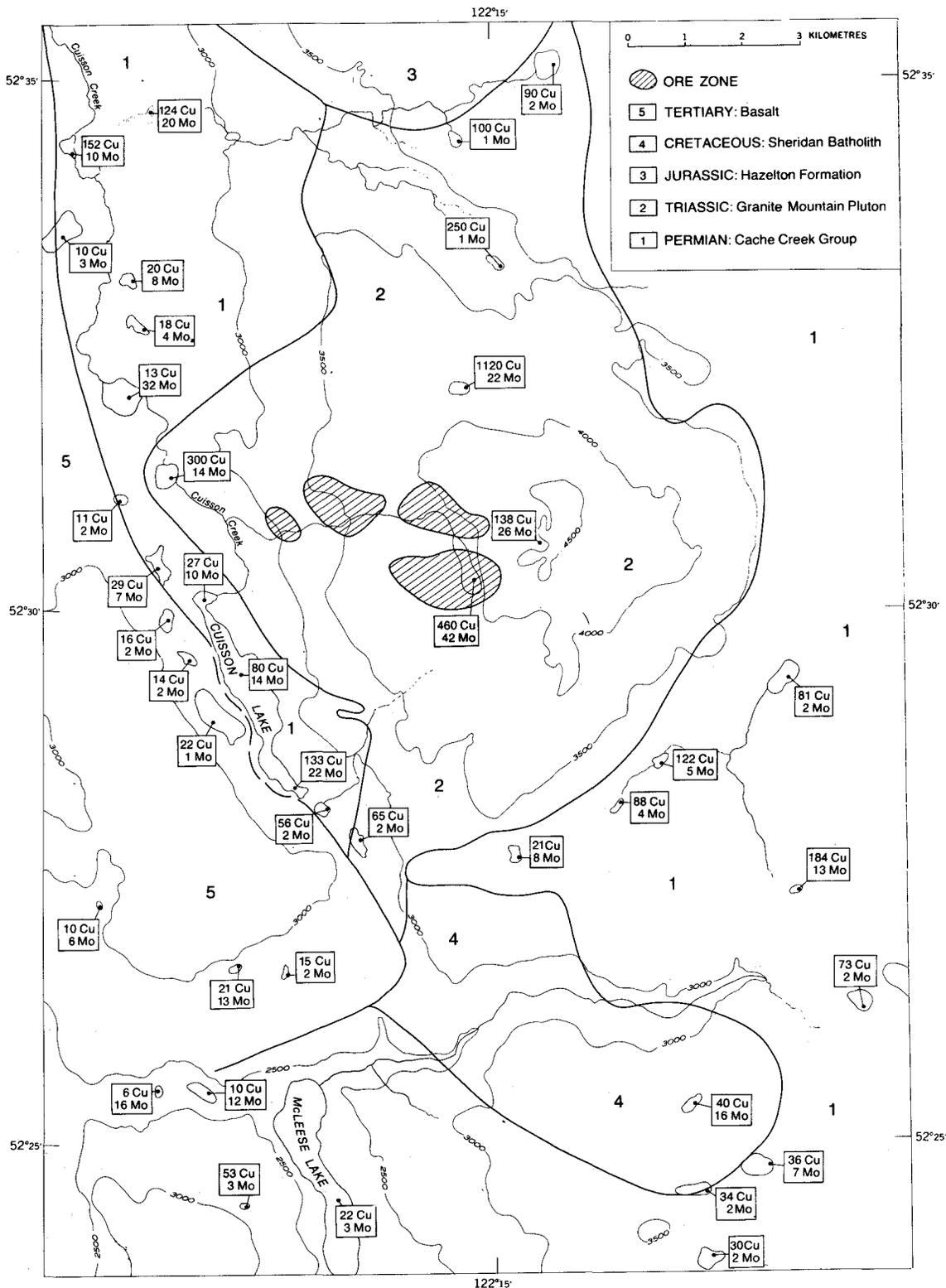
Normally, in Geological Survey of Canada-U.R.P. operations, a helicopter-sampling team is composed of three people: the pilot; a navigator-notetaker who records data and also collects the water sample; and a person in the rear compartment who collects the sediment sample. It must be emphasized that the capability of the pilot plays a significant role in sampling operations particularly in terms of co-operation in traverse planning, navigation, site selection and overall flight path utilization to minimize flight time not productively used for sampling.

On reconnaissance surveys utilizing one helicopter and two crews, 500-1000 sites may be visited each week and samples collected at almost all of these. It is not always possible to collect a satisfactory sediment sample at every lake that is visited. Routine U.R.P. lake sediment and water surveys are carried out at a rate in excess of 15 sample sites per hour, while on traverse, and 12 sites per hour, calculated on a basis of total flying time. Total time includes nonproductive ferry flights and time spent at sites where no samples were collected. When the density is increased to one

sample site per 6 km<sup>2</sup>, the sampling rate increases to 18 or 20 sites per hour. Maurice (1976) achieved 21 sites per hour on Baffin Island at a follow-up study density of one site per 1.2 km<sup>2</sup>.

On day-long helicopter traverses, to manage in an organized fashion several hundred collected samples, it is desirable to use trays or partitioned boxes to contain the bags and bottles. The trays also permit order to be maintained in the numbering sequences of bags and bottles. Although the bags are usually constructed of high wet-strength paper with water-resistant glue they will not withstand rough treatment. Plastic bags are sometimes used but require more handling for subsequent drying. Most traverse data are recorded on some form of field computer compatible cards by the navigator-notetaker. Cards of this nature have been described by Garrett (1974). Obviously, all operational procedures in the helicopter are designed to avoid errors and unnecessary time loss while carrying out satisfactory collection of sediment and water samples. Heated drying tents are required in the field for sorting and checking of sample numbers as well as drying sediment samples prior to shipping.

There is a marked absence of logistical and cost data and descriptions of equipment and procedures in most published accounts of lake sediment and water surveys. Such information on the 1974 Saskatchewan survey may be found in Hornbrook and Garrett (1976). Average costs can be estimated despite the great number of variable factors which contribute to the overall survey costs. Although the collection costs are usually the highest cost component;



**Figure 20.12.** Distribution of Cu and Mo in lake sediments in the vicinity of the Gibraltar copper-molybdenum porphyry deposit, B.C. (Cu and Mo values in ppm). (Data supplied by Rio Tinto Canadian Exploration Co. Ltd.)

sample preparation, analyses, data compilation, map production and interpretation costs can be significant in multi-element surveys. Approximate 1977 collection costs for U.R.P. lake sediment and water surveys at a density of one sample per 13 km<sup>2</sup> range from \$40.00 a site in southern developed areas to \$50.00 a site in northern or remote areas. An average cost of collection would be \$3.50 per km<sup>2</sup> for large scale reconnaissance geochemical surveys. Sample preparation and analytical costs will vary tremendously. In U.R.P. surveys, where lake sediments are disaggregated, ball milled and sieved prior to analysis for 12 or 13 elements and their organic content, and lake waters are analyzed for 2 elements and pH, these costs are significant. These costs together with data processing, base map compilation, data compilation and production of element maps and data listings may constitute an additional cost equal to up to 50 per cent of sample collection costs. Thus, it is obvious that there is no fixed quotable cost per sample site or km<sup>2</sup> unless all relevant cost factors are considered.

### **Lake Sediment Geochemistry Applied to Mineral Exploration in Canada**

The association of elevated levels of trace metals in lake sediments adjacent to mineralization was observed as early as the mid-1950s in New Brunswick and Quebec by Schmidt (1956). However, for all practical purposes, the rapid increase in the utilization of lake sediments and waters as sample media for geochemical exploration did not occur until the early 1970s.

By the mid 1970s research and development was very active in the Shield and several lake sediment reconnaissance surveys had been carried out. The application of lake sediment geochemistry in exploration is now widespread in the Canadian Shield. Some users of the method are experiencing difficulties, but this may often be attributed to inappropriate application of the method and frequently an inability to properly interpret the complex data obtained.

The most extensive use of lake sediment geochemistry in the search for mineralization has been within Canada, primarily in the Shield but also in the Cordilleran and Appalachian regions, as indicated in Figure 20.11 and summarized in Table 20.5.

### **Cordillera**

The use of lake sediments for geochemical reconnaissance in the Cordillera was initiated by M.B. Mehrtens and A.G. Troup of Rio Tinto Canadian Exploration Co. Ltd. In 1970, 8000 km<sup>2</sup> in the Quesnel area of south-central British Columbia were sampled using a float-equipped helicopter. This work demonstrated that lake sediment samples could be collected more economically than stream sediments in this heavily forested region. In total, Rio Tinto sampled 54 000 km<sup>2</sup> in British Columbia and the Yukon with the largest area covered being 30 000 km<sup>2</sup> between Quesnel and the United States-Canada border. Sampling of centre-lake sediments by means of an Ekman-Birge dredge was at an average density of one per 10 km<sup>2</sup>.

