GEOCHEMISTRY OF FERROMANGANESE OXIDE CONCRETIONS AND ASSOCIATED SEDIMENTS AND BOTTOM WATERS FROM SHEBANDOWAN LAKES, ONTARIO

by

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INTRODUCTION

On June 10th, 1966 Mr. R.A. Ryder made the first of his several discoveries of ferromanganese concretion occurrences in Shebandowan Lakes. On learning of these discoveries, Prof. D.S. Cronan decided to investigate the geochemistry of the deposits. Accordingly, field surveys were conducted over a nine day period in July 1970 with the assistance of the writer and scuba diver, Mr. R.R. Hygaard of Thunder Bay. A total of 50 concretion deposits, including Ryder's original discoveries, were located, described and sampled. Sampling at the concretion sites included taking bottom water and sediment core specimens as well as concretions. Additional sampling was made of waters influent into the Lakes, the effluent and lake bottom water at barren locations.

Subsequently, seventy two concretion samples were analyzed by atomic absorption for Fe, Mn, K, Mg, Ca, Cu, Zn, Ni and Co at the University of Ottawa geochemistry lab. Several concretion samples were subjected to Mossbauer spectroscopy, electron spin resonance and X-ray diffraction experiments. The AA analysis of 47 water samples and 20 sediment core samples, the former for Fe and Mn and the latter for Fe, Mn, Cu, Ni and Co was contracted commercially as was colorimetric determination of As in 10 concretion samples. Other work included logging of the sediment cores and examination of concretions through binocular microscope.

This work presents field and lab observations along with the analytical results and seeks to draw from them inferences regarding the geochemical environment and origin of the Shebandowan Fe-Mn concretionary deposits. In early chapters basic data, general and detailed, as available on the area, has been compiled, both to aid the current study and any future studies of the concretions and their environment. These are followed by chapters on field data and the overall interpretation.

ACKNOWLEDGEMENTS

Professor D.S. Cronan, now of the Imperial College, London, initiated and supervised this investigation, including the field work, both during and after his stay at the University of Ottawa.

Mr. R.A. Ryder, Research Scientist, Ontario Department of Lands and Forests, the original discoverer of Shebandowan concretions, extended civilities in connection with our field operation, supplied valuable data and information, and read critically parts of this report. The facilities and guidance for the Mössbauer and ESR spectroscopic experiments were provided respectively by Dr. M.C. Townsend, Mines Branch, Ottawa and Professor A. Manoogian, Department of Physics, University of Ottawa. Dr. R.G. Garrett of the Geological Survey of Canada kindly gave advice on the application of several of his own computer programs, used for determining the correlation coefficients, precision and validity of analyses. My wife spent tedious hours helping me draft figures and maps.

Special thanks are due to several staff members of the Geology Department at the University of Ottawa, notably: Mrs. Diane Garrett, for analytical procedures; Mr. E.W. Hearn, for photography and reproduction; and Mr. C. de la Fuente, for X-ray diffraction work.

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SHEBANDOWAN WATERSHED

Location and access

Shebandowan Lakes are located near the headwaters of the St. Lawrence River system about 50 miles west of Thunder Bay (Map 52 B/NE in pocket). The Lakes were first connected by a road with Lake Superior in 1870 when the Dawson horsewagon route was completed between Port Arthur and the foot of the Lower Lake, the first leg of a water-course gateway to the Canadian West. It was at that time that the outlet of Lower Lake was dammed raising the water level 2½ feet up to the Upper/Middle Lakes Narrows, flooding out a small rapid there. The watercourse route thrived for a dozen years until the completion of the Canadian Pacific Railway transcontinental track, which passes some 20 miles to the north. The present C.N.R. track, which follows the north side of Shebandowan Lakes, links Thunder Bay and Winnipeg, having been completed early in this century. A precursor of the modern highway 11 between Thunder Bay and Fort Frances already reached Shebandowan in the 1930's.

Climate

Recently published contour maps (Phillips and McCulloch, 1972) correlate climatic data averaged over the 1931-60 period between meteorological stations in the Great Lakes region. These show that the Shebandowan area enjoys a cool temperate climate with warm summers and cold winters. The mean daily temperature was +17.8C in July and -16.7C in January (Table 1). There were about 80 frost free days in a year, when for 155 consecutive days snow cover exceeded or equalled 25 mm. Annual precipitation totalled 710 mm with winter's contribution amounting to only 40% of the summer precipitation. Yearly potential evapotranspiration was about 480 mm.

Average yearly solar radiation for Winnipeg, the nearest station reporting such information, was 117,895 gcal cm^{-2} year^{-1} (16-year average) (Brunskill and Schindler, 1971).

Table 1. Climatic data for the Shebandowan Lakes drainage basin averaged over the 1931-60 period (Phillips and McCulloch, 1972)

	Jan.	Mar.	Apr.	July	Oct.	Nov.	Year
Temperature (C)							
mean	-16.7		+2.2	+17.8	+15.0		
max.	-8.9		+8.9	+25.6	+11.0		
min.	-23.9		-5.0	+11.7	-1.7		
Total precipitation (mm)	30		51	89	51		710
Snowfall (mm)	430	300				380	1980
Vapour pressure (millibars)	1.6		4.9	14.7	7.1		
Sunshine (hrs)	100		205	310	140		
Sky cover sunrise-sunset (tenths)	6.7		6.0	6.2	7.0		

Population, vegetation and land use

The only permanent community of any size in the area is the Indian village of Kashabowie, numbering perhaps 350 souls. The Inco mine and mill on Lower Lake employ about 500 workers, but these commute from the outside. During the summer season the population swells considerably with the influx of cottagers, tourists and sport fishermen.

The country was initially inhabited by the migratory Ojibwa (Chippewa) Indians, who are now the principal dwellers at Kashabowie. The area experienced its first propsecting rush in the early 1870's following the discoveries of the Moss and Coldstream mine deposits just west of the Shebandowan watershed. The currently worked Inco Ni-Cu mine was discovered in 1913. Throughout the years a relatively high level of exploration activity has been maintained, earlier for gold and iron and more recently for base metals.

The principal forest trees of the region, arranged in their order of abundance, are as follows (McInnes, 1899): banksian pine, black spruce, balsam fir, white spruce, poplar, white birch, white and red pine, white cedar and larch.

The following kinds of vegetation, commonly occurring in a similar climatic environment at the Experimental Lakes Area, over 100 miles to the northwest of Shebandowan, are noted by Brunskill and Schindler (1971):

Swamp areas - trees: black spruce, alder and larch;
shrubs: Labrador tea, swamp laurel, leather leaf, <u>Betula glandulosa</u>, bog rosemary.

Aquatic mycrophytes: <u>Equisetum fluviatile</u>, <u>Sparganium angustifolium</u>, <u>Sparganium multipedunculatum</u>, <u>Sagittaria latifolia</u>, <u>Carex</u>, <u>Calla palustris</u>, <u>Eriocaulon septangulare</u>, <u>Iris versicolor</u>, <u>Nuphar microphyllum</u>, <u>Nuphar variegatum</u>, <u>Drosera rotundifolia</u>, <u>Drosera intermedia</u>, <u>Sarracenia purpurea</u>, <u>Urticularia vulgaris</u>.

Canada Land Inventory Map 52A, covering the adjoining area, east of 90°, shows nil natural soil capability for arable culture or permanent pasture. Much of the soil is classified as stony with solid bedrock less than 3 feet below the surface. There are apparently no large-scale logging activities within the Shebandowan district, although undoubtedly much timber required for mining purposes is derived from local stands.

Physiography

The Shebandowan Lakes drainage basin (Map 3) comprises an area of 450 square miles (1,165 sq. km.). As much as three quarters of its boundary is the continental divide between the Winnipeg-Nelson river system draining into Hudson Bay and the St. Lawrence River system flowing east into the Atlantic. The remainder of the boundary divides the basin from tributaries of the effluent Shebandowan River and its downstream confluent, Kaministikwia River, which empties into Lake Superior at Thunder Bay.

The area is a rolling peneplain with total relief of 300 feet (91m) above the 1,474-foot (450m) level of Shebandowan Lakes. The topography reflects the bedrock lithology and structure, modified by Pleistocene glacial scour and deposition. Lineal features, such as ridges and depressions, are principally expressions of foliation, shearing, and faulting, best developed in the greenstone-metasedimentary terranes. The long northeasterly stretch of Upper Shebandowan Lake, the west arm of Middle Shebandowan Lake; and the south arm of Kashabowie Lake, are examples of water filled linear depressions underlain by corresponding linear tectonic features of the greenstone-metasedimentary complex.

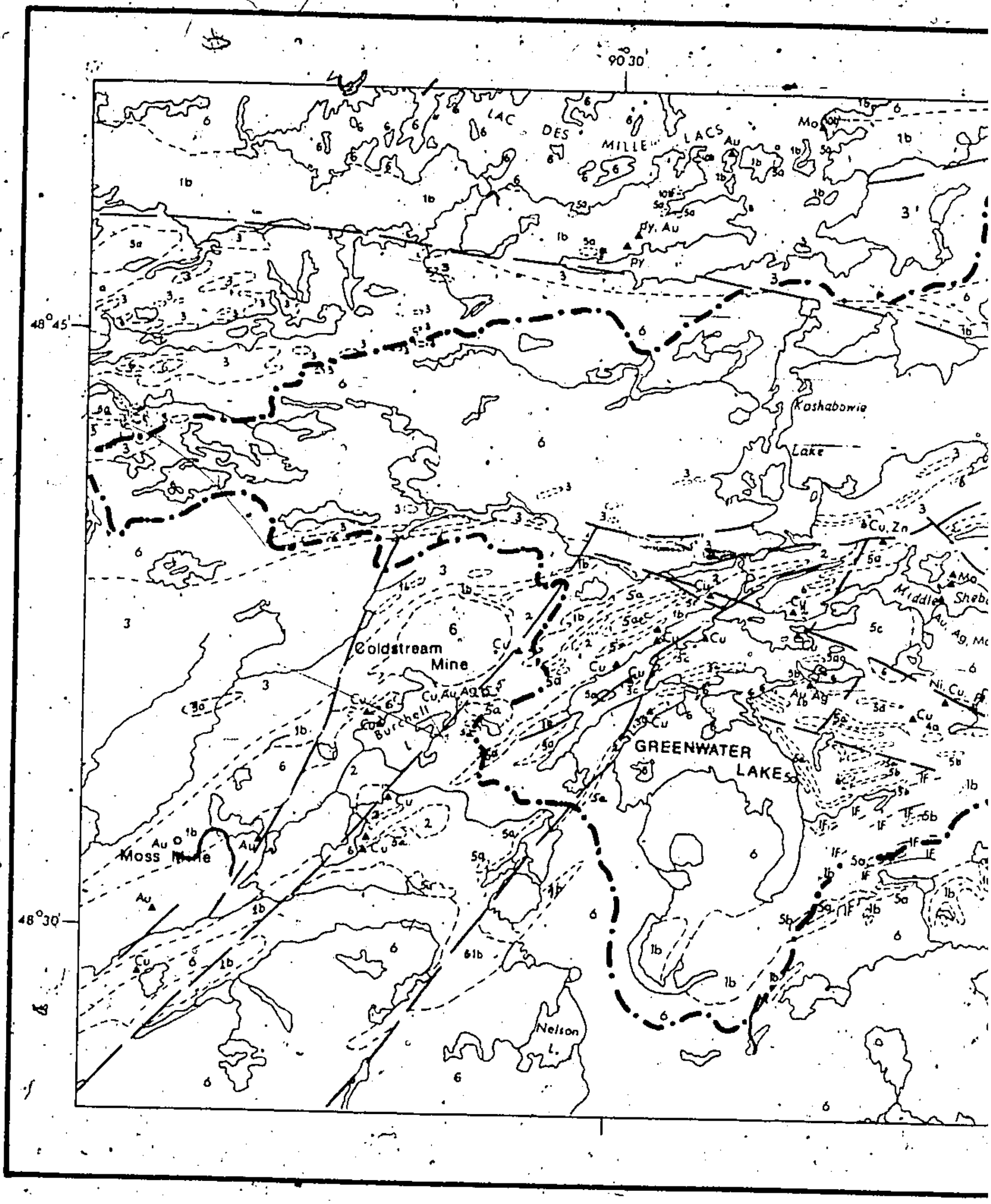
Areas underlain by granite, which tends to be massive to weakly foliated, are characterized by irregular shaped hills and basins, except where locally cut by faults.

Wherever granite is intensively fractured or foliated, as in vicinity of some contacts, it exhibits low resistance to erosion. This is well exemplified by Greenwater Lake, whose arcuate-shaped basin coincides with an underlying margin of a northeasterly batholithic projection into greenstone. Similarly, the basins of Lower and Middle Shebandowan Lakes are largely contact areas of an underlying granitic stock.

Bedrock Geology

First comprehensive mapping of the Shebandowan Lakes watershed was carried out by Tanton (1938 a,b). More detailed partial coverage has been done since by Giblin (1964) and Hodgkinson (1968). A regional compilation from these and other published and unpublished sources was made by Pye and Fenwick (1965) (Map 2). Morin (1973) completed detailed mapping of the Lakes' vicinity.

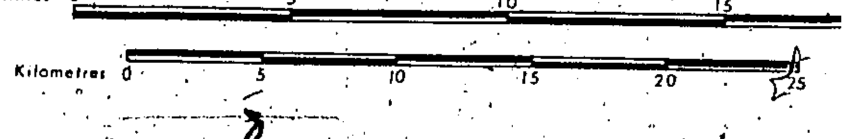
The area is underlain by Archean rocks. Potassium-argon dating indicates that metamorphism and granitic intrusion in the region occurred about 2,500 million years ago (Wanless, 1970). An east to northeast trending sequence of steeply-dipping greenstones and metasedimentary rocks, up to 12 miles wide, underlies the greater southern portion of the drainage basin that includes the Shebandowan Lakes. Except for the southern margin of another such belt near Athelstane Lake, the area to the north, 3 to 10 miles wide, is underlain by batholithic masses of younger granite.



MAP 2

GEOLOGY

SHEBANDOWAN REGI



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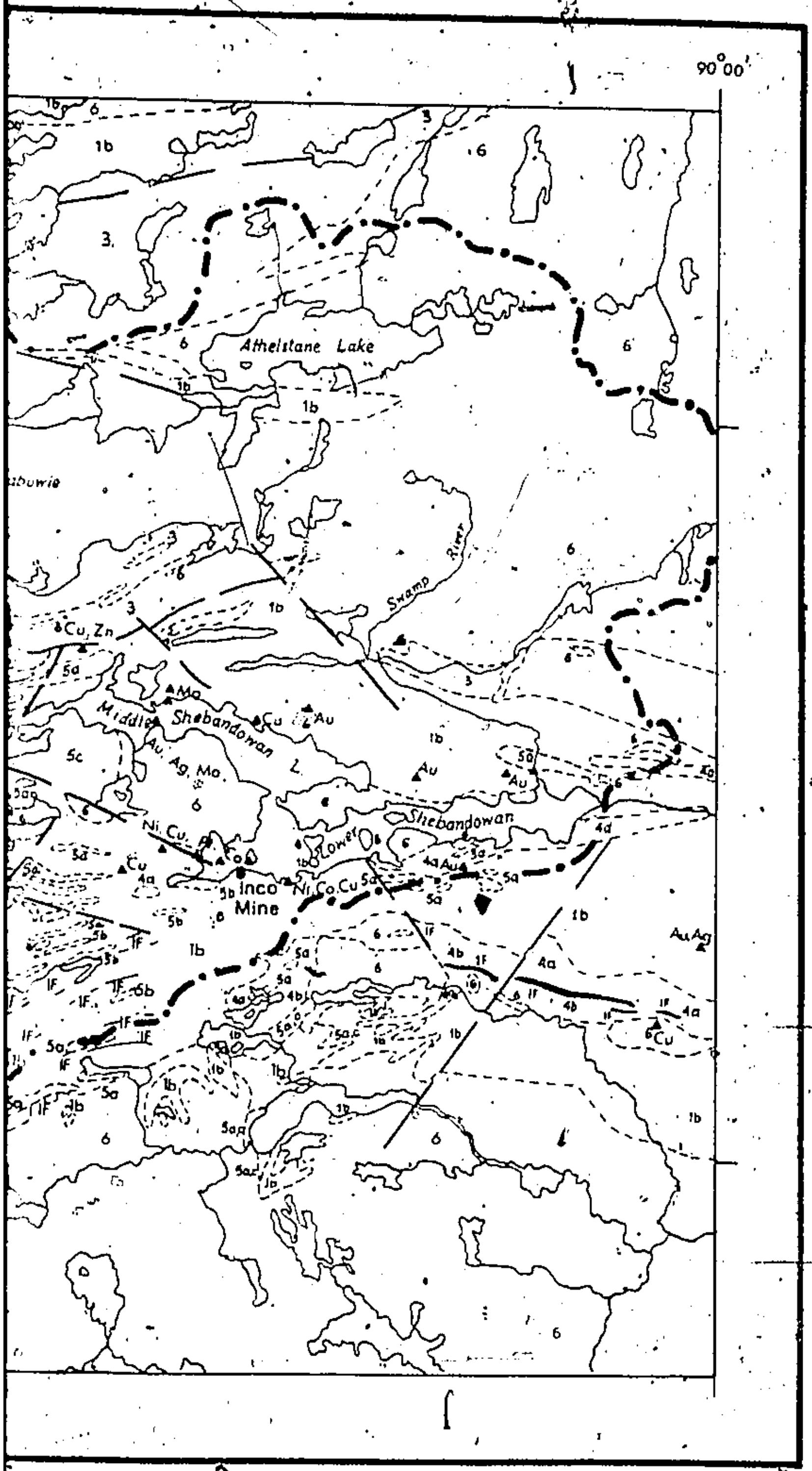