The concentrations of copper and molybdenum in lake sediments collected by Rio Tinto, from lakes around the Gibraltar copper-molybdenum porphyry deposit (326 megatonnes of 0.37% Cu and 0.01% Mo) are shown in Figure 20.12. Sampling was post-discovery, but prior to the commencement of mining and any possible contamination of the associated drainage system. These data show strong anomalies for both Cu and Mo in close proximity to the deposit, with downstream dispersion of these metals being clearly evident.

In 1970, Hoffman and Fletcher (1972) collected a few nearshore lake-bottom samples as part of a multi-media geochemical investigation in south-central British Columbia. A Cu anomaly was found associated with a known mineralized zone in syenites. These authors subsequently carried out a survey of 16 000 km<sup>2</sup> in the Nechako Plateau, British Columbia. Organic-rich centre-lake sediments were taken from 500 lakes (Hoffman and Fletcher, 1976). The survey revealed regional geochemical variations in the concentrations of a number of elements in the lake sediments directly related to variations in underlying bedrock geology. For instance, lake sediments with high levels of Ni and Cr were found up to 10 km and 20 km respectively down-ice from ultramafic intrusives. Anomalies for Cu, Mo, Pb and Zn outlined mineralization, or lithologies favourable for mineralization. While considerable variation in the trace metal content of samples collected from single lakes was found, this variation did not obscure multi-lake anomalies related to known mineralization.

In general, the number of lakes per unit area is much less in the Cordillera than in the Canadian Shield. Within the Cordillera lakes are more abundant in the interior plateaux than in the mountain ranges (Fig. 20.11). It is primarily within the plateau regions that there are sufficient lakes to allow sampling at reconnaissance densities of one site per 10 to 20 km<sup>2</sup>.

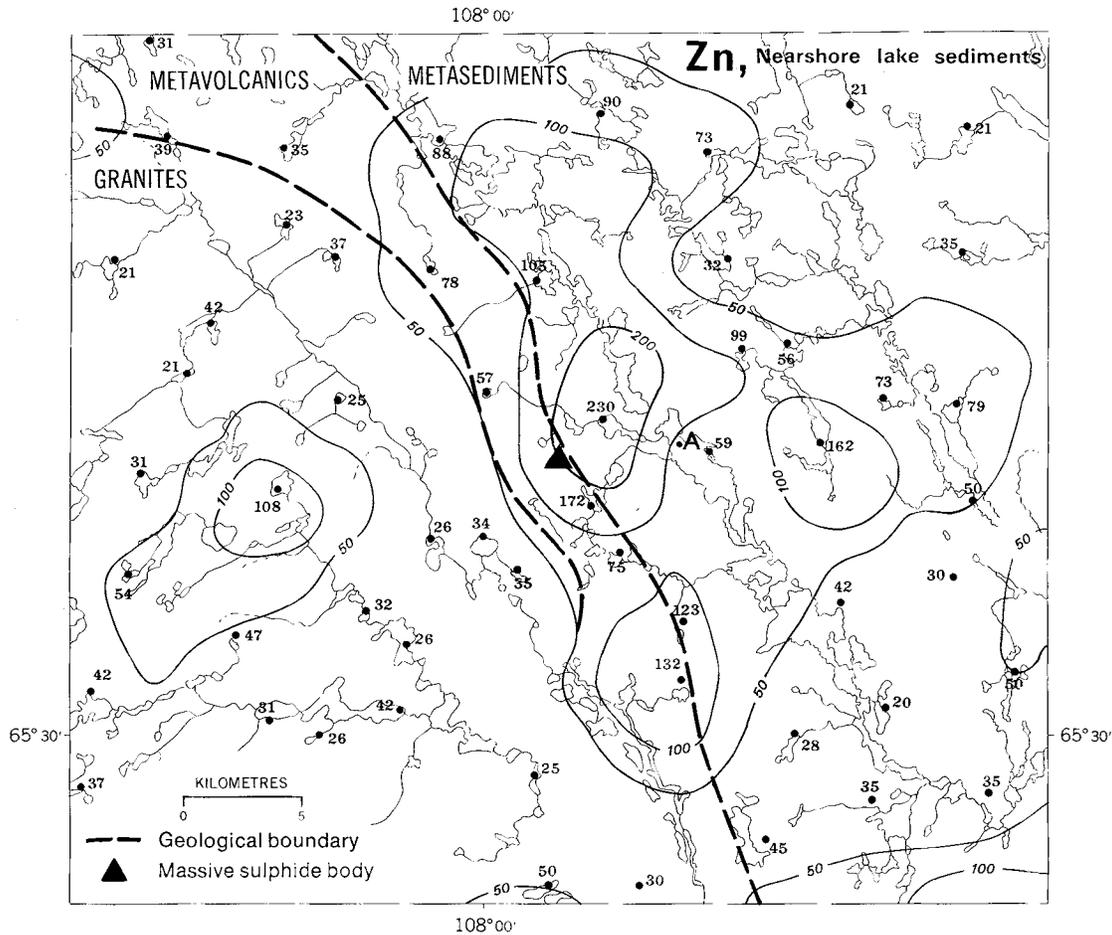
In Shield areas where low relief generally prevails, the widespread dispersion of indicator elements along drainages must largely depend on their movement in solution. It should be recognized that in parts of the Cordillera and in similar mountainous regions, mechanical transport may play a more significant role in metal movement.

### **Northern Shield**

The northern Shield is here considered to be that portion of the Canadian Shield north of latitude 60°N. Most of this region is north of the treeline and is underlain by permafrost (Fig. 20.11).

The first reported study of the use of lakeshore materials for mineral exploration in the northern Shield was by Allan (1971). In 1970 he sampled lakeshore materials from lakes in a 4000 km<sup>2</sup> area, underlain mainly by basaltic rocks, near Coppermine on the Arctic coast. The Cu content of samples collected at a density of 1 site per 26 km<sup>2</sup> indicated the widely disseminated copper mineralization that occurs within the basalts. Allan and Hornbrook (1970) and Allan (1971) found chemical weathering active in this area of continuous permafrost. A good regional correlation exists between Cu in the nearshore sediments and Cu in the associated lake waters. This discovery provided a basis for further investigations of nearshore materials for regional geochemical reconnaissance, since for application at the reconnaissance-level wide dispersion of indicator elements in the surface environment is essential, and in typical Shield terrain of low relief such dispersion must be primarily hydromorphic.

A more extensive study was carried out in 1971 by Allan, Cameron and Durham, involving the sampling of rocks, lake waters and lakeshore materials from seven areas, including some mineralized and some barren, within the Bear and Slave geological provinces of the northwestern Shield. Results from this work (Allan et al., 1973a) formed the basis for the first large scale reconnaissance survey, the Bear-Slave operation, carried out in 1972 over an area of 93 000 km<sup>2</sup>. Helicopter supported sampling of nearshore lake bottom materials at a site density of 1 per 26 km<sup>2</sup> was completed in six weeks (Allan et al., 1973b). Geochemical maps for the survey area, released in 1973 (Allan and Cameron, 1973), contained data for U, Zn, Pb, Cu, Ni, K, Fe, Mn and



**Figure 20.13.** Distribution of Zn in nearshore lake bottom materials, Agricola Lake area, N.W.T. (after Cameron and Durham, 1974b).

organic content. Follow-up work was carried out by the Geological Survey of Canada in the Bear Province (Cameron and Allan, 1973) and the east part of the Slave Province (Cameron and Durham, 1974a,b) and throughout the survey area by the mining industry. The activities in the east part of the survey area resulted in the first mineral discovery in the Shield attributable to reconnaissance level nearshore lake bottom sampling – the Agricola Lake massive sulphide body.

While this work was being carried out by the Geological Survey of Canada, students of I. Nichol at Queens University were carrying out more detailed geochemical investigations of the lake environment in the Yellowknife and Kaminak Lake regions. The former area represents a transitional environment between the northern and southern Shield, since it is forested but within the zone of discontinuous permafrost. After an initial reconnaissance survey (Nickerson, 1972) nineteen mineralized and barren areas were studied in detail (Jackson and Nichol, 1975). They found centre-lake sediments to be more useful for geochemical reconnaissance than nearshore materials because they are more homogeneous within lakes and they better reflect the presence of mineralization. Jackson and Nichol (1975) found that Fe and Mn oxide precipitates in the sediments could be an important control on the distribution of many base metals under suitable physicochemical conditions.

The Kaminak Lake area is within the zone of continuous permafrost, north of the treeline. Work commenced in 1973 and is summarized by Klassen et al. (1975). For reasons that are not presently understood no relationship was found

between lake sediment metal levels and known mineralization. Work in this region has been continued by Klassen, Shilts and co-workers at the Geological Survey of Canada emphasizing detailed physical and chemical studies of lake sediment and water regimes (Shilts et al., 1976).

As has been discussed, both nearshore materials and centre-lake sediments have been sampled for mineral exploration purposes in the northern Shield. In general, the former have **not** been produced by normal processes of lacustrine sedimentation. Instead, they are subaqueous equivalents of glacial and postglacial sediments on the margins of lakes and show similar patterned features, such as mudboils and rib and trough structures (Shilts and Dean, 1975). Like glacial and postglacial sediments, shoreline materials are heterogeneous mixtures of material from cobble to clay in size. The central, fine grained portions of both the surface (i.e. Shilts, 1971) and subaqueous (i.e. Allan, 1971) mudboils have been sampled for mineral exploration purposes.

The Canadian mining industry has made much use of various sample media from lakes for geochemical exploration in the northern Shield. The principal targets have been massive sulphides and uranium mineralization. Virtually all of this work is unpublished. In 1976, approximately \$400 000 was spent by the industry on lake sediment and lake water surveys in the Northwest Territories (W.A. Padgham, pers. comm.). This comprised two thirds of their total geochemical expenditures in the Northwest Territories.

Figure 20.13 shows a strong anomaly for Zn in lakeshore materials in the eastern part of the Slave Geological Province (Cameron and Durham, 1974b). For the region, the geometric mean Zn content of these shore deposits is 32 ppm. These data were obtained in 1972 and 1973 and the Agricola Lake Zn-Cu-Pb-Ag-Au bearing massive sulphide, near the centre of the anomaly, was discovered in 1974. It occurs in steeply-dipping metavolcanic rocks near their contact with metasedimentary strata. The extensive nature of the anomaly is caused by widely scattered mineralization, presumably related to the massive sulphide body, and by widespread dispersion of mobile base metals in the present drainage system.

More detailed data for secondary dispersion from the Agricola Lake massive sulphide body are shown in Figure 20.6. In the proximal portion of the eastward-draining lake-stream system, the waters are acid and Zn migrates in solution (Cameron, 1977). Down-drainage the pH increases as the mineralized waters mix with those of other streams. This results in precipitation of Zn in both nearshore materials and centre-lake sediments. Down-drainage from Agricola Lake there is a rapid decline in the Zn content of the nearshore materials, roughly paralleling the decline of this element in the waters, but Zn in centre-lake sediments continues to be strongly anomalous. Cameron (1977) suggested that this difference is possibly caused by the nearshore material having sorbed Zn from the waters in situ while the centre-lake sediments contain fine grained particulates that have been transported down-drainage after having sorbed Zn. The evidence of more widespread dispersion in centre-lake sediments, together with their greater homogeneity compared to nearshore materials, indicates they are more suitable than the latter for regional reconnaissance sampling. In addition, with modern sampling equipment (see Fig. 20.10), centre-lake sediments can be sampled more rapidly than nearshore materials.

Until the late-nineteen sixties it was widely believed, in North America, that chemical weathering was minimal in permafrost environments and consequently that many geochemical approaches to mineral exploration would be unsuitable in these regions. Experience in the northern Shield, the Yukon, Alaska, Scandinavia and the U.S.S.R. has shown that this is not the case. Indeed, the mobility of many elements appears to be greater in the northern Shield than in the south, one possible reason perhaps being because of a lesser amount of fixing by organic material. The studies referenced earlier in this section indicate that U, F, Zn, Cd, Cu, Ni, Co and Mo are relatively mobile in the surface environment of the northern Shield and therefore should be given prime consideration as indicator elements for reconnaissance lake sediment surveys. Less mobile elements include Pb, Ag, Au, Hg and As. Once target areas have been defined by lake sediment reconnaissance, water geochemistry using mobile indicator elements can be of considerable assistance in more precisely defining targets (Cameron and Ballantyne, 1975).

### Southern Shield

The southern Shield represents that portion of the Canadian Shield, generally south of latitude 60°N, within Alberta, Saskatchewan, Manitoba, Ontario, Labrador and Quebec (Fig. 20.11).

This region is characterized by a tremendous variation in environmental factors that influence weathering, transport and, eventually, precipitation and sedimentation of trace elements in lake sediments. Although most of the region is south of the limit of continuous permafrost more than one half lies within the zone of discontinuous permafrost and also, is south of the treeline (see Fig. 20.11).

In northern Saskatchewan lake sediment sampling began in the early 1970s and has been employed extensively in the last few years. Early work was conducted by the Saskatchewan Research Council (Arnold, 1970; Haughton et al., 1973), Saskatchewan Geological Survey, (Sibbald, 1977) and by a few exploration companies (Dunn, pers. comm.). In 1974, a 51 800 km<sup>2</sup> region of east-central Saskatchewan was covered by an organic lake-centre sediment-sampling reconnaissance program (Hornbrook et al., 1975b, 1977; Hornbrook and Garrett, 1976). The program was jointly undertaken by the Geological Survey of Canada and the Province of Saskatchewan.

Lake sediment chemical data from this program defined single and multi-element regional trends and local highs (i.e. for U and Cu-Zn-Pb) in the survey area that frequently coincided with known areas of mineralization. Several anomalous areas of unknown mineral potential were also defined. Correlation and regression studies showed that Fe, Mn and organic content do not appear to play important roles as scavengers of trace metals and therefore do not cause the occurrence of significant false anomalies. Statistical studies demonstrated that the surficial environment is not adversely affecting the raw data for interpretive purposes, and the relationship and interaction of the elements are primarily a reflection of bedrock, and geological and chemical processes. Extensive statistical treatment, beyond separation of the data on a bedrock catchment basin basis, was not required as it did not substantially improve interpretation of the data. This survey has been followed-up by Lehto et al. (1977) of the Saskatchewan Research Council and by the mineral exploration industry.

In 1975, the Saskatchewan Geological Survey undertook reconnaissance lake sediment studies along the western portion of the unconformity between Precambrian and Phanerozoic rocks. At the same time they started a four year study of lakes peripheral to the Athabasca Sandstone. Reconnaissance lake-sediment geochemistry was further studied in 1976 by the Saskatchewan Geological Survey (Rameakers and Dunn, 1977) and by the Saskatchewan Research Council (Lehto et al., 1977). The method was actively utilized by the Saskatchewan Mining and Development Corporation and many other exploration companies amounting to more than \$250 000 worth of exploration in 1976 (Dunn, pers. comm.). In 1977, under the joint Federal-Provincial Uranium Reconnaissance Program (Darnley et al., 1975), a reconnaissance lake sediment survey was carried out over a 12 000 km<sup>2</sup> area covering the north-eastern extension of the Wollaston Trend, up to the Manitoba border. These data (Geological Survey of Canada, 1978c) were released in June, 1978.

Both the Key Lake - Highrock Lake and Rabbit Lake areas provide examples of the effectiveness of reconnaissance lake sediment sampling. Tan (1977) has described the geochemical exploration program conducted during 1973 and 1974 that was part of a much larger uranium exploration program, carried out by Uranerz Exploration and Mining Limited and partners, which led to the discovery of the Key Lake uranium-nickel deposits in 1975-76. It was also pointed out that organic-rich lake sediments were more effective as a sample medium than swamp or soil material, at both the reconnaissance and detail level, and in generating distinct anomalies related to the two orebodies.

The geology and geochemistry of the eastern margin of the Athabasca basin, including the Key Lake area, which unconformably overlies crystalline basement rocks, have been described by Ramaekers and Dunn (1977). Figure 20.14 shows as yet unpublished data from lake sediment samples collected in the vicinity of Key Lake in 1975 by C.E. Dunn, Geological Survey of Saskatchewan. Sample density was one per 7 km<sup>2</sup>. Lake sediments from lakes 2-12 km down the glacial trend to

the southwest of the Key Lake uranium-nickel deposits contain up to 2000 ppm uranium. The total dispersion halo extends down-ice and drainage at least 30 km at which distance 10 ppm uranium (2.5 times background) is commonplace. Smaller associated halos of nickel, cobalt, zinc and arsenic are also present but not shown in Figure 20.15. Uranium and nickel distributions in organic-rich lake centre sediments have clearly defined the location of the Key Lake deposits and give evidence of the potential of the method in similar environments.