LEGEND

ARCHEAN

6	Granitic gneisses
5	a Gabbro, diorite, etc. b Peridote, dunite, serpentinite c Anorthosite, anorthositic gabbro
4	Metasediments, may be younger in part than 3 - a Conglomerate, arkose, greywacke, etc. b Metavolcanics with metasediments
3	Metasediments - arkose, greywacke, schists and paragneisses
2	Acid metavolcanics
1	Basic metavolcanics (a) b as above: undifferentiated metavolcs.
IF	Iron formation

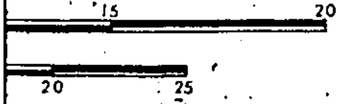
SYMBOLS

	Geological boundary
	Fault
●	Producing mine
○	Past producing mine
▲	Base metal or Mo sulphides; native Au Ag occurrences; py - pyrite

after Ont. Dept. Mines Map 2065

(Pye & Fenwick 1965)

REGION



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The northern edge of the greenstone-metasedimentary belt is comprised throughout of a band of metasediments, ½ to more than 1 mile wide. It consists of mica schists, derived from greywacke and, locally arkose, with minor metavolcanic and amphibolitic interbands. To the north the metasediments are gradational into biotite and muscovite granites, locally showing lit-par-lit banding. To the south, the east-northeast contact with the main body of metavolcanic is nowhere exposed. On the basis of discordance, lineaments, and diamond drill logs, this contact was postulated by Giblin (1964) and Hodgkinson (1968) to be a fault. Only two other, less extensive, bands of metasediments occur in the metavolcanic sequence at the east end of Lower Shebandowan Lake. They comprise conglomerate, as well as greywacke and arkose members. The larger of these two bands, extends westward six miles into the watershed along the south shore of the Lower Lake, and is up to 3/4 miles wide.

South from the faulted contact with the metasedimentary band at Kashabowie Lake, the metavolcanic sequence attains its maximum width of 11 miles along the section to southeast of Greenwater Lake. The metavolcanics, now largely chlorite, sericite, and amphibolitic schists are derived from flows and pyroclastics of rhyolitic to basaltic compositions. North of Upper and Middle Shebandowan Lakes, the acidic and basic metavolcanic have approximately equal distribution. The basics are increasingly abundant relative to the acidics farther south, until in the section east of Greenwater Lake the acidic volcanics are only rarely found.

Basic to ultrabasic rocks extensively intrude the metavolcanic sequence, where they exceed the acidic metavolcanics in total mapped area. They commonly form bodies that are grossly concordant with the intruded volcanic bands, but in one instance an irregularly shaped pluton has been mapped over an area of 4 square miles, at the east end of Upper Shebandowan Lake. Some of these bodies show differentiation. Original compositions include gabbro, quartz-gabbro, hornblendite, anorthosite and peridotite. Gabbros are the most common; they have been widely saussuritized, uralitized, and chloritized.

Acidic rocks intruding the metavolcanic sequence range from granitic to syenitic in composition and from batholithic to minor bodies in size. The boundary of a fist-like protrusion from the batholith along the south side of the belt is marked by the outside curvature of the shoreline of Greenwater Lake. This pluton of biotite granite has lineated, hornblende-rich border phases, probably resulting from magmatic assimilation of greenstone. A major stock of biotite granite underlies Middle Shebandowan Lake and its southern side, extending eastward under Lower Shebandowan

Lake and its shores. It is at least 10 miles long and up to 3½ miles wide at its western end, near Loch Macdougall. Minor acidic stocks, dykes, and sills intrude the metavolcanics, but are subordinate in terms of total mapped area to the basic intrusives.

No satisfactory interpretation of major folding in the metavolcanic-metasedimentary sequence has been proposed. The regional strike of banding and schistosity is northeast to easterly, with steep dips, suggestive of isoclinal folding. Local variations in foliation are encountered around margins of plutons. A northeasterly anticlinal axis through acid metavolcanics north of Burchell Lake has been postulated by Giblin (1964) on the basis of a few pillow-top determinations.

The major folding picture is complicated by the more evident faulting. Many essentially strike-slip faults or shears have been mapped or inferred from lineaments. At least one of these is thought to pass through the long northeasterly stretch of Upper Shebandowan Lake. Transverse faults of various strikes have been observed. Several northwesterly ones offset to the right the faulted northern metasedimentary-metavolcanic contact. The most persistent of these, and also the one with the largest horizontal displacement, of about 1½ miles, is the Crayfish Creek fault. It has been traced at least 13 miles northwest along strike from the vicinity of the Inco mine workings at Southwest Bay of Lower Shebandowan Lake.

Metal Concentrations in Bedrock

Metal concentrations in sulphide deposits have been found at a number of localities within the metavolcanic belt. Pyrite is the commonest of sulphides, its occurrence having been described as ubiquitous in the basic metavolcanics (Hodgkinson, 1968).

A sulphide deposit of major economic interest, containing nickel, copper, cobalt, and platinum metals, was brought into production by The International Nickel Company of Canada, Limited in 1972. The underground workings are located principally under the waters of Southwest Bay of Lower Shebandowan Lake. The ore zone has been traced at least 4,000 feet along a WNW strike in sheared peridotite, north of Crayfish Creek fault. The zone attains widths up to 100 feet and contains pyrite, chalcopyrite, pyrrhotite and polydimite in massive and disseminated form. Reserves are reportedly sufficient to feed a 2,500 ton per day mill for 20 years. During the early stages of production ore milled reportedly averaged 1.25% Ni. Two shafts have been put down, of which the main, or east, shaft is 2,395 feet deep.

A smaller sulphide deposit, held in 1965 by Vanguard Exploration Limited, is located on the northwest side of Upper Shebandowan Lake, 3/4 miles west of the mouth of Kashabowie River, in the vicinity of the Crayfish Creek fault. Two mineralized sections, 2,300 feet apart occur in a sheared zone striking N60°E and dipping steeply. Both zones consist of silicified greenstones, impregnated with disseminated-to-massive sulphides, chiefly pyrite, with pyrrhotite, chalcopyrite, and some sphalerite. In the west section drilling has indicated approximately 200,000 tons averaging 1.25% copper in a southwest-raking shoot about 150 feet in length and 22 feet in width, to a vertical depth of 600 feet. Associated zinc-gold-silver values are present in small amounts.

Other minor occurrences of copper, nickel, zinc, lead and molybdenum as sulphides have been found in metavolcanics, basic intrusives, and granite in the vicinity of the Shebandowan Lakes. There are also a few known minor occurrences of free gold and silver in quartz lodes.

Within the watershed, banded magnetite-hematite-silica iron formation is associated in many places with basic metavolcanics, and in a few places with the metasediments. Most extensive bands are in metavolcanics east of Greenwater Lake, where widths of up to 100 feet have been recorded, and one sequence has been traced on strike for more than 2 miles.

Surficial Geology

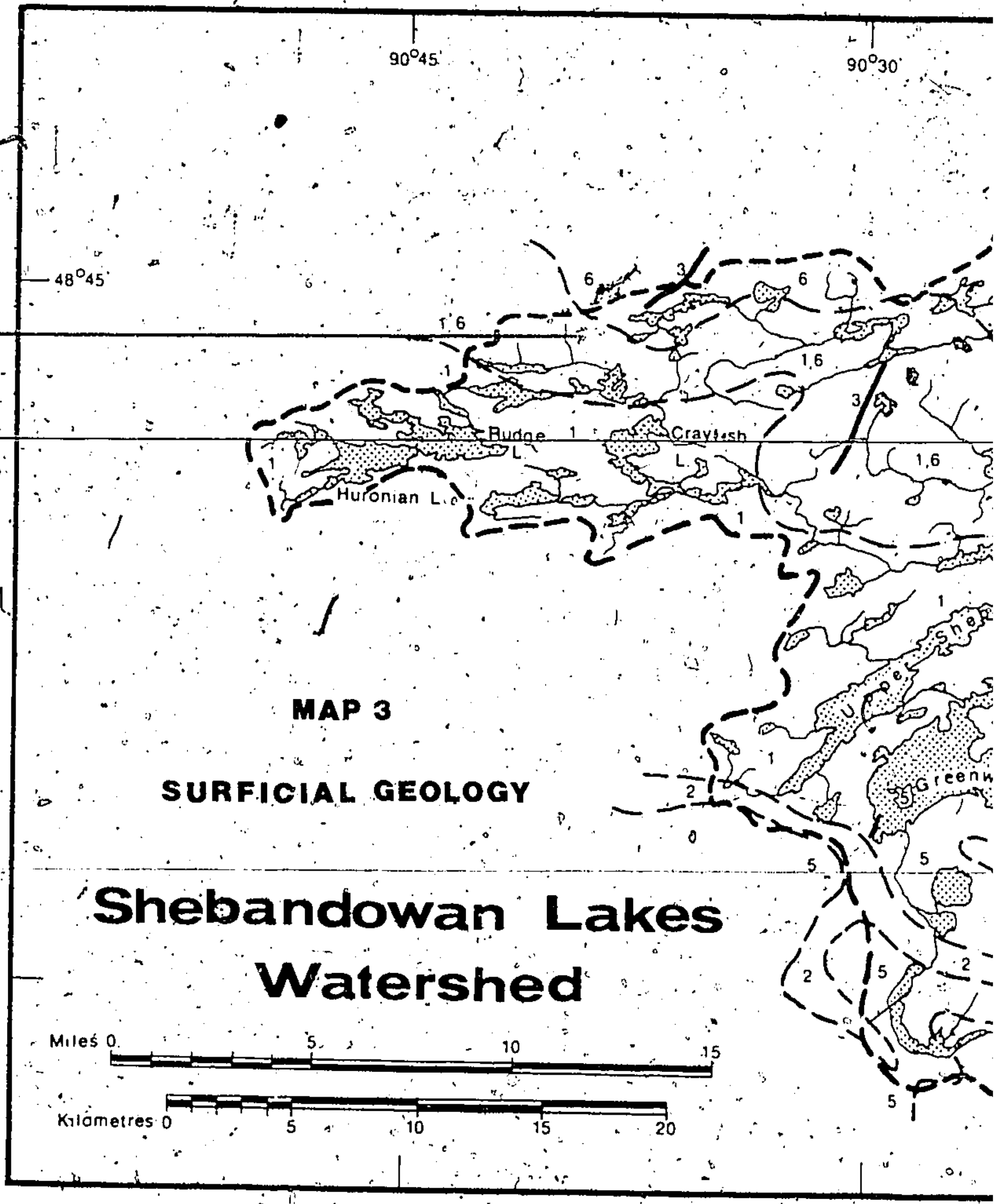
Within the past million years the region has been overridden by continental glaciers at least once during each of the four Pleistocene glacial stages (Hough, 1958), having been last cleared of ice about 12,200 years ago (Prest, 1969).

The sequence of glacial events in the region was given by Zoltai (1963, 1965a, b), based on interpretation of air photographs and field observations. Only evidence of the late phases of Wisconsin glaciation has been detected. A summary from Zoltai (1963, 1965a) follows:

(1) The earliest recorded activity was an advance south to south southwest by the Patricia ice-mass. During this phase the Shebandowan Lakes watershed area was overridden, and the ice moved across the International Boundary into northern Minnesota, where striae corresponding to this advance have been found. The ice then receded north for an undetermined distance, possibly clearing the Shebandowan area.

(2) An ensuing readvance moved the Patrician ice about 18 miles southwest of Greenwater Lake, as evidenced by northwest-trending terminal morainal ridges.

(3) The ice then withdrew to a stationary west-northwest front, marked by end moraines and extensive associated outwash deposits southwest of Upper Shebandowan Lake and on the south side of Greenwater Lake.



MAP 3

SURFICIAL GEOLOGY

Shebandowan Lakes Watershed

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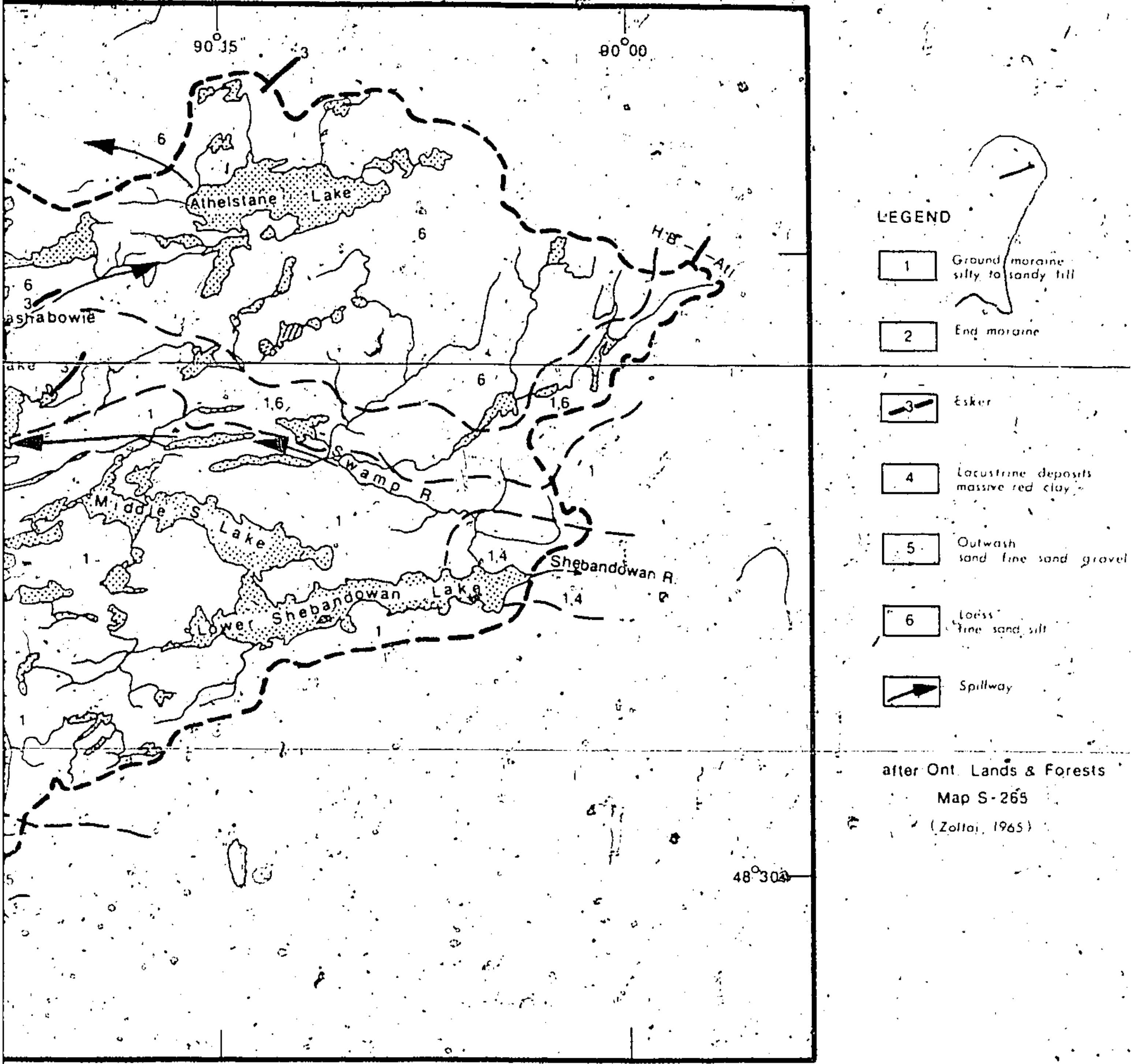

after Ont. Lands & Forests
Map S-265
(Zoltai, 1965)

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(4) The subsequent period of ablation finally cleared the present drainage basin of the Patricia ice sheet, which regrouped along a new line some 45 miles farther north. Contemporaneously, surges from two other continental ice masses, the Hudson Bay from the northeast and the Superior from the east, advanced to within 16 miles of the east end of Lower Shebandowan Lake. The three ice masses formed an interlobate system, correlated in time with the Valders maximum, approximately 11,800 years BP (Prest, 1969). The southerly flow of the Kaministikwia-Shebandowan river system was dammed by the Superior lobe, resulting in glacial Lake Kaministikwia in the wedge between the Hudsonian and Superior ice margins. The west end of this lake may have extended over the present Lower and Middle Shebandowan Lakes basins. The drainage was reversed, a westward spillway having been postulated along the north side of Shebandowan Lakes, through Kashabowie Lake to Athelstane Lake and Lac des Mille Lacs; and southwestward thence to glacial Lake Agassiz in the vicinity of Atikokan. At this time red, stone-free massive glaciolacustrine clays were deposited. They have spotty occurrence within the area as discontinuous lenses and lumps less than 1 foot thick.