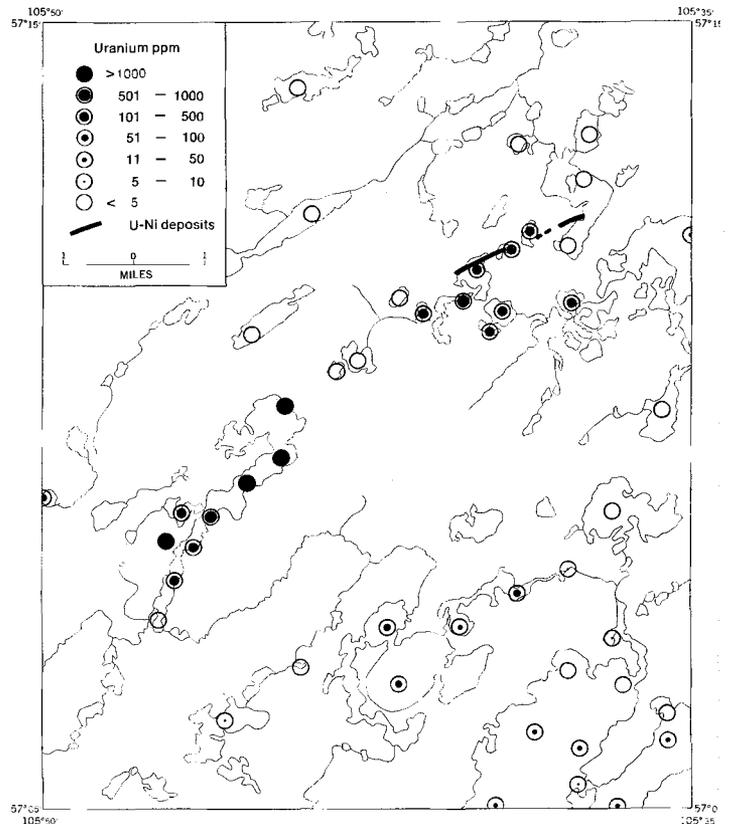
The Rabbit Lake uranium deposit has given rise to markedly different geochemical patterns (Ramaekers and Dunn, 1977). Uranium is present in excess of 1000 ppm in the sediments of Rabbit Lake itself, and several hundred ppm in the neighbouring lakes to the east, but is only marginally anomalous 5 km from Rabbit Lake where its waters eventually drain into Wollaston Lake. In another lake sediment survey carried out by Cameron and Ballantyne (1977) in the Rabbit Lake area a large regional U anomaly was outlined (an area of 216 km<sup>2</sup> as enclosed by the 5 ppm contour in Fig. 20.15). The anomalous lakes trend down-ice from the deposit and appear to be an example of the glacial dispersion of uranium-bearing detritus, followed by leaching of the U from this detritus into the lake system. In addition, it is possible that satellite deposits of U could also be influencing the distribution patterns of U in the lake sediments. Lake waters within the area of anomalous sediments are also anomalous in U and F. In Saskatchewan, centre-lake bottom sediment sampling has been extensively and successfully employed over the last few years, more so than in other areas of the Canadian Shield.

Extensive glaciolacustrine sediments formed by Lake Agassiz have rendered much of the Province of Manitoba, except for the northern part, unsuitable for routine reconnaissance lake sediment surveys. The diverse influence of glaciolacustrine sediments in inhibiting geochemical response in the Abitibi Clay Belt of Ontario and Quebec has been described by Gleeson and Hornbrook (1975a). Lake sediment surveys have been used for mineral exploration in Manitoba but there are very few published accounts of such work other than that by Clews (1975) at Fox Lake and by Bradshaw (1975) at Wintering Lake.

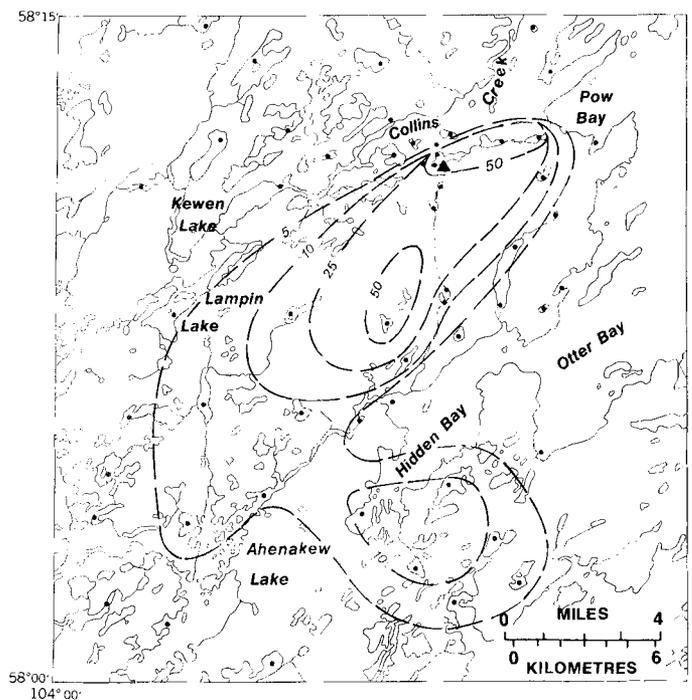
In Manitoba, utilization of lake sediment geochemistry for mineral exploration by the mining industry received a major impetus as a result of the lake sediment surveys carried out under the joint Federal-Provincial Uranium Reconnaissance Program in 1975 and 1976.

In these reconnaissance surveys centre-lake organic-rich sediments from the profundal basins of suitable lakes, and surface lake waters, were collected at an average density of 1 sample per 13 km<sup>2</sup>. The 1975 survey (Hornbrook et al., 1976a, b, c and d) and the 1976 survey (Geological Survey of Canada, 1977b) covered 87 300 km<sup>2</sup> of northern Manitoba north of latitude 58°N and west of longitude 95°W. The most interesting resultant dispersion patterns were those exhibited by uranium and associated elements in the northwest corner of the survey area (NTS 64N) along the extension of the Wollaston Trend. This particular area has undergone very active exploration and follow-up activities.

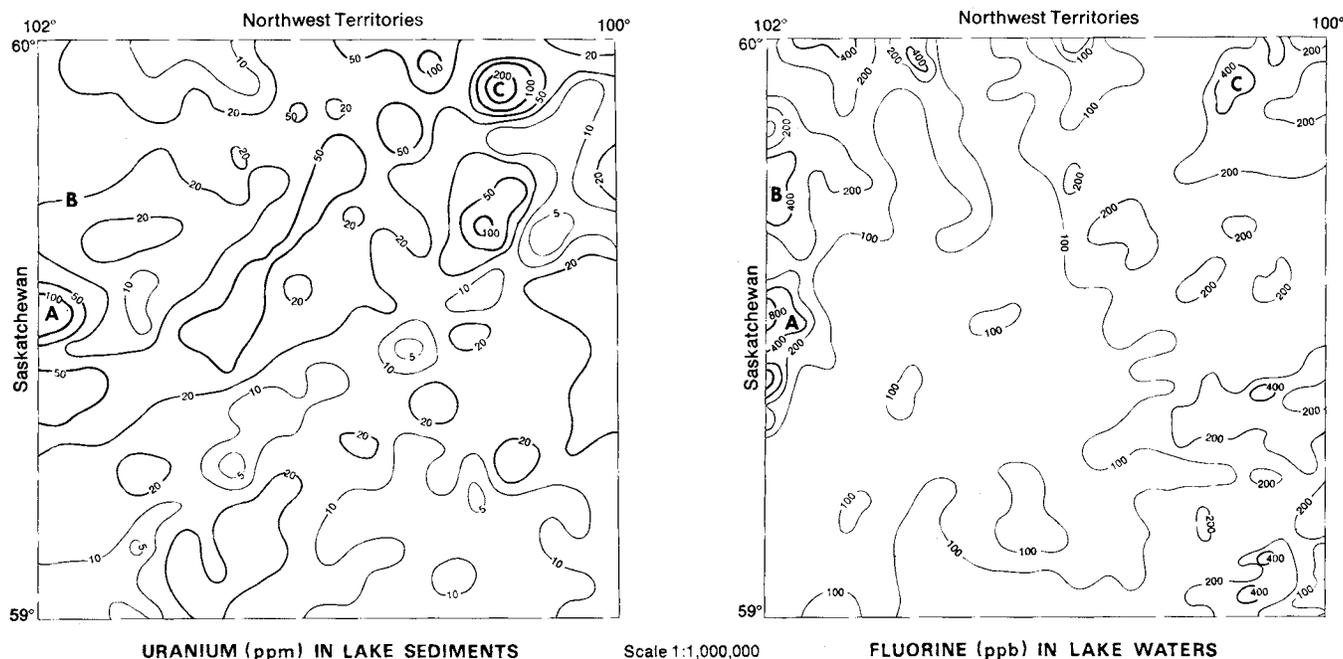
To evaluate the 1975 reconnaissance data, follow-up surveys were conducted in selected areas by the Geological Survey of Canada (Coker, 1976). Follow-up survey methods included: high density (1 site per km<sup>2</sup>) lake sediment and water sampling; airborne gamma-ray spectrometry surveys by the Geological Survey Skyvan (1 km line spacing) and a helicopter-mounted McPhar Spectra 1 four-channel spectrometer (0.25 km line spacing); and ground investigations where overburden and bedrock were sampled. An association was found to exist between uranium and



**Figure 20.14.** Distribution of U in lake sediments in the vicinity of the Key Lake U-Ni deposit, Saskatchewan. (Data supplied by C.E. Dunn, Geological Survey of Saskatchewan.)



**Figure 20.15.** Uranium (ppm) in lake sediments near the Rabbit Lake uranium deposit, Saskatchewan (after Cameron and Ballantyne, 1977). Location of deposit shown by solid triangle.



**Figure 20.16.** Distribution of U in lake sediments and F in lake waters (sample density 1 site per 13 km<sup>2</sup>) northwestern Manitoba (64N).

fluorine in lakes within the Hudsonian granitoid bodies in the area (see A, B and C in Fig. 20.16). At a detailed sampling scale of one sample per km<sup>2</sup>, uranium and fluorine results were found to define precisely the extent of the granitoid bodies, even indicating zoning within them. The association of other elements with uranium was felt to be useful for discriminating between high level regional uranium anomalies related to elevated uranium levels in bedrock (U association with F) and other relatively lower levels of uranium of possible economic significance (U alone or associated with Ni and As) within the geological environment of northwestern Manitoba.

Active follow-up studies by the mineral exploration industry has continued into 1977 with positive results. Detailed lake sediment and water sampling has been used in conjunction with other geological, geochemical and geophysical follow-up methods.

In recent years a great deal of lake sediment work has been carried out in Ontario. Among the earliest regional surveys was that of Hornbrook and Gleeson (1972, 1973) and Gleeson and Hornbrook (1975a,b) where 34 000 km<sup>2</sup> were sampled at a density of one sample per 8 km<sup>2</sup> in the Abitibi Clay Belt of Ontario and Quebec. This survey demonstrated the limitations of lake sediment geochemical response in a clay terrain. Jonasson (1976) began intensive research into the hydrogeochemistry of two small lakes in the Lanark area of southeastern Ontario in 1970 and eventually isolated and summarized many of the complex problems in the application and interpretation of lake sediment geochemistry. Contemporaneously, lake sediment and water investigations were being carried out in Ontario by Coker (1974), Coker and Nichol (1975, 1976), and by Timperley and Allan (1974). In northwestern Ontario, Coker investigated the nature of and factors affecting trace element accumulation in lake sediments in order to reevaluate the feasibility of using lake sediments for reconnaissance mineral exploration. Investigations were carried out in the following areas: Sturgeon Lake, Upper Manitou Lake, Shebandowan Lake and Manitouwadge Lake. This work revealed that the deepest central region of a lake basin provides the most representative and homogeneous source of sample media.

Interpretation of the regional lake sediment chemical data demonstrated that the distribution of individual metals generally failed to identify adjacent mineralization due to the complex physicochemistry of the lake environment. However, element compositions, when ratioed with manganese (Zn/Mn, Ni/Mn), or when regression analysis was employed, could identify lakes adjacent to massive sulphide or Ni-Cu mineralization (Coker, 1974). Such data manipulation may often be required to remove the effects on trace element distributions in lake sediments caused by coprecipitation or varying pH (see previous discussion). The work of Timperley and Allan (1974) in the Red Lake – Uchi Lake area was concerned with investigating the use of gyttja as a prospecting medium and with providing some idea of the overall physicochemical system involved in the lake regime. Brunskill et al. (1971) investigated the relationship of the chemistry of the surface lake sediments to that of the overburden and bedrock in the Experimental Lakes Area in northwestern Ontario. Closs (1975) carried out an orientation survey to examine the geochemistry of lake sediments in the Elliot Lake region. His work showed that contamination from mining activity can be a problem and that correlation analysis and regression analysis are an approach to data evaluation that should not be overlooked in order to recover a maximum of information from the data. The work of Allan and Timperley (1975) was specifically concerned with centres of intensive mining activity (i.e. Sudbury) and the resultant contaminating effect from such activity on the chemistry of lake sediments. They found widespread evidence of heavy metal contamination in the upper 5 to 10 cm of the lake sediment column. In their conclusions they emphasized that the use of dredging devices should be avoided for sampling and that samples should be collected by coring-type devices, at least 10 cm below the lake sediment surface, to prevent the inclusion of contaminated sample media.

In the Grenville geological province west of Ottawa near Renfrew, Ontario an orientation survey was carried out to permit testing of geochemical methods to ascertain their responses to typical Grenville geological and environmental influences. This survey, by Coker and Jonasson (1977a,b)

provided the basis for the 22 300 km<sup>2</sup> reconnaissance centre-lake bottom sediment and surface lake water survey completed in 1976. The reconnaissance survey was a joint undertaking with the Ontario Government under the Federal-Provincial Uranium Reconnaissance Program (Geological Survey of Canada, 1977a).

In the orientation survey, 246 lake sediment and 276 lake water samples were collected from all bodies of water in the area including lakes of all sizes, ponds, beaver dammed ponds, true swamps and flooded marshes. Data from the 1150 km<sup>2</sup> area (NTS 31F 07) are presented in Figure 20.17. This detailed level of sampling proved efficient in outlining favourable geology and perhaps certain structures with possible mineral potential. Exact correspondence of sediment and water uranium anomalies is not achieved. However, examined together, they reinforce each other and do outline geological features; for example, the Hurd Lake granite, where there is an annulus of elevated uranium values in both water and sediments. Field inspection with scintillometers confirmed the presence of radioactive mineralization in pegmatites and skarns peripheral to the Hurd Lake granite.

A definite value was found in interpreting the hydrogeochemical dispersion patterns in terms of elemental association (a simplistic cluster analysis, grouping values greater than the mean plus one standard deviation) based on a knowledge of the trace and minor-element chemistry of known mineral assemblages in the area. The same scale of sampling also seemed to be of value in seeking lead-zinc prospects in Grenville marble and skarns and also for locating new molybdenum occurrences in metamorphosed sediments. The broad extent of the anomalies outlined indicates that reconnaissance scale lake sediment geochemical sampling at 1 site per 13 km<sup>2</sup>, using lakes, the larger ponds and true swamps, would be successful in locating zones of interest for detailed follow-up surveys.

Other than the work of Schmidt (1956), Hornbrook and Gleeson (1972, 1973), Gleeson and Hornbrook (1975a) and Allan and Timperley (1975) there is very little published on lake sediment geochemistry in Quebec. The early investigations of Schmidt (1956) in the Chibougamau area, Quebec revealed that the anomalous distribution of metals in lake sediments was related to adjacent mineralization. Hornbrook and Gleeson's work has been previously described. Allan and Timperley's (1975) Chibougamau area studies were concerned primarily with industrial heavy metal contamination and their approach and conclusions are similar to that described for their Sudbury, Ontario investigations. However, lake sediment sampling has and is being, used by the exploration industry in Quebec but their data remain unpublished to date. For example, the James Bay Development Corporation used centre-lake bottom sediments to explore over 100 000 km<sup>2</sup> during 1973-75 and this work is continuing. Minatidis and Slatt (1976) have demonstrated the usefulness of nearshore sediments as a follow-up technique after reconnaissance surveying. Their work in the Kaipokok region of Labrador defined U and Cu enriched zones, some of which were known and others which represent new discoveries. Thus, systematic nearshore sampling of materials around the periphery of several lakes in a mineralized area may provide a rapid method of delineating local mineral-rich areas.

### Appalachia

Schmidt (1956) carried out geochemical investigations near Bathurst, New Brunswick where, similar to his work at Chibougamau, Quebec, the presence of anomalous metal contents in lake sediments related to adjacent mineralization, was observed. In 1972, on insular Newfoundland, lake sediment orientation studies were carried out in the New Bay Pond area by Hornbrook and in the Daniel's Harbour area by

Pond area by Hornbrook and in the Daniel's Harbour area by Hornbrook and Davenport (Hornbrook et al., 1975a). In 1973, following the orientation studies, a reconnaissance centre-lake sediment survey was carried out over 7800 km<sup>2</sup> on Lower Paleozoic carbonate rocks in western Newfoundland, including the Daniel's Harbour area (Davenport et al., 1974, 1975).