(5) Both the eastern ice sheets eventually receded allowing the draining of Lake Kaministikwia. About

this time, thin but extensive loess deposits were formed. They now cover the north part of the watershed around Athelstane and Kashabowie Lakes.

The gross distribution of glacial deposits within the Shebandowan Lakes watershed is shown on Map 3. The thickest deposits are associated with terminal moraine in the south part of the area. Several diamond drill holes, collared in this material about 5 miles west of the southwest end of Upper Lake, failed to reach bedrock at depths of 200 feet or more (Giblin, 1964). Ground morainic till is the most generally distributed glacial deposit, averaging 3 to 8 feet (1.0 to 2.6m) in thickness. Glaciolacustrine clays, in lumpy aggregates, are found mixed with it near the east end of Lower Lake. The southern boundary of loess admixed with till is approximately marked by the railway line. Farther north loess becomes predominant attaining an average thickness of about 20 inches (51 cm).

Swamps and peat deposits cover about 5 per cent of the area. They are extensively developed in outwash near Greenwater Lake and along the lower courses of some streams, notably Swamp River. Unfortunately nothing is known about other recent sedimentation along the watercourses and in the lake basins.

Soils

No published pedological information is available on the watershed area itself. However, findings within the surrounding region (Hills and Morwick, 1964, Brunskill and Schindler, 1971, and Zoltai 1965c) point to the predominant development of weak podzolic and brunisol soil profiles. These soils are characteristic of the cool, moist climate and associated coniferous forests. They consist principally of a surface mor of acid matted material derived from trees, partially decomposed organic substances, and fungal hyphae, overlying an intensively leached ashlike grey horizon, succeeded by a reddish-brown layer enriched in oxidized compounds of iron derived from above.

In a region east of Kenora, over 100 miles to the northwest, Brunskill and Schindler (1971) observed little or no soil on hilltops and hill slopes, but lower lying areas often had brunisols, 10 to 30 cm thick, covering bedrock. Greater thicknesses of orthic brunisols were observed in areas underlain by sand and boulder till. One such profile consisted of a mor layer 10-20 cm thick, exhibiting a sharp contact with underlying light gray A horizon about 20-25 cm in thickness. A reddish-brown B layer of sand 30-50 cm thick, beneath the grey layer, graded into C horizon of clean quartz and feldspar sand. The organic and leached horizons were found to be very acid. pH values of 4.0-4.5 were obtained in some darkly coloured soil waters.

Hills and Morwick (1944) found weakly developed podzol the most widely distributed soil in the forested uplands of the region. A typical profile is described as follows:

Horizon	Depth	Description
A_0	0.6-2.5 cm	Fairly compact fibrous mat of leaf litter. pH 5.2.
A_2	2.5-6.3 cm	Ashlike gray structureless leached sand. pH 4.8.
B_2	2.5-6.3 cm	Iron brown layer with slight cohesion of particles (Orterde); layer of accumulation, high in iron. pH 5.0.
B_3	7.6-20.3 cm	Yellow-brown structureless layer. pH 5.3.
C		Slightly weathered, coarse parent materials. pH 5.5.

On the poorly drained flats organic matter accumulates to from half-bog and bog soils. The following is a generalized description of a half-bog soils (Hills and Morwick 1944).

Peat Horizon -	15.3-92.5 cm of woody or mossy peat grading from the living plant materials into a deeper, slightly decomposed section; just above the mineral soil there is a thin layer somewhat more decomposed. pH 4.5.

Podzolized Horizon -	Under imperfect though not poor drainage conditions where the peat layer is shallow, a light gray leached horizon may occur just beneath the peat layer. This ranges from 0 to 7.6 cm in depth. pH 6.0.
Glei Horizon -	(a) In heavy soils this is a grayish layer often with a bluish tint. It is very plastic when wet, brittle when dry. pH 7.0. (b) In the lighter soils this is a dark reddish-brown compact layer. While mottlings are common to both heavy and light soils they are more common in the latter. pH 6.5.

SHEBANDOWAN LAKES

Lake Morphometry

Upper, Middle and Lower Shebandowan Lakes are arbitrary divisions of essentially a single Lake. However, downstream surface flow of water, noted in July 1970 at the Upper-Middle Narrows, suggested a slight difference in levels of these two lakes. The surface elevation of Middle and Lower Lakes was given by Tanton (1938a) at 1,474 feet (450m) ASL. The Lakes are now controlled by three dams; one at the outlet of Lower and one above the inlet of each of the main tributaries of Upper Lake, Kashabowie River and Greenwater Creek. For this reason it is difficult to attribute any part of water fluctuation to natural causes per se. During the open water season (May 15 to November 15) in 1970 the water level at Rossmere Bay varied by 52.6 cm (R.A. Ryder, unpublished data).

The outlines are irregular in detail, but generally the lake system is long and narrow, with west-east extension. The composite length is about 30 miles, while the straight line joining the head of Upper Lake with the outlet at Lower Lake measures 22½ miles. Maximum width is 1.5 miles, minimum width about 40 feet (at Upper-Middle Narrows), the average being between .5 and 1 mile. The surface water area is 22.8 square miles (59 sq. km.).

The system is fed by number of streams, of which Kashabowie River, Swamp River and Greenwater Creek, in that order, drain the largest areas and contribute the most water.

There are numerous islands, particularly in Upper Lake, which also has the most highly indented shorelines. The shoreline totals 146 miles. The shores are low to moderately steep. In places, especially along the East Arm of Upper Lake and along the south side of Middle Lake, hills rise to 200 feet or more above the lake within 1,000 feet of ~~the shore. Bedrock is widely exposed or thinly covered.~~ Inflowing creeks have swamps commonly associated at their mouths. Elsewhere, much of the shore is heavily wooded except where cleared for cottage and recreation areas, particularly along the north sides of Lower and Middle Lakes.

Bathymetry of the Lakes is known from an unpublished contour map by Ontario Dept. of Lands and Forests, based on surveys in 1964 and 1965. Unfortunately it shows ~~few data points and faulty contouring renders it unacceptable~~ for reproduction here. However it shows clearly that the Lakes are divided into several basins (Fig. 4). For convenience five bathymetric subdivisions are proposed. First covers the five mile stretch from the southwest end of Upper Lake, which for the most part is uniformly shallow, averaging around 15 feet (4.6 m) in depth. The next five miles, to the Upper-Middle Narrows, display the most pronounced rugosity within the watercourse bottom and also include the greatest depth recorded, 124 feet (38 m). The average depth within this interval is perhaps 30 feet (9.2 m). Over the next 1.6 miles (2.6 km), to the gap west of Kabaigon I., mean depth is about 20 feet (6.1m). The most persistent and regular deep basin extends over the next nine miles of the watercourse, to the gap south of Castor I. The average depth here is around 40 feet (12.2m). The last seven miles, to the outlet, are rather uniformly shallow at 10 to 15 feet (3-4.6m).

The rate of discharge from the lakes system, measured in 1970 fluctuated from 915 cu. ft./sec. in July, to 99 in August, 46 in September, and 313 in October (Rasberry et al., 1971). This is equivalent to a daily outflow of about 296 x 10^6 ft^3 (8.38 x $10^6 m^3$). No data are available regarding water income of the Lakes. Presumably as much as 90% is brought by influent streams, and the remainder by precipitation, with negligible contribution from groundwater and springs.

Shebandowan Lakes are located in the south central part of their 450 square mile (1,165 sq. km) drainage basin (Map 3), whose approximate centre is at the intersection of 48° 40' north latitude and 90° 20' west longitude. The long axis of the basin is approximately 41 miles (66 km) in length and extends from about 89° 57' to about 90° [illegible] west longitude. The area of the watershed includes all of Haines township, parts of Hagey, Conacher, Lamport, Begin, and Ames townships, and part of Abitibi Block No. 2. The remainder, about half the area, is unsurveyed territory.

Table II. Dimensions of Shebandowan Lakes

Factor		Value
Area		
Drainage area		450 sq mi (1,165 km^2)
Surface area		22.8 sq mi (14,952 ac., 59 km^2)
Length (composite)		30 mi (48 km)
longest straight line, ENE		22.5 mi (36 km)
Prevailing winds		east to northeast
Width		
maximum width		1.5 mi (2.4 km)
maximum width (U/M Narrows)		40 ft (12 m)
mean width		.5-1.0 mi (.8-1.6 km)
Depth		
maximum (Upper L)		124 ft (38 m)
Sub-basin means		
1. U Upper L	approx.	15 ft (4.6 m)
2. M&L Upper L	"	30 ft (9.2 m)
3. U Middle L	"	20 ft (6.1 m)
4. M&L Middle, U Lower L	"	40 ft (12.2 m)
5. L Lower L	"	12 ft (3.7 m)
Shoreline (composite length)		146 mi (235 km)
Effluent discharge - 1970 open season		296×10^6 ft^3 (8.38×10^6 m^3) daily

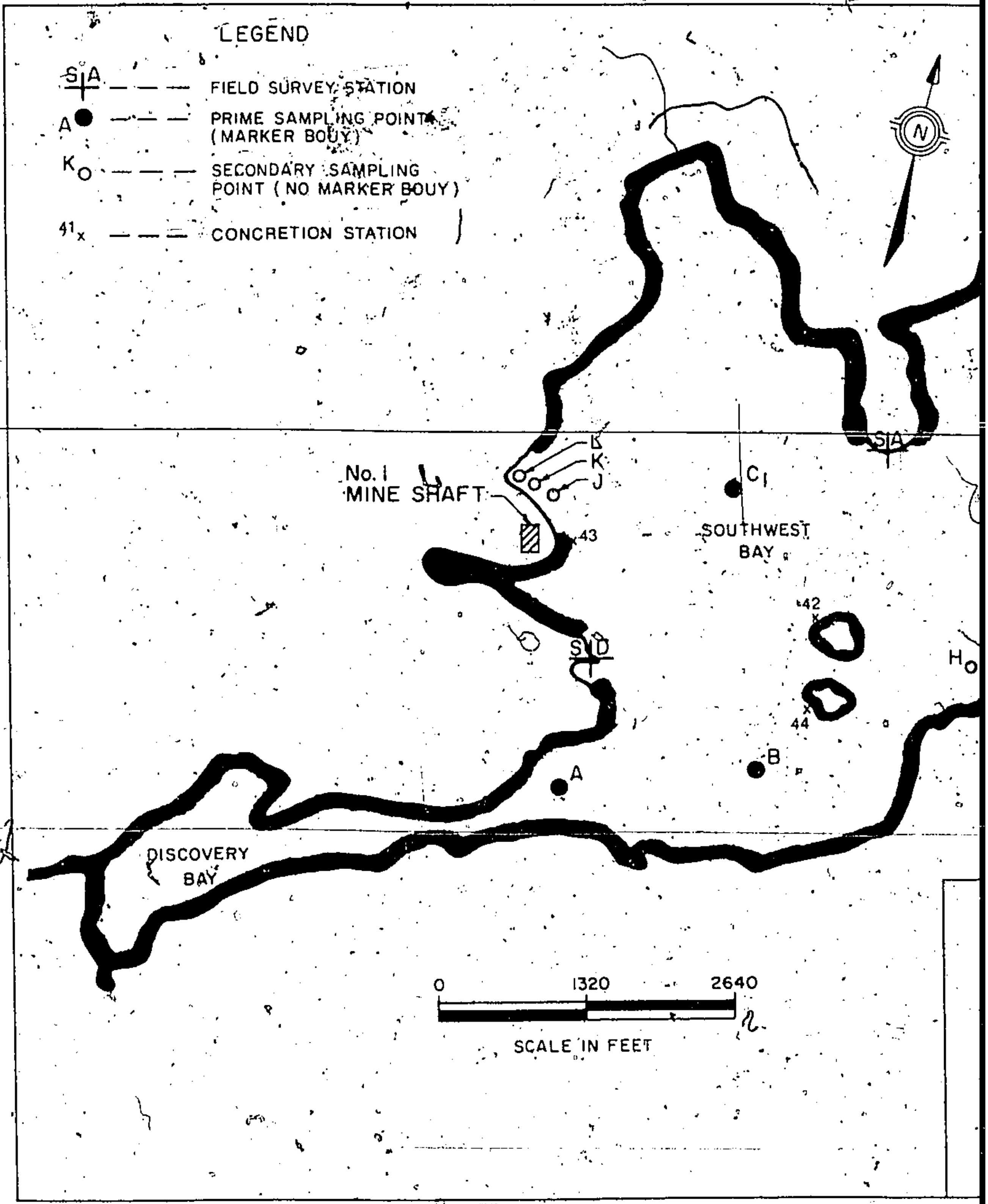
Lake Chemistry

The properties of Shebandowan Lakes' water were first studied in some detail by R.A. Ryder (pers. commun.) in the mid-1950's, but the data have been lost. Nevertheless these studies showed that the deepest sub-basins (L Upper, M and L Middle) underwent thermal stratification in the summer when the thermocline was gradually depressed to its maximum depth in September. The stratified deep basins exhibited an orthograde distribution of oxygen. The remaining sub-basins were not thermally stratified and their water mixed freely throughout the year.

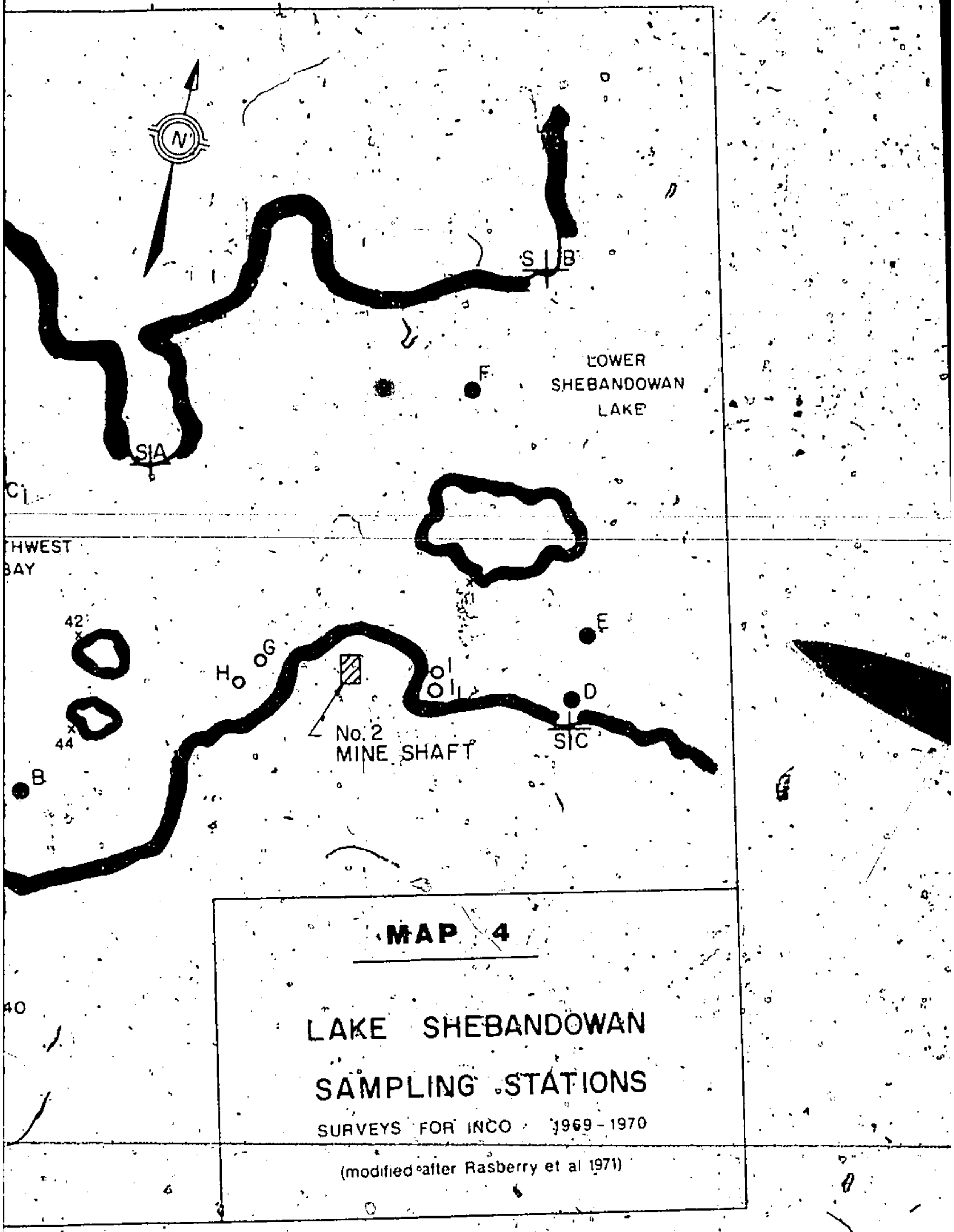
The only data obtained on lake water during the course of our survey, apart from analyses of bottom water sampled at some of the concretion sites, were kindly gathered by Mr. Ryder at concretion Stations 1 and 5 (Appendix VII). At Station 1, located in Three Mile Bay, an offshoot of the M Upper basin, there was virtually no stratification to a depth of 7.2 m, whereas at Station 5 in M Lower basin a thermocline was well developed, particularly between depths of 6 and 8 m. No change in the oxygen content, from top to bottom, was indicated at either station.