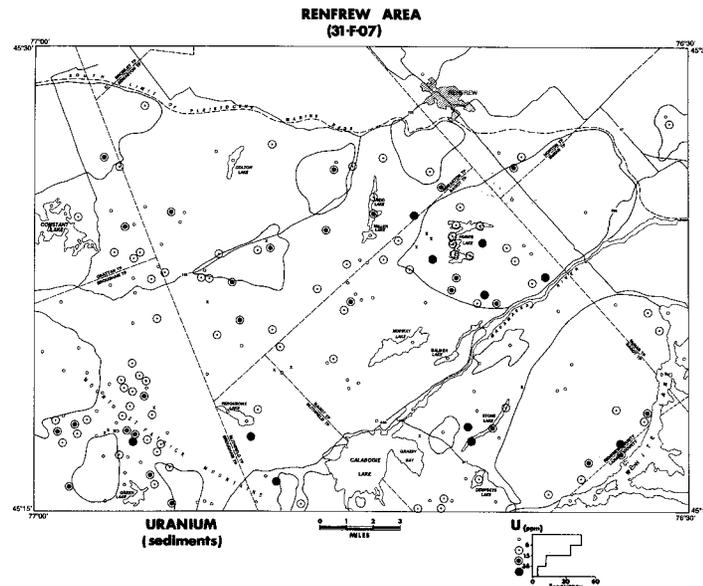
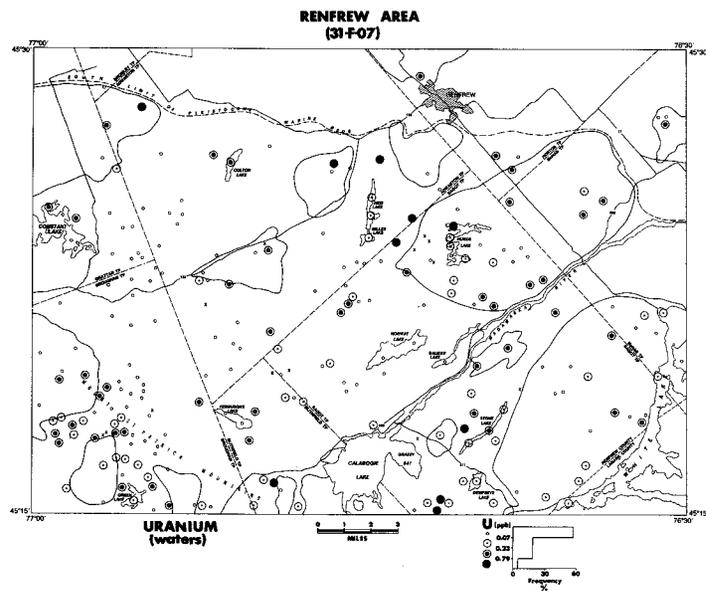
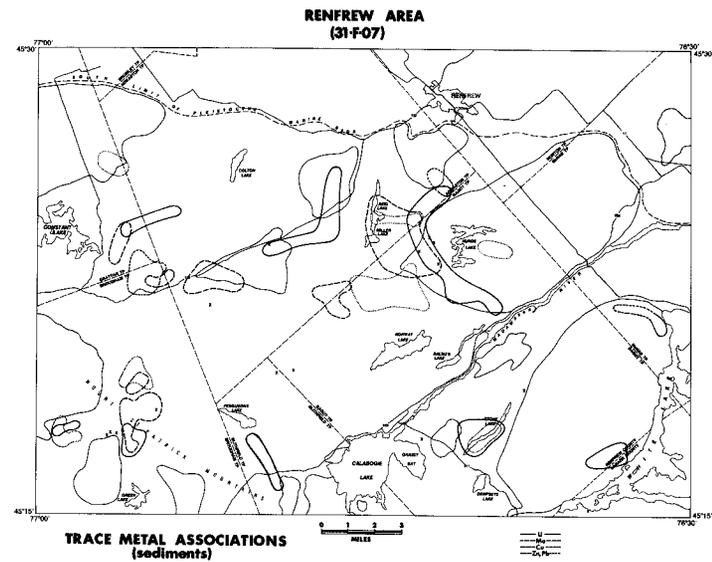
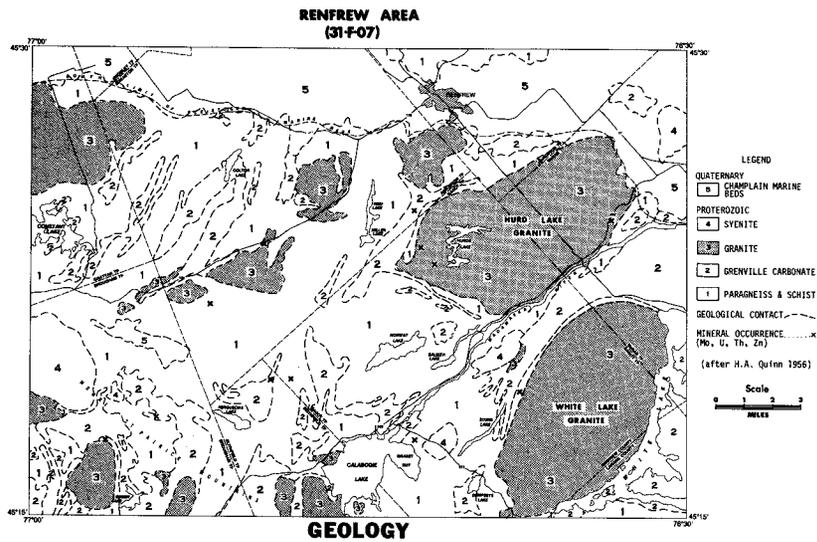
The Daniel's Harbour orientation study successfully determined optimum procedures for reconnaissance geochemical exploration for zinc mineralization in the St. George and Table Head groups of carbonate rocks. Figure 20.18 shows that the distribution of zinc in organic centre-lake bottom sediments, collected over 900 km<sup>2</sup> at an average density of one sample per 5.2 km<sup>2</sup>, has delineated the Daniel's Harbour locality containing known zinc deposits. This study was carried out prior to the development of the zinc deposits by Newfoundland Zinc Mines Ltd.

The frequency distribution of the zinc data is lognormal and the contour intervals in Figure 20.18 were arbitrarily chosen at 0.5, 1.5, 2.5, 3.5 standard deviations above the mean (150, 400, 1000, 2700 ppm Zn respectively). The major zinc deposits and related showings are revealed by a multi-station anomaly where the lake sediments contain zinc concentrations ranging from 6250 to 14 500 ppm. Only one of the sampled lakes may have been contaminated by trenching on an adjacent showing. Other weaker zinc anomalies are present along the eastern margin of the study area where zinc showings are known to occur. Zinc content of samples is weakly correlated with the iron and organic content. It is not correlated with the manganese content. However, similar zinc distribution patterns can be produced by plotting either untreated zinc data or residual zinc data after regression with iron and/or organic content.

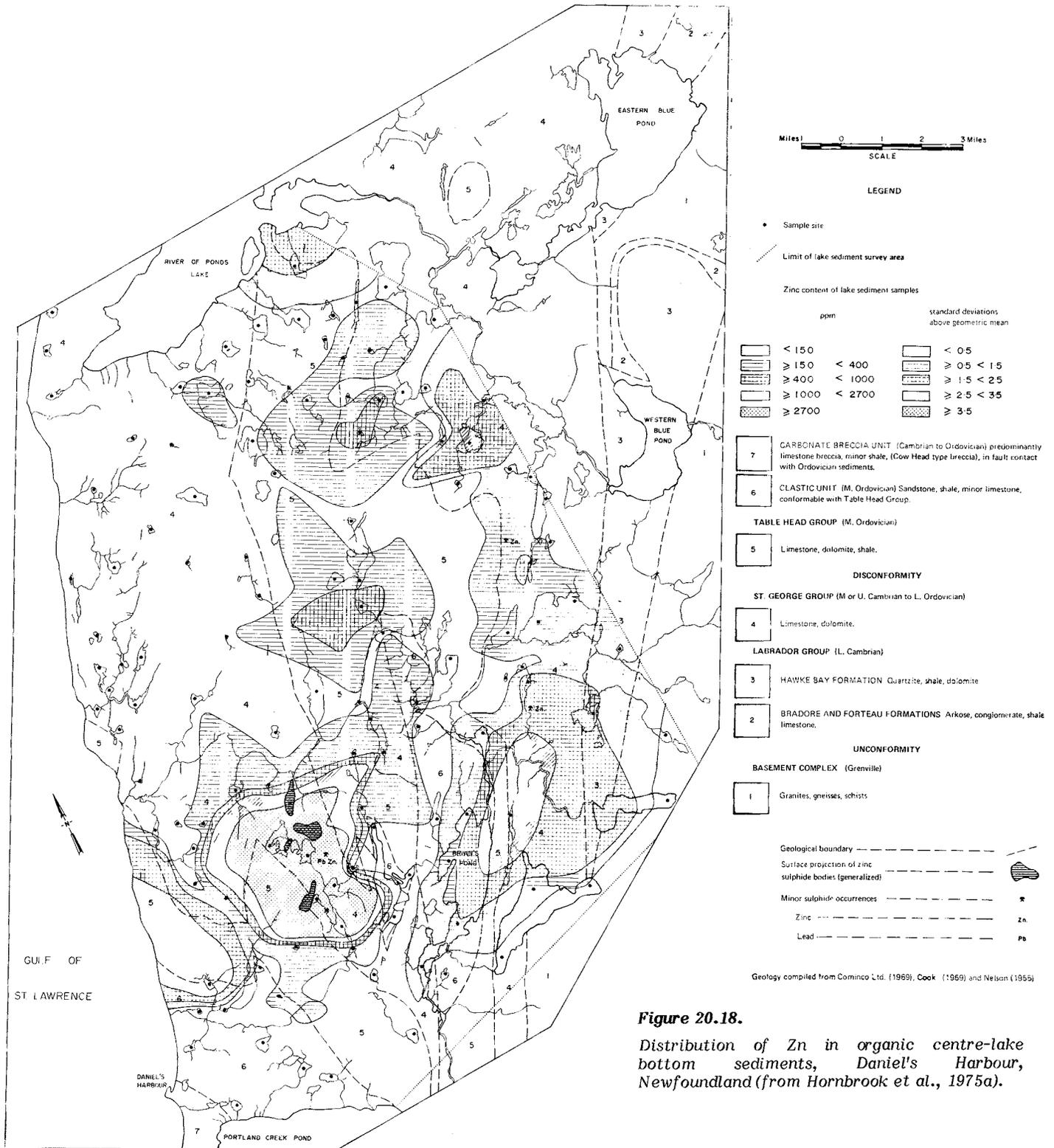
In the 1973 reconnaissance area, known zinc and lead mineralization typically occurs as clusters of pods or veins which may occupy an area of several square kilometres. In the Daniel's Harbour area, a sufficient number of zinc sulphide bodies fortuitously subcrop and supply zinc in detectable amounts to adjacent lakes, but in other more remote areas of the reconnaissance survey this may not be the case. To maximize the possibility of detecting anomalies due to mineralization, where only a small portion of a deposit intersects the bedrock surface, the reconnaissance survey sample density was increased to an average of one sample per 2.6 km<sup>2</sup>.