Detailed data on a small area of the Lakes system, Southwest Bay of Lower Shebandowan Lake, come as a result of water quality study commissioned by Inco in the vicinity of their mine and carried out during the open seasons of 1969 and 1970 (Lumsden et al. 1970 and Rasberry et al. 1971). Analytical results and ranges from stations monitored in 1970 are reproduced in Table III, with a key to locations provided by Map 4.

The results show rather uniform water quality throughout the area monitored and throughout its depth. They differ little in values for the same parameters obtained in


LEGEND
S|A — FIELD SURVEY STATION
A ● — PRIME SAMPLING POINT (MARKER BOUY)
K O — SECONDARY SAMPLING POINT (NO MARKER BOUY)
41x — CONCRETION STATION
N
S|A
L
K
J
C1
No. 1 MINE SHAFT
43
SOUTHWEST BAY
42
44
S|D
H
A
B
DISCOVERY BAY
0
1320
2640
SCALE IN FEET

1 of



MAP 4

LAKE SHEBANDOWAN SAMPLING STATIONS

SURVEYS FOR INCO 1969 - 1970

(modified after Rasberry et al 1971)

2of2

1969, variations being of the order expected due to seasonal variations.

The pH of the water showed little departure from neutral throughout the 1970 season. The water had little colour, low turbidity, and was extremely soft with a total carbonate hardness of about 27 mg/l. Total dissolved solids concentration was minimal. The metal concentration was likewise low, considered due to natural origin and not to contamination issuing from the mine workings on the underlying orebodies which had been under development for several years.

It is to be noted that the average of total iron values in the Inco study area are exceeded by factors of 2 or more by bottom water values obtained from concretion sites (compare Table III and Appendix III). Actually the Inco figures based on sampling in July, 1970, within a day or two of our sampling at the concretion sites, are at the low end of the iron ranges. For example, contemporaneous sampling at Inco station E (25 ft. depth) and at concretion station 41 (15-20 ft depth) yielded respective total Fe values of .02 and .105 mg/l. The stations are about 1,100 feet apart.

While the quality of the Southwest Bay water remained essentially uniform throughout the two seasons, variation was noted in temperature and dissolved oxygen content. Variation was greatest at the deepest station, F,

AVERAGE ANALYTICAL RESULTS AND RANGES FOR 1970

RESULTS IN MILLIGRAMS PER LITRE
(except pH value and where stated)

DESCRIPTION	pH VALUE (at lab)	TEMPERATURE °C	TURBIDITY J.T.U.	COLOUR °HAZEN	CONDUCTIVITY µMHOS	DISSOLVED OXYGEN
LAKE STATION A at 3'-0"	7·00 6·80 - 7·20	13·5 3·0 - 21·0	5 5 - 5	15 15 - 15	60·0 59·0 - 61·5	10·1 9·2 - 10
LAKE STATION A at 10'-0"	6·96 6·80 - 7·10	13·2 3·0 - 19·4	5 5 - 5	15 15 - 15	58·1 57·8 - 58·5	9·9 9·2 - 10
LAKE STATION B at 3'-0"	7·00 6·90 - 7·10	13·4 3·0 - 21·2	5 5 - 6	15 15 - 15	57·4 56·0 - 58·0	10·0 9·2 - 10·
LAKE STATION B at 15'-0"	7·01 6·85 - 7·10	13·1 3·2 - 19·0	5 5 - 5	15 15 - 15	57·6 56·5 - 58·0	9·7 9·1 - 10·
LAKE STATION C at 3'-0"	6·98 6·80 - 7·15	13·8 3·8 - 21·0	5 5 - 5	15 15 - 15	56·5 56·0 - 57·0	9·9 9·1 - 10·
LAKE STATION C at 25'-0"	7·04 6·90 - 7·20	12·8 4·0 - 18·0	5 5 - 5	15 15 - 15	58·9 56·5 - 65·0	9·4 8·7 - 10·
LAKE STATION D at 3'-0"	7·01 6·80 - 7·15	13·8 3·0 - 20·5	5 5 - 5	15 15 - 15	56·3 55·5 - 57·5	10·3 9·2 - 11·
LAKE STATION D at 15'-0"	7·05 6·95 - 7·15	13·6 3·2 - 20·0	5 5 - 5	15 15 - 15	56·1 56·0 - 56·5	9·8 9·2 - 10·
LAKE STATION E at 3'-0"	7·03 6·90 - 7·15	13·7 3·1 - 20·2	5 5 - 5	15 15 - 15	56·1 55·0 - 57·0	10·0 9·3 - 10
LAKE STATION E at 25'-0"	7·06 6·95 - 7·20	12·3 3·5 - 17·5	5 5 - 5	15 15 - 15	57·0 56·0 - 57·5	9·7 7·9 - 11·
LAKE STATION F at 3'-0"	7·03 6·90 - 7·25	13·5 3·0 - 20·0	5 5 - 5	15 15 - 15	55·4 54·5 - 57·0	10·1 9·5 - 10
LAKE STATION F at 30'-0"	6·93 6·65 - 7·20	11·1 3·8 - 14·5	5 5 - 5	15 15 - 15	56·1 55·0 - 57·0	8·7 7·0 - 10·
STATION No. 2, OUTLET FROM LAKE	7·39 6·90 - 7·60	18·9 9·8 - 24·0	11 5 - 20	26 15 - 50	58·3 56·5 - 59·5	10·5 9·8 - 11·

1 of

OR 1970

TABLE III

REPRODUCED FRO

CONDUCTIVITY µMHOS	DISSOLVED OXYGEN	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY $CaCO_3$	TOTAL HARDNESS $CaCO_3$	CHLORIDE Cl	SULPHATE SO_4	TOTAL NITROGEN N	ORTHO-PHOSPHATE P	TOTAL
60·0 59·0-61·5	10·1 9·2-10·8	65 54-76	0 0-1	65 53-76	20·8 20·5-21·0	26·9 25·0-30·0	1·31 1·00-1·50	7·8 7·8-8·0	0·338 0·279-0·440		0·0 <0·005
58·1 57·8-58·5	9·9 9·2-10·2	66·5 56-76	0 0-2	66 54-76	20·7 20·0-21·0	26·9 25·0-[illegible]	1·38 1·00-1·75	7·6 7·0-8·0	0·401 0·242-0·550		0·0 <0·00
57·4 56·0-58·0	10·0 9·2-10·3	66 58-78	0 0-3	65 58-78	20·5 20·0-21·0	26·6 25·5-28·0	1·19 0·75-1·50	7·1 6·0-8·1	0·353 0·322-0·412		0·0 <0·006
57·6 56·5-58·0	9·7 9·1-10·2	60 54-72	0 0-1	60 53-72	20·3 20·0-20·5	26·5 25·0-28·5	1·19 1·00-1·50	7·3 6·0-8·5	0·267 0·255-0·282		0·0 <0·006
56·5 56·0-57·0	9·9 9·1-10·2	63 60-72	0 0-1	62·5 59-71	20·3 20·0-20·8	26·0 25·0-28·0	1·25 0·75-1·75	7·2 5·8-8·2	0·296 0·196-0·382		0· <0·006
58·9 56·5-63·0	9·4 8·7-10·2	60·5 54-72	0 0-1	60 54-70	20·2 19·5-20·5	27·5 25·0-31·5	1·38 1·00-2·00	7·0 6·0-8·1	0·196 0·179-0·212		0·1 <0·0
56·3 55·5-57·5	10·3 9·2-11·4	58 48-64	0 0-1	57·5 47-64	20·0 19·5-20·5	25·9 25·0-28·0	1·13 0·50-1·75	6·7 5·5-7·2	0·255 0·160-0·388		0· <0·015
56·1 56·0-56·5	9·8 9·2-10·4	55 48-66	0 0-1	55 48-66	20·0 19·5-20·5	25·8 24·0-27·5	1·38 1·00-2·00	6·9 6·0-7·4	0·341 0·159-0·792		0· <0·05
56·1 55·0-57·0	10·0 9·5-10·5	50 34-72	1 0-2	49 33-71	20·2 19·5-21·0	26·5 25·0-28·0	1·13 0·75-1·50	7·0 6·0-7·8	0·258 0·140-0·389		0· <0·05
57·0 56·0-57·5	9·7 7·9-11·2	45·5 38-52	0 0-1	45 38-52	19·8 19·0-20·5	26·0 24·0-28·0	1·31 1·00-1·75	6·8 5·8-7·3	0·233 0·127-0·322		0· <0·0
55·4 54·5-57·0	10·1 9·5-10·5	44·5 32-58	0 0-1	44 32-58	19·8 19·0-20·5	25·4 24·0-27·0	1·13 0·75-1·50	6·8 5·5-7·6	0·291 0·209-0·454		0· <0·0
56·1 55·0-57·0	8·7 7·0-10·4	44 36-52	0 0-2	43·5 36-52	20·3 20·0-21·0	25·3 23·0-27·0	1·25 0·75-1·75	6·9 6·0-[illegible]	0·309 [illegible]-0·404		0· <0·0
58·3 56·9-59·5	10·5 9·8-11·5	66 52-84	3 1-4	64·3 49-83	20·8 20·5-21·0	26·4 25·5-28·0	1·19 0·75-1·50	7·9 6·6-9·0	0·461 0·290-0·644		0 <0·0

TABLE III

REPRODUCED FROM [illegible] RASBERRY ET AL 197

SULPHATE SO_4	TOTAL NITROGEN N	ORTHO-PHOSPHATE P	TOTAL PHOSPHORUS P	TOTAL COPPER Cu	TOTAL NICKEL Ni	TOTAL ZINC Zn	TOTAL IRON Fe	TOTAL CADMIUM Cd	SULPHIDE S	SILICA SiO_2
7·8 7·8-8·0	0·338 0·279-0·440		0·017 <0·003-0·032	0·037 0·021-0·073	<0·01 <0·01-<0·01	0·030 0·018-0·042	0·05 0·05-0·08			4·25 3·70-5·00
7·6 7·0-8·0	0·401 0·242-0·550		0·018 <0·003-0·032	0·030 0·018-0·037	<0·01 <0·01-<0·01	0·022 0·018-0·028	0·05 0·04-0·08			4·30 3·80-5·00
7·1 0-8·1	0·353 0·322-0·412		0·018 <0·003-0·032	0·037 0·025-0·048	<0·01 <0·01-<0·01	0·028 0·023-0·030	0·05 0·04-0·08			4·20 3·84-4·40
7·3 0-8·5	0·267 0·235-0·282		0·016 <0·003-0·028	0·052 0·030-0·073	<0·01 <0·01-<0·01	0·022 0·020-0·028	0·05 0·04-0·07			4·15 3·80-4·40
7·2 2-8·2	0·296 0·188-0·382		0·020 <0·003-0·042	0·060 0·048-0·073	<0·01 <0·01-<0·01	0·027 0·013-0·035	0·06 0·04-0·11			4·16 3·80-4·44
7·0 ·0-8·1	0·196 0·178-0·212		0·021 <0·003-0·044	0·049 0·044-0·082	<0·01 <0·01-<0·01	0·025 0·021-0·028	0·04 0·02-0·05			4·14 3·90-4·30
6·7 -7·2	0·255 0·160-0·388		0·021 <0·003-0·038	0·062 0·040-0·088	<0·01 <0·01-<0·01	0·035 0·023-0·048	0·05 0·02-0·08			4·05 3·70-4·30
6·9 -7·4	0·341 0·158-0·792		0·020 <0·003-0·038	0·039 0·028-0·048	<0·01 <0·01-<0·01	0·030 0·023-0·035	0·04 0·02-0·08			4·10 3·70-4·50
7·0 7·8	0·258 0·140-0·389		0·019 <0·003-0·030	0·060 0·028-0·092	<0·01 <0·01-<0·01	0·037 0·033-0·043	0·04 0·02-0·08			4·06 3·84-4·40
6·8 7·3	0·233 0·127-0·322		0·023 <0·003-0·048	0·026 0·019-0·040	<0·01 <0·01-<0·01	0·029 0·016-0·048	0·05 0·02-0·06			4·11 3·84-4·40
6·8 7·6	0·291 0·209-0·454		0·024 <0·003-0·048	0·045 0·035-0·057	<0·01 <0·01-<0·01	0·057 0·025-0·081	0·04 0·02-0·08			4·17 3·80-4·44
9	0·309 0·188-0·404		0·024 <0·003-0·056	0·035 0·032-0·041	<0·01 <0·01-<0·01	0·032 0·024-0·042	0·04 0·03-0·05			4·22 3·90-4·60
7·9 9·0	0·461 0·290-0·644		0·022 <0·003-0·044	0·022 0·013-0·033	<0·01 <0·01-<0·01	0·009 0·008-0·012	0·11 0·05-0·21			3·88 2·52-4·60

3 of 3

36 feet deep. This is illustrated in Fig. 1 for parts of 1969 and 1970 seasons. Climatic disparity between these years and wide time (monthly) separations in the data points account for the incongruity implied by isopleths for the two corresponding periods. In 1970 water temperatures declined earlier than in 1969 and were markedly lower in September and October. A slight temperature inversion, not noticeable in Fig. 1a, occurred in both 1969 and 1970. The 1969 isotherms, based on data collected between May 22 and October 23, start and end vertically, suggesting a dimictic regime with spring and autumn turnovers. It is clear that thermal stratification took place, with steepest gradients recorded in August, both in 1969 and 1970, below a depth of 6m. Available measurements of dissolved oxygen content show downward oxygen depletion, least concentration occurring in August both years at the lowest horizon of determination, 9.1 m. In 1969 this corresponded to about 64% saturation and in 1970 to about 75% (Hutchinson, 1957). At all times deep water conditions within the study area were reported adequately aerobic to sustain fish life.