The distribution of zinc in the reconnaissance survey detects the zinc deposits and related showings of Newfoundland Zinc Mines Ltd. and duplicates the results of the orientation study data from the previous year. Elsewhere in the total reconnaissance survey area numerous other zinc anomalies were found and are described in Davenport et al. (1974).

From 1974 to 1976 the Newfoundland Department of Mines and Energy have carried out four more lake sediment surveys totalling 11 800 km<sup>2</sup>. These are: Burlington Peninsula, 1300 km<sup>2</sup>, Davenport and Butler (1975, 1976) and Davenport et al. (1976b); southwestern Newfoundland, 1800 km<sup>2</sup>, McArthur et al. (1975); Burrin Peninsula, Davenport et al. (1976a); Avalon Peninsula, 4800 km<sup>2</sup>, Davenport and Butler (1976), Davenport et al. (1975, 1976). These surveys were directed toward base metal exploration and were therefore carried out at sample densities ranging from one sample per 2.7 km<sup>2</sup> up to 5.3 km<sup>2</sup>. The centre-lake bottom sediment and surface lake water surveys, begun in 1977, are to cover 24 000 km<sup>2</sup> of insular Newfoundland and 144 000 km<sup>2</sup> of Labrador and are to be completed in 1978. Coverage in 1977 was 73 000 km<sup>2</sup> in Labrador and 17 400 km<sup>2</sup> on insular Newfoundland. The 1977-78 surveys are carried out under the Federal-Provincial Uranium Reconnaissance



**Figure 20.17.** General geology, distribution of U in waters and in sediments and the association of trace metals in lake sediments, Renfrew area (31F 07), Ontario (from Coker and Jonasson, 1977a).



**Figure 20.18.**

Distribution of Zn in organic centre-lake bottom sediments, Daniel's Harbour, Newfoundland (from Hornbrook et al., 1975a).

Program. Follow-up surveys will be carried out to assess the data by the Geological Survey of Canada and the Newfoundland Department of Mines and Energy.

**National Geochemical Reconnaissance**

It is only relatively recently that geochemical surveys that are national in scope, and complimentary to national geological and geophysical surveys, have been undertaken. In Canada the first National Geochemical Reconnaissance (N.G.R.) surveys commenced in 1975, the immediate stimulus being the Federal-Provincial Uranium Reconnaissance Program (U.R.P.). In the Shield, and in similar terrain, such as insular Newfoundland, the primary sampling media are lake sediments and waters. The lake sediments are analyzed for U, Zn, Cu, Pb, Ni, Co, Mo, Ag, As, Hg, Mn, Fe and loss-on-ignition (L.O.I.). Waters are measured for U, F and pH. Areas sampled under the auspices of the N.G.R.-U.R.P. programs for lake sediments and waters, to the end of 1977 are shown on Figure 20.19 (Hornbrook et al., 1976a, b, c, d, e, f, g, h, i; Geological Survey of Canada 1977a, b, c, d and 1978a, b, c, d, e).

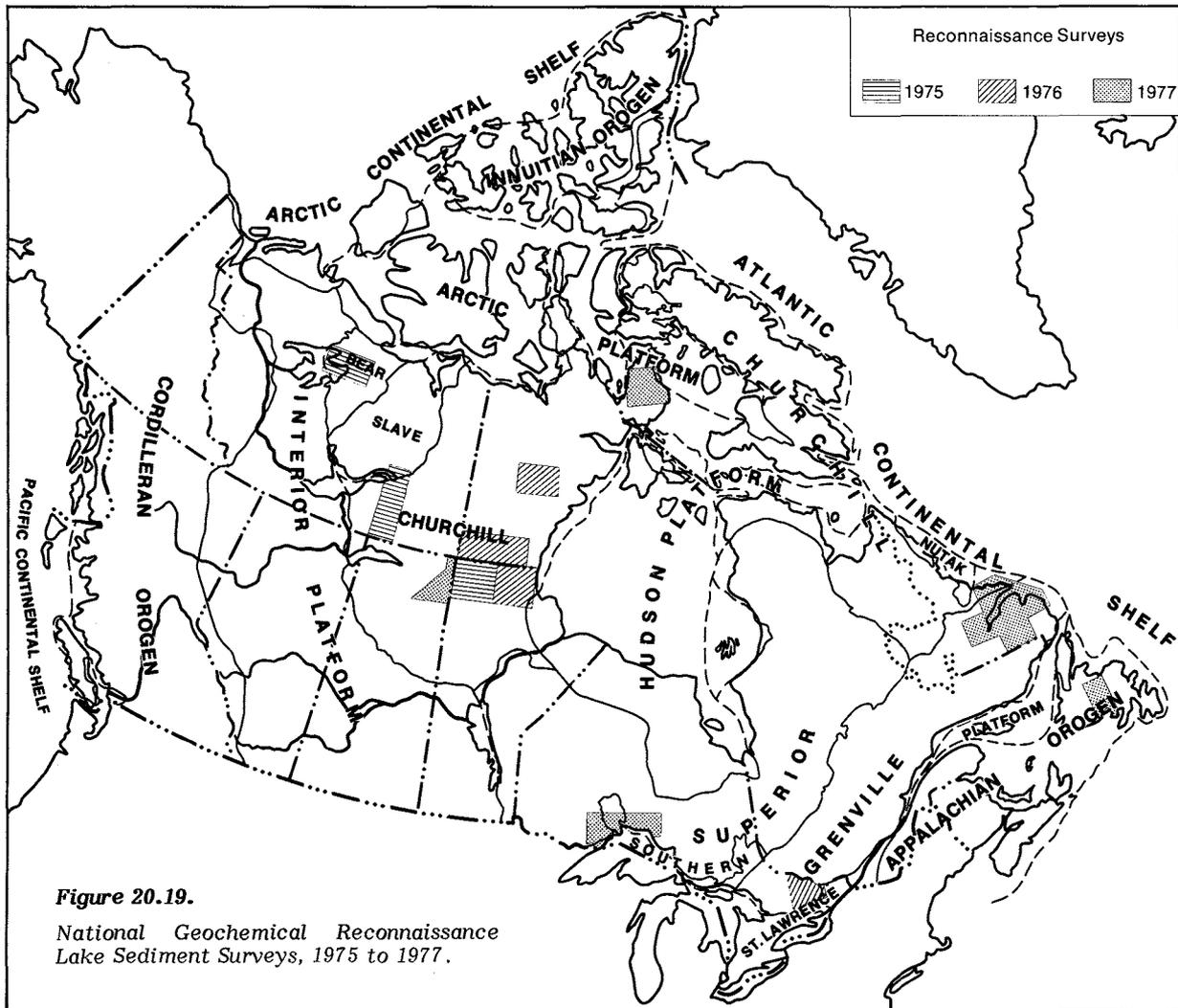
The sampling density for this reconnaissance work is an important consideration as it must provide an adequate level of information, but at the same time have wide enough spacing that costs and speed of coverage are reasonable. The chosen compromise was one sample per 13 km<sup>2</sup>. It is not the aim of the program to identify individual ore deposits, but rather to delineate regional trends where mineralization is

likely to occur. Despite this, the sample spacing has proven sufficient to outline anomalous lake sediments associated with a number of uranium and base metals deposits.

In addition to the short-term objectives of the Uranium Reconnaissance Program, the National Geochemical Reconnaissance data will provide a long-term data base for a variety of geoscientific and environmental purposes. In order that the data be consistent from year to year, standardized sampling and analytical techniques are used and quality control of the data is emphasized. Thus each batch of 20 analyses contains the following:

16 Routine Reconnaissance samples

- 1 Cell Duplicate Sample. This is collected from the same 13 km<sup>2</sup> grid cell as one of the reconnaissance samples, but from a different lake. The two samples allow the measurement of within-cell sampling variance.
- 1 Lake Duplicate Sample. Collected from the same lake as the cell duplicate sample. Allows estimation of within-lake sampling variance.
- 1 Analytical Duplicate Sample. A split from one of the routine reconnaissance samples. Allows estimation of analytical variance.
- 1 Control Reference Samples. A standard sample inserted to measure the analytical accuracy of the batch.