The water quality at the Lower Lake outlet (station 2, Table III), also monitored for Inco, was similar in many respects to that of Southwest Bay. The total iron, however, was double to triple that of the Bay stations (but was still

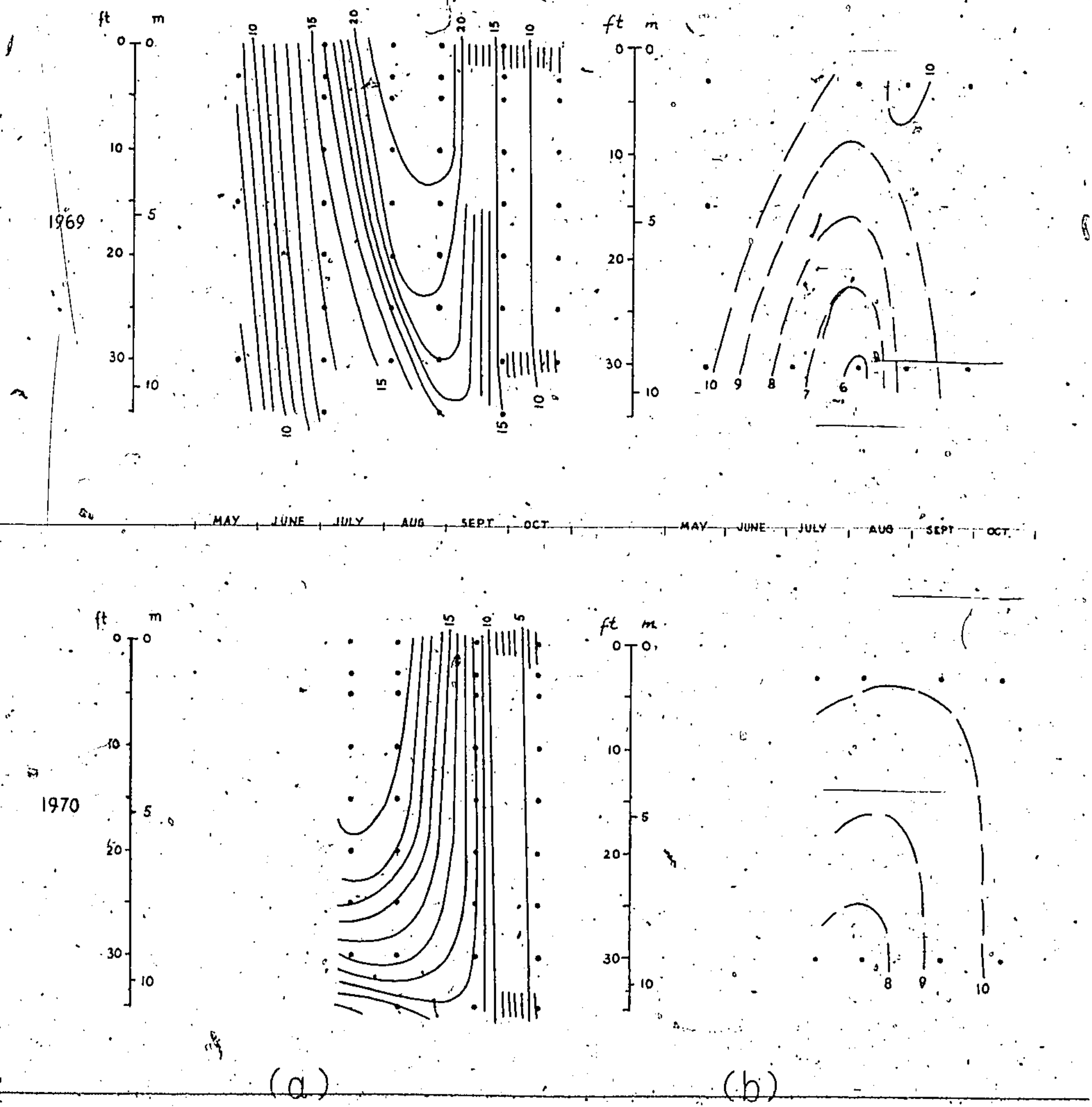


Fig. 1. Variation in water temperature(a) and dissolved oxygen content(b) with depth at Station F, Southwest Bay, Lower Shebandowan Lake. Contour intervals: a) 1C, b) 1mg/l. Data points and values from Lumsden et al. 1970 and Rasberry et al. 1971.

exceeded by factors from less than two to three by values realized from contemporaneous sampling in this area during the concretion survey). Iron-rich input by Swamp River, influent only 1½ miles above the outlet, is likely responsible for this. Nitrogen was 50-60% higher, while phosphorus rose significantly above Southwest Bay's levels in 1969 but not in 1970. These rises have been attributed to manmade effluents from the cottage areas on Lower Lake. Copper content was only about half that in Southwest Bay water; zinc, only slightly less than the lake stations' average in 1969, plummeted to a fourth their value in 1970. No ready explanation comes to account for the decreased copper values and the anomalous inter-seasonal fluctuation in the zinc content.

Productivity

For data on productivity and biotic activity in Shebandowan Lakes, one must again rely on work by Lumsden et al. 1970 and Rasberry et al. 1971, confined to Southwest Bay. Identification and enumeration of the genera of phytoplankton and benthic fauna was carried out several times during the open seasons of 1969 and 1970 at stations A to L (Map 5).

Appendix V shows the distribution of phytoplankton in 1970. Their concentration was said to have been similar to the preceding year, when total counts averaged about 45 cells per millilitre. The Southwest Bay phytoplankton consisted almost entirely of free-floating varieties of algae and diatoms. Zooplankton which included protozans and rotifers occurred in 1970 in concentrations of only about 1 per millilitre.

The surveys indicated that the essential nutrients, nitrogen and phosphorus and others, such as sulphur and silica, were present in adequate concentrations to support algal blooms, but no such blooms were observed. In fact the Southwest Bay productivity was low. The authors thus concluded that deficiency of some other element or elements; possibly carbon, may limit the productivity of the lake.

Trophism

While examining components of phytoplankton in Southwest Bay, Rasberry et al. (1971) noted excess in the number and population of species indicative of oligotrophy over those usually associated with mesotrophic conditions.. This fact combined with overall low productivity led them to conclude that the lake is basically oligotrophic.

The difference in mean depth between lake basins can moderate the availability of ambient nutrient levels resulting in different trophic levels of the basins. To account for this phenomenon the morphoedaphic index

$\left(\frac{\text{total dissolved solids (ppm)}}{\text{mean depth (ft.)}}\right)$ (Ryder, 1965) may be used to indicate relative trophism within such a multibasin system as Shebandowan Lakes. Mr. Ryder has kindly furnished some unpublished TDS figures from his own sampling throughout the Lakes system which showed considerable variation between seasons and even during the same season. Using "rounded" averages of Ryder's TDS figures for each of the morphometric subdivisions proposed above, morphoedaphic indices of trophism for each sub-basin are indicated in the following table.

Table IV. Relative trophism of Shebandowan Lakes sub-basins as indicated by morpheodaphic indices

Sub-basin	Mileage	Approx. Mean Depth (ft.)	TDS (ppm)	MEI
U Upper L	0 - 5.3	15	60	4.0
M&L Upper L	5.3 - 10.2	30	60	2.0
U Middle L	10.2 - 11.8	20	60	3.0
M&L Middle & U Lower L	11.8 - 20.0	40	60	1.5
L Lower L	20.0 - 27.4	12	50	4.2

The above figures reflect the classical view that morphometric factors influence trophism of lacustrine basins, ceteris paribus.

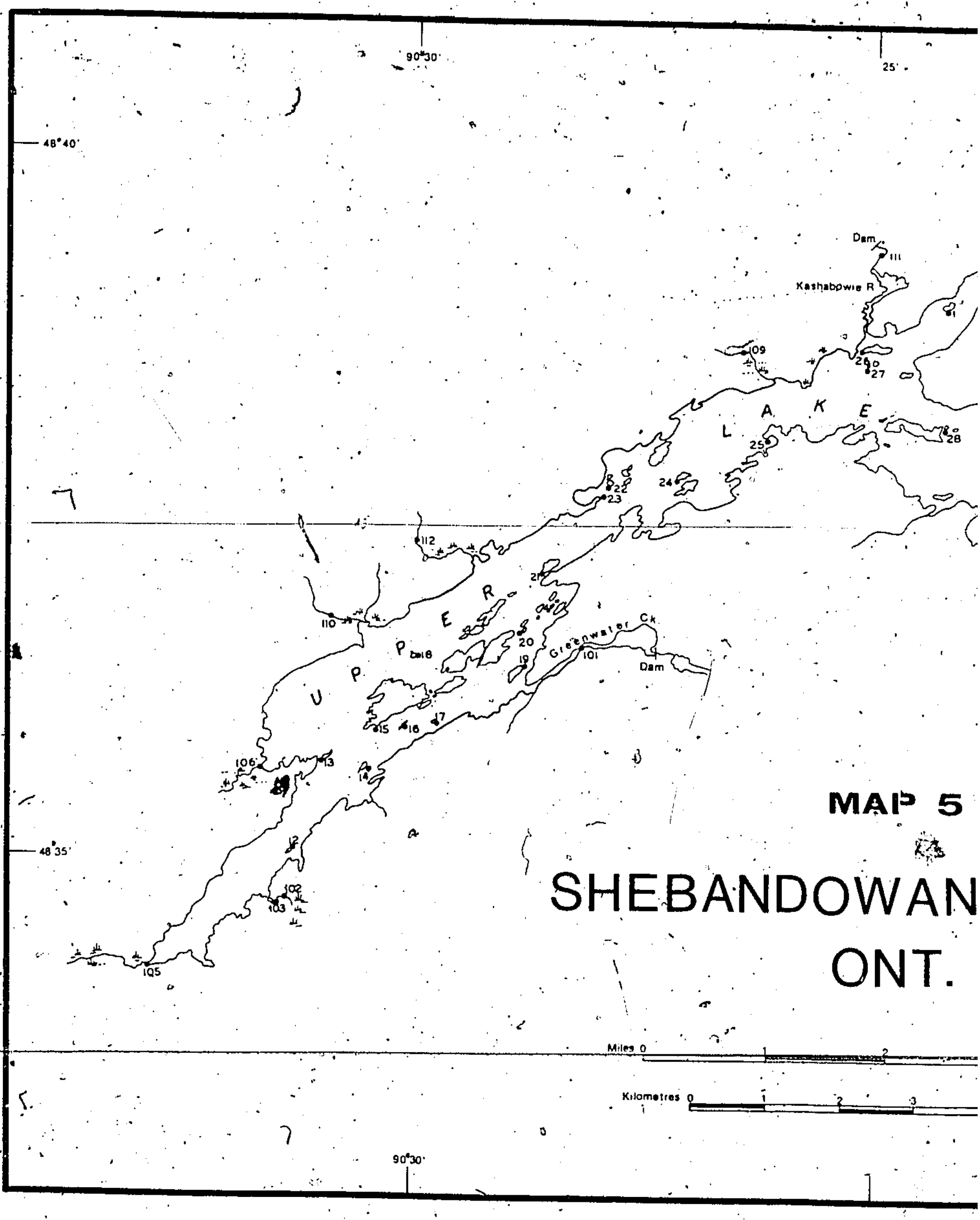
Ryder's personal view is that the lake system's status is in a flux due to cultural eutrophication. Twenty years ago it would certainly be classified as oligotrophic. Today it can perhaps be considered as mesotrophic especially the L Lower basin, proceeding towards eutrophic.

FIELD SURVEY

Between 12 and 20 July 1970 the Lakes were explored for concretion deposits with the view of obtaining a fairly even representation throughout the watercourse. This was accomplished by budgeting exploration and sampling time accordingly. Fifty deposits were located at stations numbered 1 to 50 on Map 5. Concretion specimens were collected at all stations, except station 36. Bottom water samples were obtained at 28 concretion stations and at 2 barren locations, while sediment core was recovered at 20 concretion sites.

Upon locating a deposit the diver was instructed to outline its dimensions and gauge its range of depth, using a wrist-type aneroid depth indicator. This gauge unfortunately proved inaccurate, resulting in a number of probable overestimates of depth (see Fig. 4) particularly in U Upper L. A description of the bottom, the types of concretions present, their distribution, relative concentration and disposition with respect to the sediment, associated plant growths and other pertinent observations were relayed to the boat.

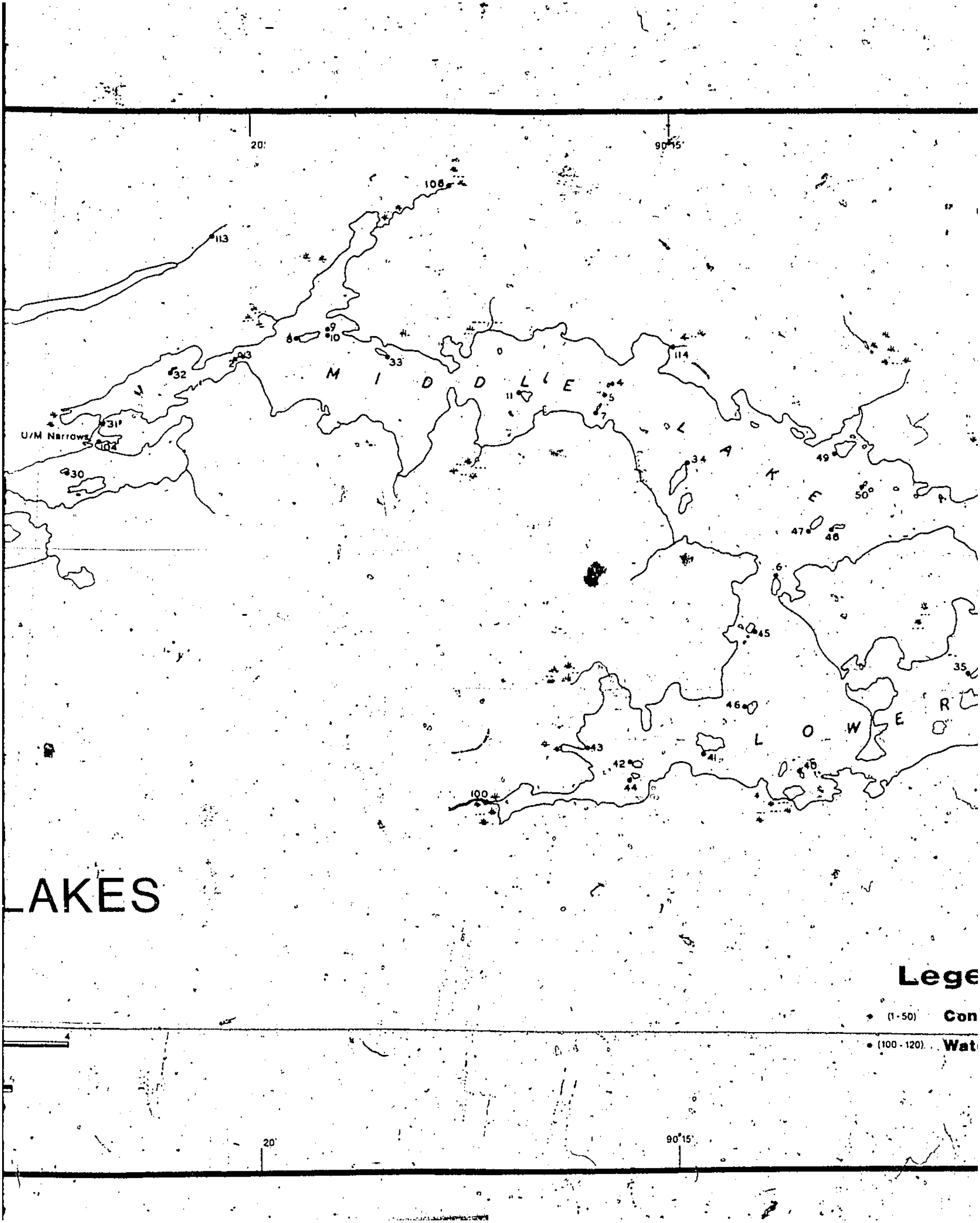
Concretion specimens brought in were placed in polythene lined paper bags and later air dried. Longitudinal traverses, whereby specimens were collected at regular intervals along the long axis of deposit, were made at five stations, and a cross traverse was additionally completed at one station.

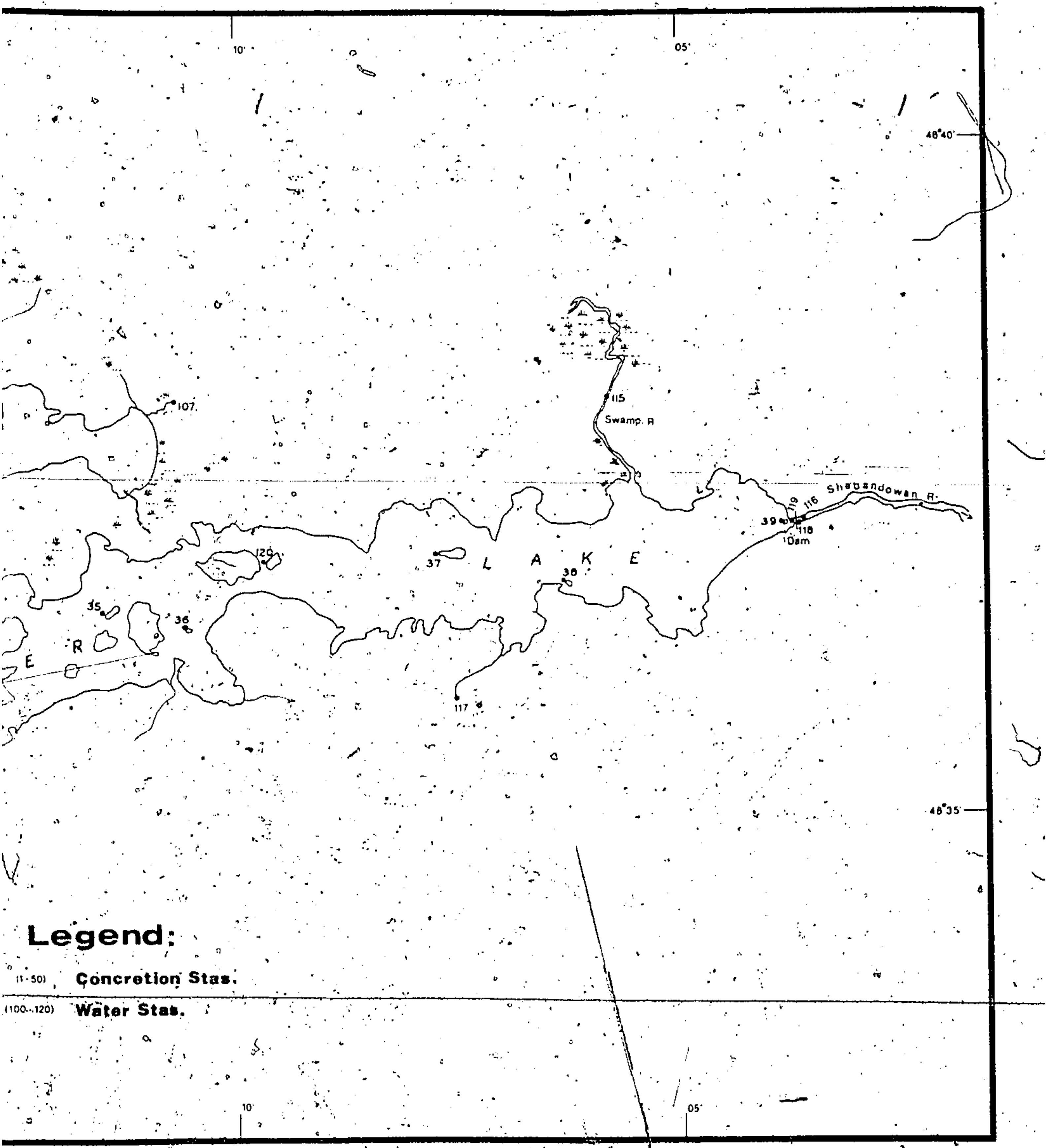


MAP 5

SHEBANDOWAN

ONT.


20'
90°15'
108
113
9
8
10
2
3
33
32
M I D D L E
L A K E
114
4
5
11
7
U/M Narrows
31
104
30
34
49
50
47
48
6
45
35
46
L O W E R
43
42
41
40
44
100
LAKES
Lege
(1-50) Con
(100-120) Wat
20'
90°15'

10'
05'
48°40'
48°35'
107
115
Swamp. R
Shebandowan R.
119
116
39
118
Dam
120
37
L A K E
38
35
36
E
R
117
10'
05'
Legend:
(1-50) Concretion Stas.
(100-120) Water Stas.

Bottom water samples were collected in clean 1-litre plastic bottles and acidified with a few drops of HNO_3. Sediment cores were retrieved in 2-inch diameter plastic tubing, drained, cut to size, sealed at both ends and kept frozen on return to camp.

Running water from 16 influent streams was also sampled. Where possible, the water was collected from the central part of the stream channel, about 1 foot below the surface. In addition, three water specimens were taken at the outlet of the Lakes, one just above the dam and two below All water sampling sites, other than those coincident with concretion sites, bear the numbers 100 to 120 on Map 5.

CONCRETIONS

Physical features of deposits

While perhaps only a fraction of the existing Shebandowan deposits was located in the course of the field survey, they were found in every lake sub-basin (Map 5 and Fig. 4). They occur at depths estimated at 6 to 40 feet, essentially in littoral areas. Some of the station depth estimates appear to have been inflated, especially in the U Upper basin, where several estimates exceed the maximum depths indicated in the bathymetric survey. No exploration was done below 60 feet, which was the diver's limit.

The concretion deposits occur commonly along the sides and point extensions of islands or in isolated shoals. They do not seem to favour particular geographic situations or orientation and usually occur within a vertical range of 5 feet, with a maximum relief of 30 feet estimated at Station 8. Most frequently the long axes of deposits are isobathic, paralleling adjoining shore outlines, but occasionally, as at Stations 8 and 34, they plunge on the extension of an island or headland. The size of deposits vary from a few concretions to fields 600 feet long (Sta. 5) and up to 40 feet wide. Population per unit area is usually greater in larger deposits.

For the most part, the sediment underlying concretions is sand interspersed with coarser fractions. An exception was found throughout the U Upper basin, where rock debris of gravel to cobble fraction, often in shingle-like aggregates of chlorite schist fragments, commonly comprises the supporting surface. In fact no sediment core could be sampled there with the 2-inch plastic tubing available for the purpose. Nowhere did dark organic silt form the concretion substrate, although several deposits were observed to terminate at the sand-silt line, whose depth was variable.

Aquatic vegetation associated with the deposits ranged from unidentified emergent mycrophytes, rooted near the sand-silt line, to small growths implanted on either or both the uppersides and undersides of the oxidate crusts and their nuclei. Examination of specimens has revealed small sponges, algae and fungi attached to the oxide surfaces, occasionally on the undersides (Pl. IV). A short-cropped dark green moss-like alga (?) was the most common observed rooted growth, found particularly on upper sides of mushroom and top ring type concretions. Virtually all specimen upper sides were littered with phytoplankton debris - principally segmented stalks of diatoms, but also filaments and membranes, presumably also of organic origin.

Physical aspects of concretions

Although many colourful terms have been used in the literature (Naumann 1930, Ljunggren 1953, Strakhov 1966, and Terasmae 1971) to describe morphologies of lake concretions,

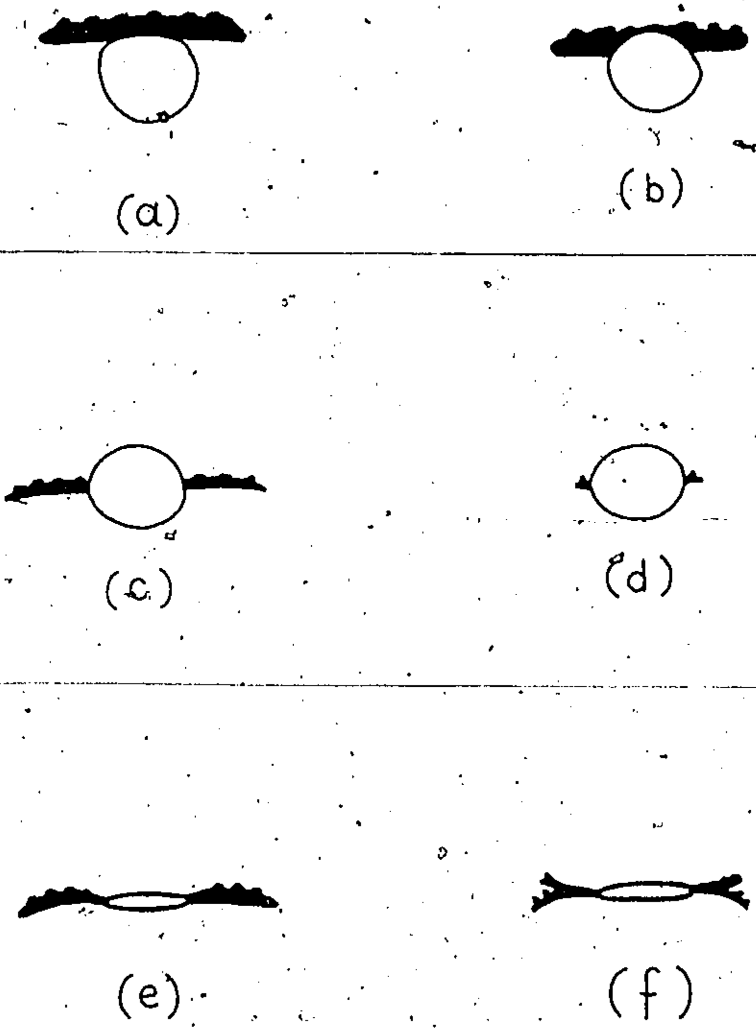


Fig. 2. Schematic vertical cross-sections of common morphological variants of concentric concretions: a) mushroom, b) top ring, c) saturnine, d) equatorial skirt, e) disc or concave-down saucer, f) doubly-concave, hourglass section.

all are probably variants of one of: a) spherical to lumpy nodules and micronodules forming in or atop the sediment; b) ring or discoid concretions, developing at the sediment-water interface; and c) pavement-type deposits representing coalescence of either a) or b).

All concretions found in Shebandowan Lakes, with possibly one exception, are of b) type, developing just above and parallel to the sediment surface. The nucleus is a pebble broken concretion fragment, or sand.

The extent of concentric growth is extremely variable within a given deposit, suggesting the existence of different ages within a population group or different rates of growth. U Upper basin deposits showed as a whole poorest concretion development.

The diameter of the nucleus in the plane of the ring growth seldom exceeds 10 cm in well developed concretions although thin oxide rings have been observed on boulders. A vast majority of concretions have a total ring diameter, oxide plus seed, of 10 cm or less; within this range the oxide portion is often considerably greater than the nucleus. The oxide is seldom more than 5 mm thick, and averages perhaps 2 mm, except where ridging develops (Fig. 2f) along the leading edges, and occasionally when considerable vertical accretion results from probable progressive rising of the nucleus above the sediment with concomitant elutriation of

Legend: Plates I-III

T - top view

S - upright side view

B - bottom view

Where two or more views of a concretion are shown, S represents 90°-up rotation of the lower edge of T; B is a 180° rotation of T commenced by raising the left edge.

PLATE I

1. Large discoid concretion showing concentric banding. Note downcurl and upperside ridge in side view, with small botryoides on upper side of the downcurl.

2. Equatorial skirt, giving rise to a saturnine aspect. The oxide extends upward through 2 cm, growing sideward in several fronts. Unusually deep down-concavity and height are probably due to progressive emergence of the granitic nucleus in sand. A small rock fragment is partly engulfed by the bottom oxide rim.

3. A "pulley" peppered with oxide globuli in the angle between the active edges. Both top and bottom portions inside these edges have a smeared appearance, probably due to partial re-solution.

4. Polygonal fracturing and veining in the nucleus, an old concretion fragment.

5. Well developed fracturing and healing by oxide material along radial and concentric directions. The veins stand out in relief by as much as 1 mm, suggesting partial dissolution of the concretion, evidently more soluble than the injected material. The veins stop at the active edge, although fracturing does not, implying growth at the edge subsequent to veining. A granitic pebble nucleus.

6. Underside of a concave-down concretion developed about an old concretion fragment.

PLATE I

the substrate (Pl. III-I). As described elsewhere (Manheim 1965, Troup 1969, Terasmae 1971) the nucleus above and below the plane of concretion growth is usually free of oxide film. There is evidence that partial dissolution of concretions, due to periodic lowering of redox potentials above and continuing redox potential deficiency below tends to maintain a thin oxide growth parallel to the interface. Exceptions to this, particularly on the uppersides, are noted below. Typically, the concretions exhibit a concave-down growth habit, ~~with~~ down-curling of the oxide edges (Pl. I-1, 2,6; Fig. 2e). This is probably illustrative of the tendency to feed on the substrate, but progressive downward growth at the edges may require winnowing of the sediment by bottom currents to maintain the rims of concretions at the sediment surface.

Most discoid specimens exhibit a flat initial growth habit with subsequent gentle curling down to the extent of up to 1-2 cm with respect to the upright axis. The nature of the growths is manifested by the development of concentric relief on both top and bottom sides (Pl. I-1) which gave rise in the past to comparison of concretions with dried apricots and excrement of cattle (Moore 1910, Ells 1898). The relief is usually better preserved on the uppersides, whereas the bottomside is often blurred, smoothed, or ropy (compare Pl. III-2b and -2t), possibly due to partial dissolution. A single upperside concentric ridge is frequently strongly developed and, if present near the edge, may, in conjunction with the downcurl, give rise to pulley type structure (Pls. I-3, II-3; Fig. 2f). The upperside ridge is often steep and inward relative to the downcurl (Pl. III-2T), therefore hatlike in side-upright view. Both the downcurl and the upperside ridge may represent active growth edges, drawing on material supply from interstitial and overlying water respectively as judged from their different orientation. The advancing fronts are normally thicker than inner oxide ridges (rarely more than 2 mm thick), suggesting that partial dissolution occurs or that shrinking accompanies the ageing process.

The typical mammillary growth habit of the colloidal Fe-Mn oxides/hydroxides becomes evident on close inspection. The active fronts appear under the microscope as a loose meshwork of tiny globules. The presence of larger botryoides, usually of a diameter less than 1 mm, to the side, i.e., in the angle between the downcurl and upperside ridge of pulley-type concretions (Pls. I-3, II-3), suggests coalescence in time of small to larger globules. Original structures, however, seem to be blurred or obliterated by solution, as observed in the generally smooth inner banding (Pl. I-1) on both top and bottom surfaces. Exception is often found on the uppersides (Pl. III-2T) where much of the surface,

PLATE II

1. Slaglike concretion, one of a number found only in Station 8, an intergranular cementation by Fe-Mn oxides of in situ eroded hunks of sand. The presence of rounded holes and arcuate sculpturing of lump surfaces testifies to powerful or prolonged bottom current action at a depth of about 20 feet below the lake surface.

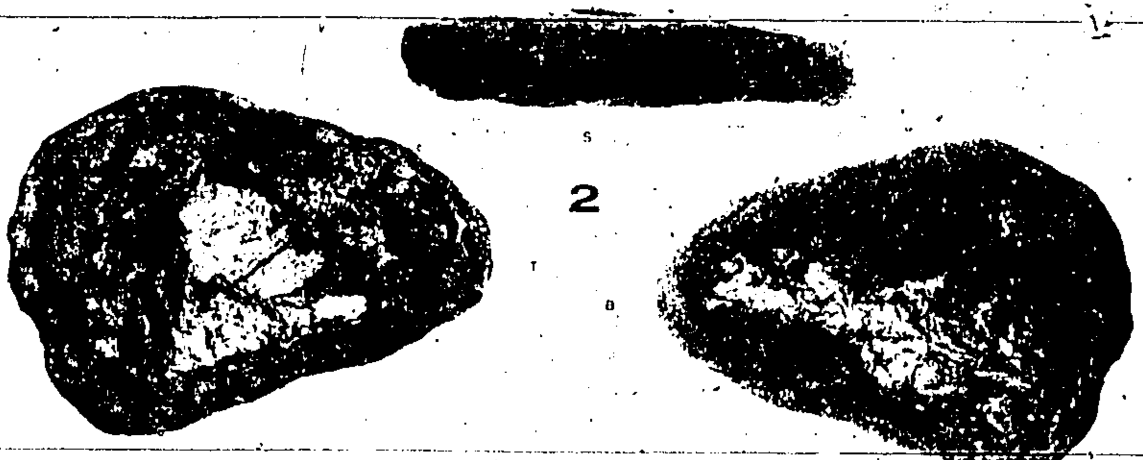
2. Wedge-shaped granitic cobble encrusted evenly on top and bottom by botryoidal oxides, one of the enigmatic specimens from Station 1 showing little evidence of re-solution on either side, with apparently active oxide growth in all directions.

3. Pulley type concretion.

4. A "mushroom" from Station 9, formed at the apex of a gabbroic cobble, shows heavy development of botryoides on the upper surface, but smoothed and ropy underside, without downcurl. The cap is up to 6 mm thick, considerably thicker than the central discoid portion of No. 3. The mushroom cap is thought to have accreted largely upward into the water, which probably supplied most of the Fe and Mn.