In 1977, N.G.R.-U.R.P. surveys were carried out over 230 000 km<sup>2</sup> of Canada and of this 142 000 km<sup>2</sup> were by lake sediment and water surveys. Sampling is carried out during the summer months and data released by the Geological Survey of Canada, and appropriate provincial or territorial governments, during the spring or early summer of the following year.

### **Lake Sediment Geochemistry Applied to Mineral Exploration in the United States of America and Fennoscandia**

There is very little published information on the use of lake sediment geochemistry in mineral exploration outside that in Canada.

#### **United States of America**

About the only published account of the application of lake-sediment geochemistry for mineral exploration in the United States of America is the work of Meineke et al. (1976) carried out in 1974-75 over a portion of the Precambrian Shield in Minnesota. The survey involved the collection of some 275 lake sediment samples from 75 lakes over an area of 520 km<sup>2</sup> in the eastern Lake Vermilion-Ely area, St. Louis and Lake counties, Minnesota. Several significant anomalies were located by the survey. Anomalous Cu was found in a lake near an interesting copper prospect. Copper, Pb, Ti and Zn appear to reflect bedrock composition; Cr, Mg, and Ni reflect both bedrock composition and glacial dispersion.

In addition, the United States Energy Research and Development Administration (ERDA) commenced reconnaissance lake sediment surveys in 1976 in Alaska in support of the National Uranium Resource Evaluation Program (NURE) (Sharp and Aamodt, 1976). By the end of the 1979 field season most of Alaska will have been sampled. Both centre-lake sediments and waters are being collected at a density of one site per 23 km<sup>2</sup>.

The mineral exploration industry has carried out reconnaissance lake sediment surveys in the Cordillera, Precambrian Shield and Appalachia of the United States of America, although to date there are no published accounts of these surveys.

#### **Fennoscandia**

There are portions of the Fennoscandian Precambrian Shield very similar in nature to the Canadian Precambrian Shield and consequently amenable to the application of lake sediment geochemistry for mineral exploration.

The Geological Survey of Finland has been particularly active in studying the application of lake sediment geochemical methods (Bjorklund et al., 1976; Bjorklund and Tenhola, 1976; and Tenhola, 1976). Organic-rich sediments were collected by the G.S.F. over a 6000 km<sup>2</sup> area in Karelia, eastern Finland. In addition to several small anomalies, the investigations indicated an extended zone of anomalously high uranium in lake sediments along the contact between Karelian schists and Pre-Karelian rocks. It was also found that central lake sediment samples may sometimes fail to indicate small isolated mineral occurrences in adjacent bedrock. A comparison between lake and stream sediments indicated that stream sediments may be used to complement lake sediment grids in areas of low lake density in the area studied.

In addition to the active use of the lake sediment method in Finland, similar work is being carried out on a modest scale in Norway and Sweden. In the northwestern U.S.S.R. helicopter supported lake sediment surveys are reportedly being carried out (L.K. Kauranne, pers. comm.).

### **SUMMARY**

The application of lake sediment and water geochemistry to mineral exploration did not begin until the late 1960s and early 1970s. Since that time there has been a rapid increase in the application of the technique, particularly within the Canadian Precambrian Shield, but also within the Cordilleran and Appalachian regions of North America and the Precambrian Shield of Fennoscandia.

The success of this exploration technique may be attributed to the demonstrated ability of lake sediments to reflect the presence of nearby mineralization. In addition, centre-lake sediments are usually homogeneous and may be sampled relatively easily and economically.

It is evident that while the technique is viable for reconnaissance-level mineral exploration in several regions, there is clearly still much work to be done to understand the processes operative on trace metals within the lacustrine environment itself, and within lakes located in different physiographic, climatic-geographic, and geological environments. A knowledge of the processes by which a metal is mobilized, transported, precipitated, and possibly remobilized, is of prime concern in order to comprehend possible controls on that metal's dispersion, accumulation and fixation into lake bottom materials.

In lakes having aquatic flora and fauna as a significant source of organic matter, or in which waters are highly productive and sedimentation is rapid, the influence of organisms on trace element distribution may be significant. In the flat-lying, tree-covered terrain characteristic of the southern Canadian Shield and Fennoscandian Shield, and in the terrain of the North American Appalachia, the incidence of organic matter is high and metal-organic interactions are predominant. The presence of organic matter can enhance trace element mobility, by forming mobile-soluble organic complexes or retard it, by direct precipitation of insoluble organic complexes or sulphides. The occurrence of abundant swamps or marshes around or in close proximity to a lake may restrict trace element movement into the lake itself. By contrast, lakes from Shield areas above the treeline and from the alpine Cordilleran regions are fed by waters derived mainly from snowmelt and containing very little dissolved organic material. Here, absorption of metals directly onto clays, rock flour, and hydrous metal oxides and dissolution of mineral particles are the predominant water-sediment interactions.

Under oxidizing conditions, hydrous oxides of iron and manganese are excellent scavengers of trace elements; however, under reducing conditions they are solubilized and may result in increases in concentrations of cations and anions in overlying waters. The scavenging effect of both iron and manganese hydroxide precipitates on trace metals in the lacustrine environment and the resulting false anomalies in lake sediments has been noted. Iron and manganese oxides are certainly important species in organic systems but their role as direct absorbers of metal ions is generally overshadowed by competition from the more reactive humic materials and organo-clays or obscured by coatings of organic matter. Moreover, these oxides are unstable in reducing organic-rich sediments.

In general, the stratigraphy of lake-bottom materials from northern and southern Canadian Shield lakes is very similar. There is an upper strata of gel-like sediment, containing a variable quantity of organic material, which has formed since the recession of the glaciers. This modern organic sediment is thickest and contains the greatest amount of organic material in lakes of the southern Shield and is relatively thin, areally restricted, and sometimes absent in lakes of the northern Shield. It is invariably present in lake centres in the southern Shield and Appalachians and occurs in

the centres of most lakes in the northern Shield and Cordillera. In contrast to centre-lake sites, surveys collecting material from the mineral sediment found around the margins of lakes are not necessarily collecting modern organic lake sediments, but are most often collecting glacial, glacial-lacustrine or marine sediments, or soils which have been subjected to some reworking, including wave action and, in addition, in the north of the Shield, to various periglacial processes.

Most trace metals tend to be enriched in the modern organic sediments, a factor which is most probably due to the nature of the metal-organic binding strength and perhaps increased ion-exchange capacity of organic sediments over inorganic types. As a result, the highest and most uniform concentrations of trace metals generally occur in the modern-organic sediment found in the deep central areas (profundal basins) of most lakes. In general, it appears that a profundal sediment is a homogeneous sample medium which does not exhibit severe matrix problems. It has also been shown that in certain situations (i.e. insufficient density of suitability sized lakes, relatively locally derived till) systematic nearshore sampling of materials around the periphery of several lakes in a mineralized area may provide a rapid method of delineating local mineral-rich areas.

The range of physicochemical-limnological conditions present within the lacustrine environment should emphasize the complexity of this regime. Variations in these conditions in different geographic – climatic and geological environments, with respect to mineralization, can affect the nature of metal transport, and accumulation in lake bottom materials.

Water sampling is often an integral part of a lake sediment survey as a knowledge of the distribution of many elements in the sediments often needs to be supplemented by information on their distribution in the overlying waters. This additional information can often provide some insight into the effects of variations in certain physicochemical factors (pH, Eh, alkalinity, Mn, Fe and organics, etc.) which might inhibit or prolong the dispersion of a given trace element in solution in the lacustrine environment. Therefore, an improved data base for interpretation of lake sediment data can often be obtained by the collection and analyses of both lake waters and sediments. Surface lake waters can generally be collected at a much faster, and hence cheaper, rate than lake sediments. However, the analytical methods currently available enable only selected elements (i.e. U, Zn, Cu etc.), generally present at very low levels (ppb or less), to be determined with relatively low precision.

The sample density employed should be a function of the type and objectives of the survey modified by a knowledge of the mobility of the different elements in the surface environment and their distribution in rocks around the intended target. If mobile elements are used as indicators, wide interval reconnaissance surveys (1 sample per 5 to 20 km<sup>2</sup>) are often adequate. But use of immobile elements as the principal indicators will require more detailed sampling even for reconnaissance.

At the reconnaissance level of sampling, gross bedrock differences can be discerned and regional trends are clearly outlined frequently depicting appropriate element associations. As a follow-up to reconnaissance-level sampling, detailed sampling at 1 sample per km<sup>2</sup> or several per individual lake, at inflows and around the margins where groundwater is thought to play a role, have proved effective in outlining potential economic mineralization.

Sophisticated computer processing of lake water and sediment data is not always necessary although suitable computer programs for data compilation, sorting and simple statistical determinations can often simplify and clarify the data for interpretation. In many instances the interelement relationships have been found to be of more interpretative value than the absolute magnitude of a single element in a given sediment or water sample. However, in the more complex limnological environments it may be necessary to adopt involved interpretational techniques such as metal ratios or regression analyses to screen out non-significant features of the data and focus attention on components of the data related to mineralization.

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\* Numerals refer to Table 20.5.

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