PLATE II

1



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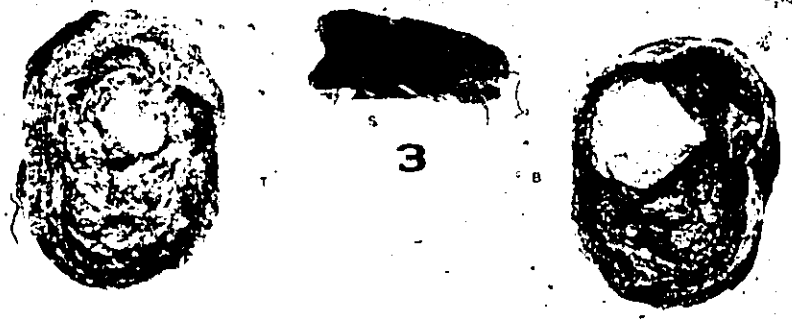

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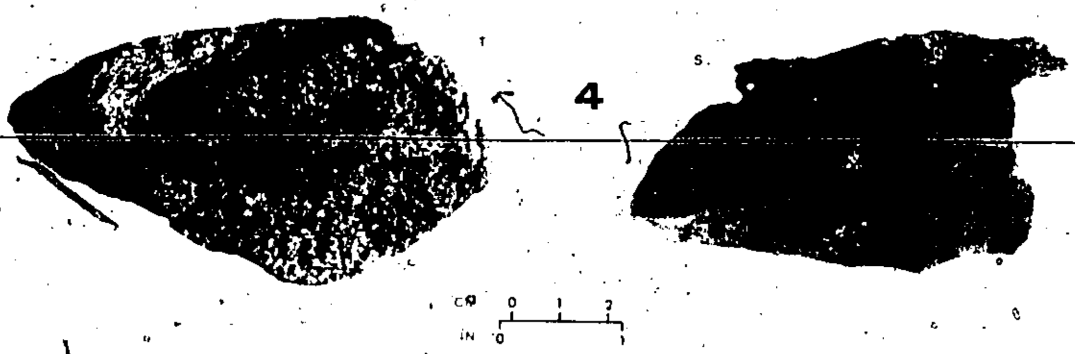


4

especially on the outside of the main ridges, is peppered with globules. This exception becomes a rule in the case of mushroom and top ring morphologies (Fig. 2a, b; Pls. II-4, III-4) in which the presence of thick botryoidal hemispheres individually as much as 3 mm thick on the uppersides, is distinctively countered by smooth, ropy, underside textures. Downcurl is commonly absent. The crusts on these concretions are thickened accordingly. The presence of botryoides on upperside surfaces may suggest supply of Fe and Mn from superjacent water. Explanation of the high proportion of material supply by bottom rather than interstitial water to the mushroom and top ring, as opposed to the equatorial or bottom ring concretions, could well be found in the differing sizes and cross-sectional shapes of the nuclei relative to sediment-water interface (Fig. 2). The mushrooms develop around the apices of large pebbles or cobbles (and populate the shallowest portions of deposits since they constitute the coarsest fraction of littoral sediments). Most upward-diffusing ions could conveivably be deflected at the equatorial portion of the mushroom and top ring concretion seeds and oxidized and precipitated in the flanking top sediment (Fig. 2a, b). In case of the other concretions (whose nuclei are immersed above their "equator" in the sediment) concentration would actually be enhanced at the nuclei edges (2c, d, e, f). The absence of apparent upperside dissolution in top rings and mushrooms is undoubtedly a consequence of their occurrence in the shallowest zone of deposits where high Eh-pH is promoted by abundance of dissolved atmospheric oxygen and photosynthetic activity.

In Shebandowan, the presence of botryoides on the lower concretion surfaces (Pls. II-2, IV) although rarely observed, indicates that similar growths occur on the undersides of the concretion as occur above. Their restricted occurrence, however, and the presence instead of smeared or ropy concentric structures is probably due to partial dissolution of previously precipitated oxide at contact with the reducing substrate.

Several specimens, dredged up from stations 1 and 5 consisted of unusually (up to 1 cm and more) thick and fresh-looking crusts with botryoids strongly developed on all surfaces. While essentially flat and concentric like other concretions, these had small overgrown nuclei, or, at times, no palpable seeds. Unlike concretions hitherto described they exhibited no effects of partial dissolution, indicating highly oxidizing conditions throughout their depositional history (Pl. IV). Unfortunately, their microenvironment was not studied to determine in what way it differed from that of the associated common concretions in the same deposit. It appears that they have formed at a rapid rate very recently, under special very localized conditions that have by-passed their nearby, more ordinary, neighbours.

Fracturing and consequent veining by oxide material is a common feature of concretions (Pls. I-3,4,5,6; II-3; III-2,3). The main sets are, in order of frequency of occurrence, radial, concentric, and polygonal. The fractures are usually hairline, and, if radial, often extend to the edges without apparent widening. Veining almost invariably stands out in relief, as much as 1 mm, but does not extend to the "active" upperside and downcurl edges, even if the fracturing does. This is taken as evidence that weathering, probably dissolution, has occurred once or periodically. The vein material, which stands out, much as quartz veins do in weathered outcrops of carbonate rock, is presumably more resistant to dissolution because of its greater compositional purity than that of the main concretion oxide aggregate, or because of its higher Fe content. Veining has not been observed in fresh and heavily botryoidal surfaces, such as uppersides of mushroom and top ring concretions. Fracturing, being a feature of concretions thinned by dissolution, may well be a major factor in their eventual destruction.

Peculiar, slaglike concretions (Pl. II-1) made up part of the field in Station 8 which contained also the more common discoid and mushroom types, the former on the downslope and the latter on the upslope. These specimens

PLATE III

1. Oxide growth, having a composite height of nearly 3 cm, showing multi-decker ring development, probably due to a progressive rise of the granitic nucleus in sand. Note the globuli-ridden upperside contrasting with a ropy, dissolved, underside. Concretion comes from Station 39, the shallowest deposit, occurring at depths estimated at 6-9 feet.

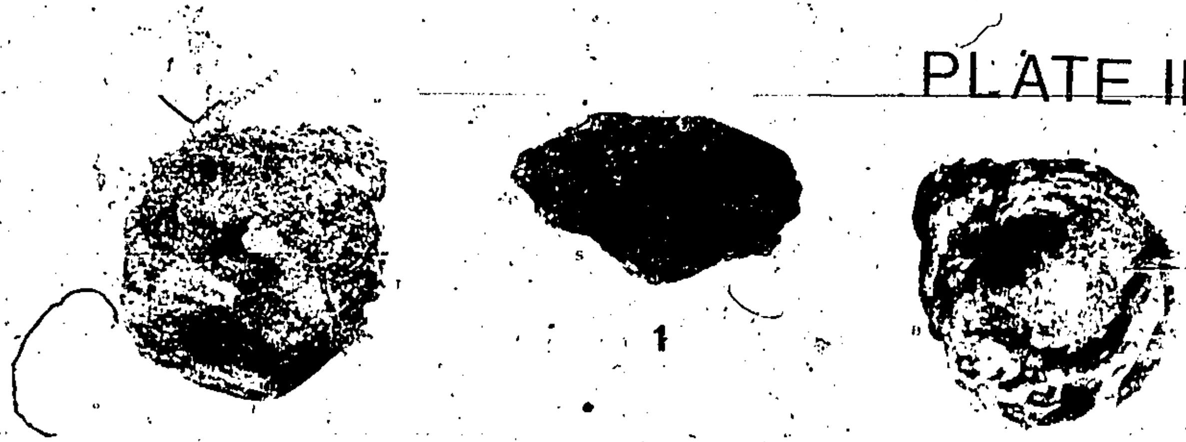
2. A large hat-like concretion, with the upperside ridge located considerably inward relative to the downcurl (c.f. pulley, Pl. II-3). The presence of globuli throughout the upper surface is not common and possibly suggests a "reactivation" of the central portion.

3. Apparently separate concretions of similar size stuck together after gliding one upon the other; but possibly a single concretion with asymmetrical development of upper and lower folds.

4. Top-ring concretion - oblique topside view. The dark, nearly upright line on the cobble represents a trace of a former equatorial ring, obliterated in the reducing substrate after the cobble was turned about 90° in the sand.

5. Equatorial skirt superimposed on a top ring following an upward adjustment of the cobble's position in the substrate.

PLATE III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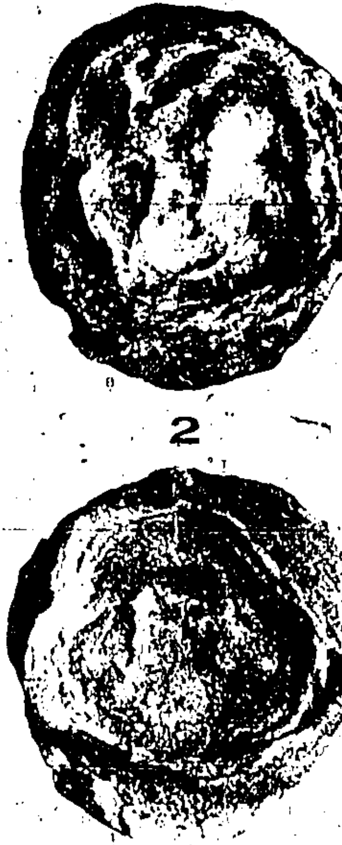
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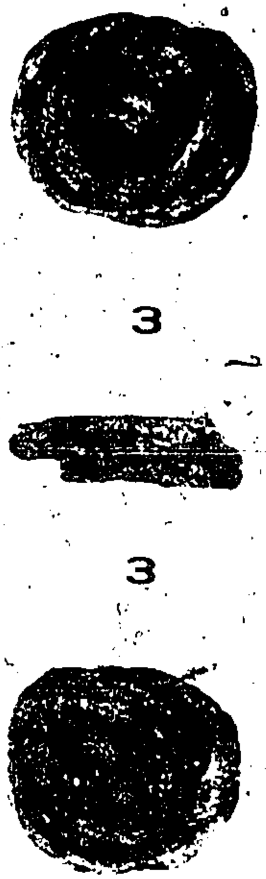
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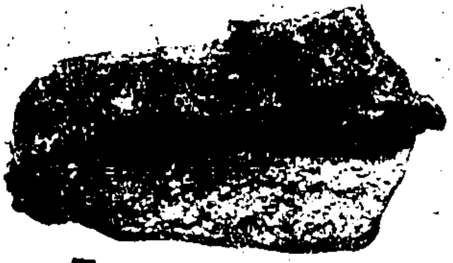
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consist of apparently subaerially eroded chunks of in situ hardpan sand, probably glacially deposited, which have been permeated and cemented by the Fe-Mn oxides through a vertical height of several centimetres. The degree of penetration of the oxides has been somewhat variable resulting in a splotchy distribution. The unusually large vertical reach of the oxides in these lumps is probably due to the high permeability of the sandy seeds. Alternatively, this vertical thickness could be explained by gradual accretion from the top down accompanied by winnowing of the supporting sediment. The highest anomalous values in Ca, K, Mg and Co, Ni and Cu of all the Shebandowan concretion analyses was obtained in one of these specimens (TR 8-12, Table VI), which may possibly be due to their relative old age.

In summary, the common Shebandowan discoid concretions grow concentrically at the sediment-water interface. They tend to bifurcate radially, probably illustrative of both interstitial and superjacent water sources, with somewhat larger material supply from interstitial than overlying water. In most cases undersides of concretions exhibit partial dissolution on contact with a reducing substrate. Partial recurring dissolution, due to changing Eh-pH conditions, also takes place on the uppersides accounting for the discoid morphology and limiting thickness of concretions.

Mushroom and top ring types form thicker growths due to high-proportion accretion from above, which is relatively unchecked by upperside dissolution in their shallow, high Eh-pH environment. Radial, concentric and polygonal fracturing and cementation by oxide material is a common feature. Thinning by dissolution combined with fracturing may be responsible for a limit to the size concretions can attain without suffering destruction.

Mineralogy of Concretions

Several crystalline phases have been identified in lacustrine concretions. Ljunggren's (1955b) X-ray diffraction studies of western Swedish ores suggested the presence of goethite (α-FeOOH) and the closely related minerals, birnessite (δ-MnO_2) and manganous manganite. X-ray work has also disclosed the presence of goethite and birnessite in nodules from Lake George, N.Y. (Schoettle and Friedman 1971), and of goethite from Kawagama Lake, Ont. (Terasmae 1971). However in numerous reported cases X-ray diffraction failed to resolve any crystalline phases in crusts, suggesting the presence of amorphous minerals or ultrafine crystal particles.

Among minerals reportedly identified in nodules and micronodules of the Karelian Lake Punnus-Yarvi were the following: hydroferrichlorite, hydrogoethite, vivianite psilomelane-wad (Shterenberg et al., 1970). In Eningi-Lampi Lake of the same region, Varentsov (1972) found birnessite, goethite, hydrogoethite and amorphous hydroxides of Fe in nodules and crusts.

Several powdered Shebandowan concretion samples were subjected to spectroscopic investigations by Mössbauer, X-ray diffraction and electron spin resonance techniques. The Mössbauer experiment showed the presence of two or more ferric oxhydroxide phases in the three samples studied, and in one of these the occurrence of goethite in microcrystalline particles. The presence of goethite but not of common manganese minerals in three samples was indicated by the X-ray diffraction method. ESR spectra of two samples disclosed broad absorption curves with nearly identical g values of 2.97 and 2.90; this was interpreted as due to Fe (III) in similar crystal fields (Prof. A. Manoogian, pers. comm.), but no identification was possible.

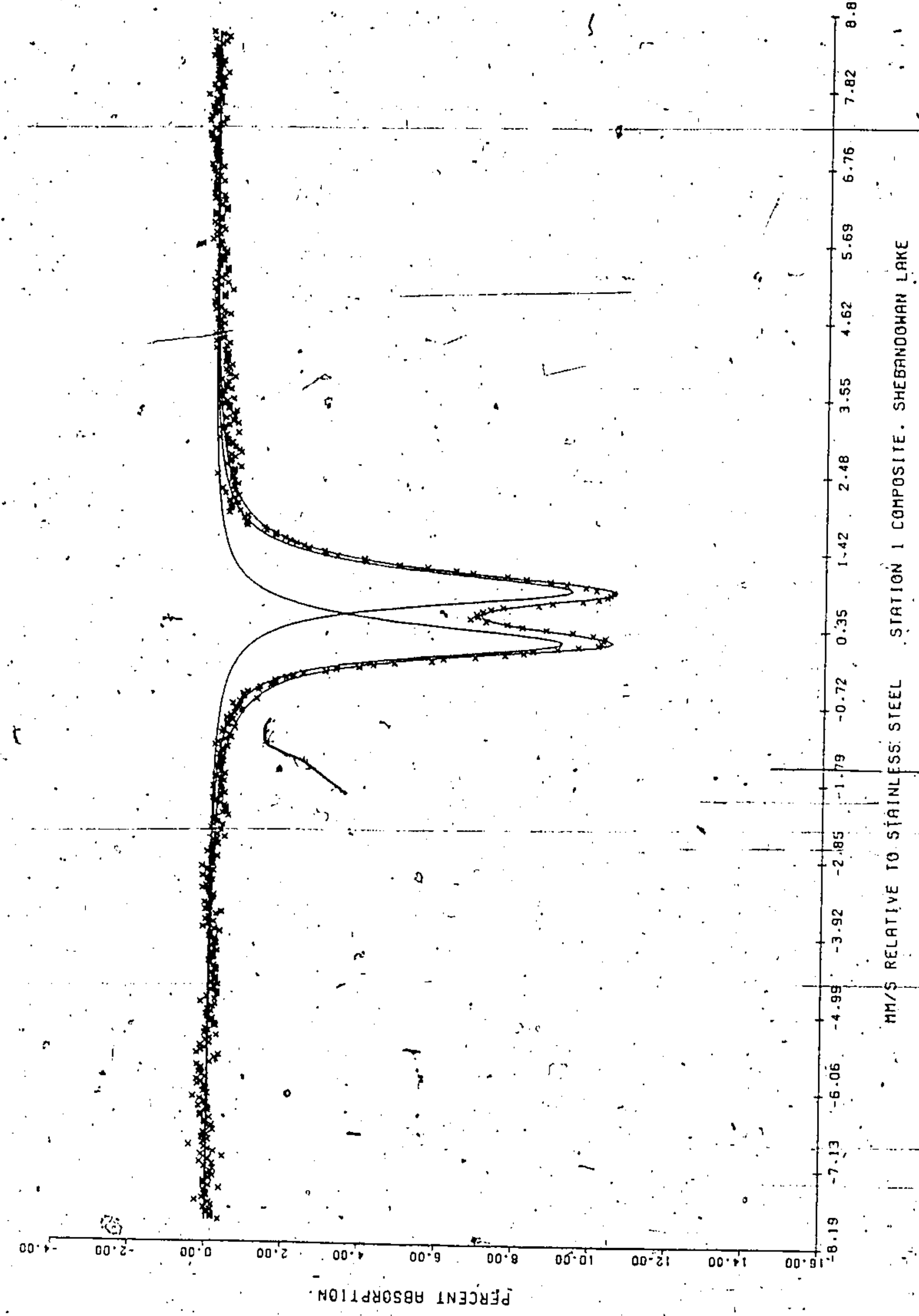
The results of the Mössbauer and X-ray diffraction experiments are detailed below.

Mössbauer Spectra

The Mössbauer effect is a particularly useful technique for obtaining data on the chemical form, structure and particle size of iron in microcrystalline particles, such as usually make up Fe-Mn concretions. This information can be gained even when methods of X-ray diffraction fail. Marine nodules have been studied with the use of the Mössbauer technique by Gager (1968), Johnson and Glasby (1969), Hrynkiewicz et al. (1970), Herzenberg (1969), Burns and Brown (1972) and Carpenter and Wakeham (1973). The latter authors also studied lake concretions, including a Shebandowan specimen, in their work. In all cases nearly identical quadrupole doublet spectra, like the upper two in Fig. 6, were obtained, suggesting the presence of a mixture of ferric oxyhydroxides in paramagnetic or superparamagnetic phases.

Since several Fe (III) oxide minerals have isomer shifts close to the observed shifts of nodules, an unambiguous identification of the iron minerals was not possible. Johnson and Glasby (1969) suggested that the iron oxide phase of nodules may be present as a mixture of α-FeOOH (goethite) and γ-FeOOH (lepidocrocite) but that other mixtures of Fe and Mn oxides may also account for the spectrum. This conclusion was criticized by Herzenberg and Riley (1969) and Hrynkiewicz et al., (1970) who suggested instead the presence of hydrated iron oxide gels as the causative source.

Mössbauer spectra of composite concretion samples from stations 1, 4 and 39 were obtained in room temperature runs, using the facilities of Mines Branch, Department of Energy, Mines and Resources in Ottawa. The spectra are shown in Fig. 6. Those of Sta 1 and 4 are similar quadrupole


MM/S RELATIVE TO STAINLESS STEEL
STATION 1 COMPOSITE. SHEBANDOWAN LAKE
PERCENT ABSORPTION
-8.19
-7.13
-6.06
-4.99
-3.92
-2.85
-1.79
-0.72
0.35
1.42
2.48
3.55
4.62
5.69
6.76
7.82
8.89
-4.00
-2.00
0.00
2.00
4.00
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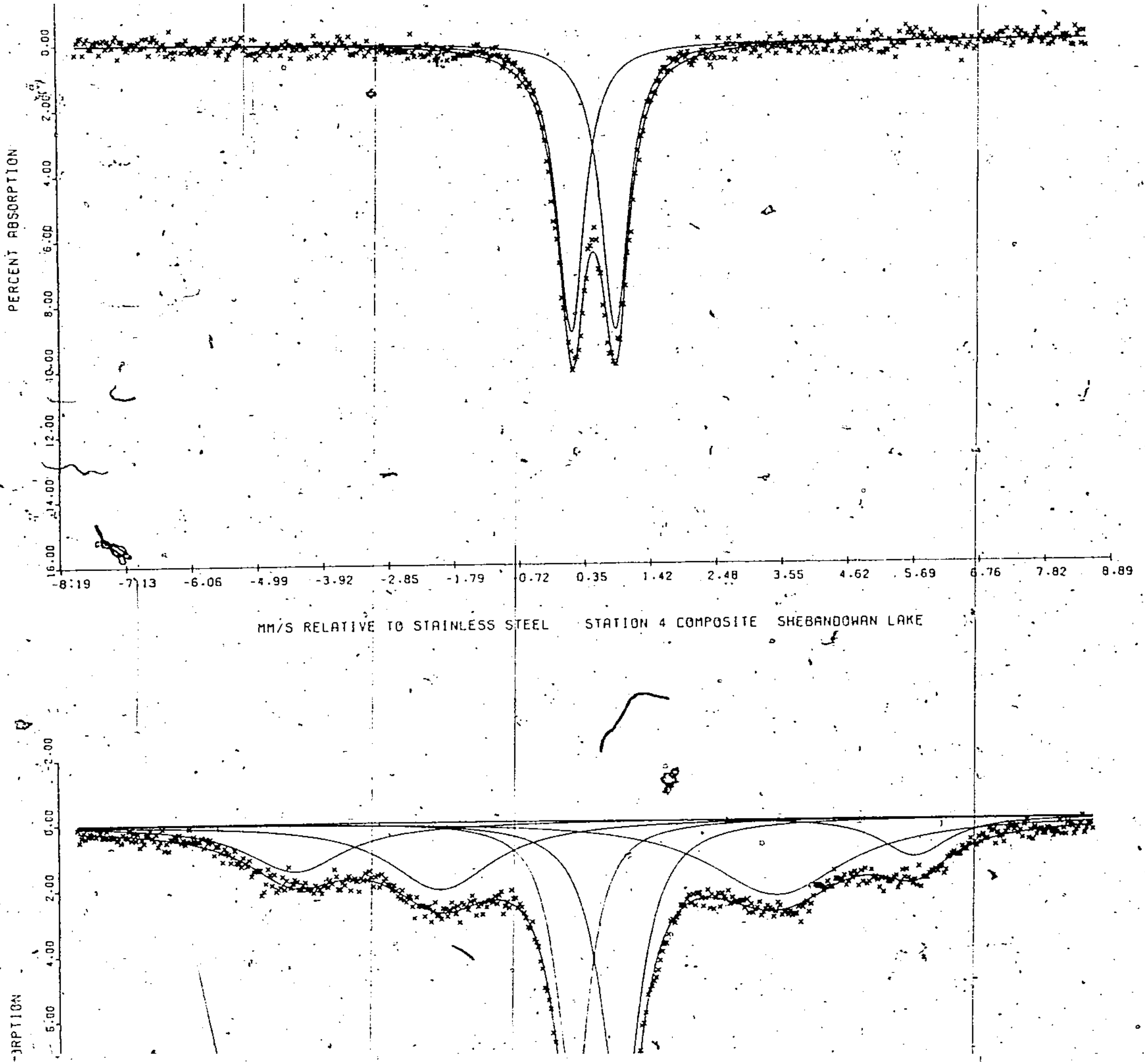
8.00
10.00
12.00
14.00
16.00

1 of


PERCENT ABSORPTION
0.00
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-6.06
-4.99
-3.92
-2.85
-1.79
-0.72
0.35
1.42
2.48
3.55
4.62
5.69
6.76
7.82
8.89
MM/S RELATIVE TO STAINLESS STEEL
STATION 4 COMPOSITE SHEBANDOWAN LAKE
-2.00
0.00
2.00
4.00
6.00
-ORPTION

2 of

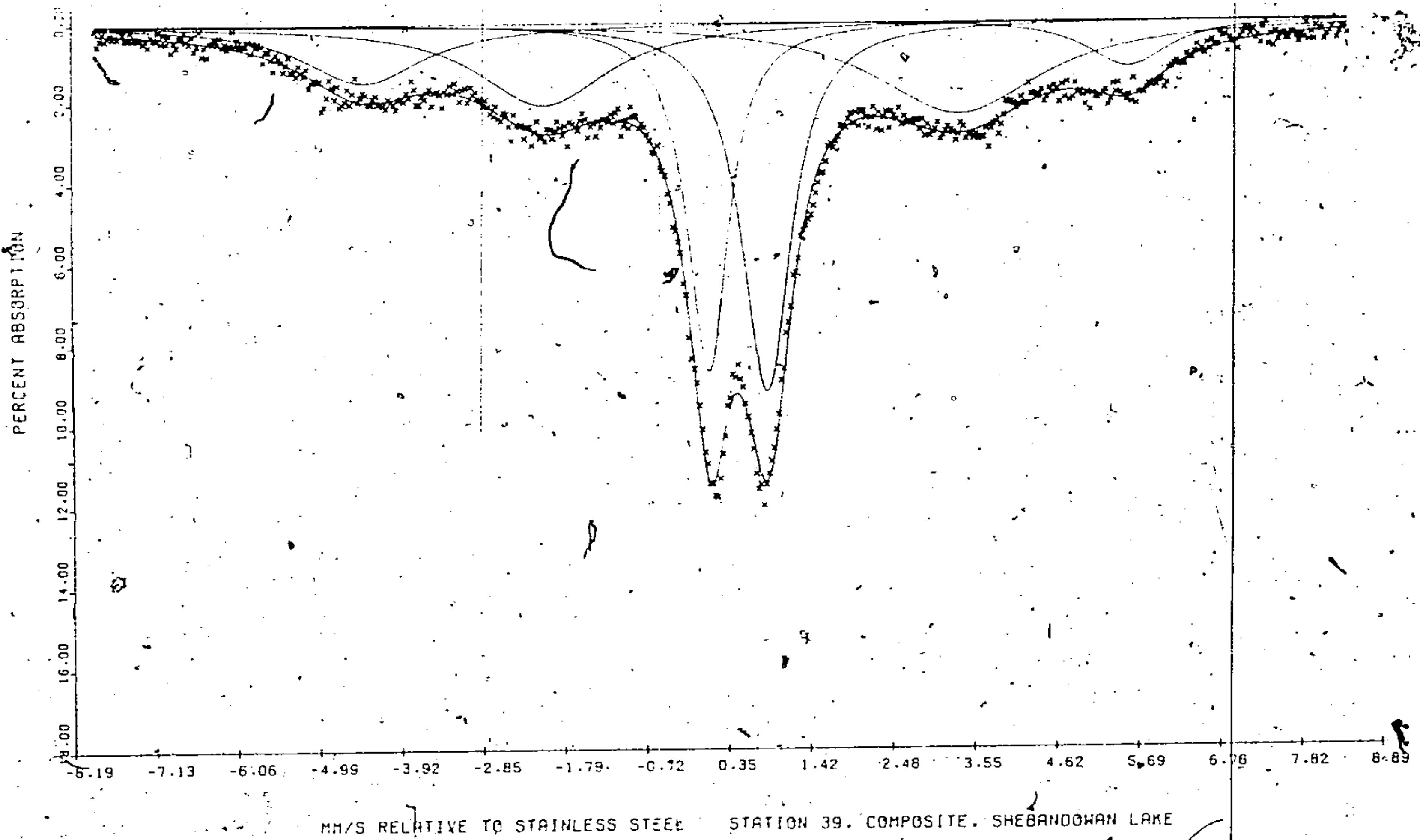

Fig. 3. Mossbauer Spectra of Three Shebandowan Station Composite Concretion Samples

3of3

doublets showing splitting of .72 and .71 mm/sec respectively, ~~with corresponding isomer shifts of 0.50 and 0.49~~ mm/sec, consistent with a high spin ferric compound. As was the case with previously studied marine nodules, these values do not fit the values of corresponding parameters in the known ferric oxyhydroxides. Therefore a combination of two or more minerals probably account for the spectra. These could include goethite (superparamagnetic), lepidocrocite (paramagnetic or superparamagnetic), or ferric oxide hydrate gels, but other ferric-bearing phases could also be present.

The spectrum of Sta 39 is different than any previously reported from ferromanganese nodules or concretions, although a similar pattern was obtained from a ferruginous Red Sea sediment (Herzenberg, 1969). Here a collapsing Zeeman structure of bulk goethite is clearly indicated, with contribution from other phase(s) modifying the central peaks. Comparison with experiments on pure synthetic α-FeOOH suggests a mean particle size of less than 200Å, probably in the range of 100 to 160Å (Van der Kraan and Van Leof 1966, and Shinjo 1966). In our natural sample, however, where purity of the goethite is not assured, substitution of Fe (III) by other ion(s) could cause the hyperfine field reduction in large particles. The population ratio in the Sta 39 sample of Fe (III) in goethite to Fe (III) in other phases cannot be estimated closely from peak intensities because of the irregularity of the hyperfine spectrum, but is probably more than 3 to 1. An equivalent portion of goethite to the sum of other ferric oxyhydroxide minerals in the sample can be inferred, assuming the spectrum to be almost entirely due to phases of essentially the same chemical composition. The internal field of goethite in the sample was found to be in the range of $3.0-3.12\times10^5$ oe by using Fe foil as a standard. This collapsing field value is expectedly less than 3.64×10^5 oe for the undisturbed hyperfine field. No detectable amounts of ferrous iron were indicated in any of the three Shebandowan spectra.

X-ray Diffraction Analysis

X-ray diffraction scanning, using Fe radiation, with Mn filter, was carried out on both whole-sample powders and their acid-insoluble residues from Stas 23, 39 and 40 and TR 8-12. The work was done by Mr. C. de la Fuente, technician at the Department of Geology, University of Ottawa.

The prime objective of these tests was to determine whether or not the high anomalous trace metal values obtained in chemical analyses of TR 8-12 and Sta 40 could be attributed to adsorption by clay minerals present in unusually high amounts. The method however failed to discern any specific clay minerals.

In addition, the X.R.D. patterns were perused for peaks of some common Fe and Mn oxide and oxyhydroxide minerals. Of these, only goethite (α-FeOOH) peaks were positively identified in whole-samples of Stas 23, 39 and 40, but not of TR 8-12. No reflections were observed from such minerals as birnessite or todorokite. The corroboration of the Mossbauer result on Sta 39 is interesting. The Mossbauer spectrum had indicated the presence of goethite in particles of ultrafine mean size, such as would not be expected to be recorded by X-ray diffraction. It is therefore assumed that a wide range of goethite size components make up the average in the powdered sample, including particles large enough to be discerned by the X-ray method.

No attempt was made to identify minerals responsible for the numerous other peaks recorded. Some of the highest-intensity profiles were due to quartz, strongly evident in all but the spectrum of Sta 23 whole-sample. Grains of detritals, often monomineralic, especially of quartz and feldspars, are commonly found engulfed in the oxide growths.

Concretion Analyses

Air dried concretions were cleaned of loosely attached sand particles and other foreign material. The oxidate growths were detached from nuclei and ground in porcelain pestle and mortar. Four concretions were used to make up each composite station sample and single concretions to make up traverse samples. Approximately 0.5 g portions were weighed out for analysis. These were digested in hot 50% HCl. The insoluble fraction was filtered off and the residue weighed after the filter was burned (for 15 minutes in a box furnace at 1,000°C). The soluble fraction was diluted to 1N. Analyses were made on a Techtron 4 atomic absorption unit which necessitated further dilution of some soluble fractions and of standards. Mn, Fe, Cu, Zn, Ni, Co and K were determined directly, while Ca and Mg were determined after addition of La. A total of 72 samples were analyzed, with each element calculated as percentage dry weight of the soluble fraction (Table VI). No determinations were made for Pb after three pilot analyses showed its content to be negligible. Ten samples were analyzed colorimetrically for their As content following digestion in $HNO_3 - HClO_4$, by Bondar-Clegg & Co. Ltd.

Replicate analyses of 69 samples gave precisions indicated in Table V. The precision is expressed as percentage of the mean at one standard deviation. The reliability of these analyses was further tested by computing ratios of data variance to analytical variance. At the 95% confidence level the analytical errors were found significantly smaller than the overall data variability using the method of Garrett (1969, 1973).

Table V. Precisions and significance of concretion analyses

	Fe	Mn	K	Ca	Mg	Cu	Zn	Ni	Co
Precision - % of mean at 1-sigma	2.3	3.5	10.2	7.3	9.3	7.4	4.8	7.3	5.7
Differences between variance ratios and Fisher's table value (1.492) at 95% level	6.1	176.5	29.7	12.0	14.5	37.0	20.7	10.7	10.3

Chemical Composition

Analyses of 72 Shebandowan concretions are presented in Table VI along with Fe/Mn ratios, means, maxima, minima and standard deviations of analyses. Average composition of stations weighted on per concretion basis and mean values for all 49 stations are also given.

The data show the concretions to be iron-rich with Fe content from 35.0 to 49.8%, having a mean value of 42.5%. Mn ranges from 1.36 to 12.7%, averaging 6.30%. Thus although Mn analyses vary by a factor of 9.3, compared to only 1.4 for Fe, the variances of the two elements are ~~nearly~~ equal. A plot of Fe versus Mn of all analyses is given in Fig. 5a. The largest maximum/minimum analytic ratios are for K and Mg, 23.1 and 17.0 respectively. These figures are lower for the remaining elements, the highest being 6.4 for Cu.

TABLE VI. Composition of the soluble fraction of oxidate portions of Shebandowan concretions (As and Insol. Residue expressed as fraction of the whole sample). Sta - refers to a composite sample of four concretions; Tr - identifies a traverse sample of a single concretion; first numbers identify stations.

Sample	Fe%	Mn%	Fe/Mn	K ppm	Ca%	Mg ppm	Cu ppm	Zn ppm	Ni ppm	Co ppm	Insol. %	As ppm
Sta. 1	41.7	9.03	4.62	478	0.559	1030	40	213	117	156	19.6	4
Tr. 1-36	44.3	7.34	6.04	279	0.558	740	31	283	132	125	6.9	
Tr. 1-41	40.5	9.07	4.46	437	0.657	1040	42	237	140	137	14.6	
Tr. 1-47	39.2	11.30	3.47	530	0.708	954	35	217	129	152	15.4	
Tr. 1-54	39.7	6.16	6.44	331	0.575	676	28	227	87	123	11.8	
Tr. 1-55	39.7	10.00	3.97	545	0.654	1300	36	191	119	139	23.9	
Tr. 1-61	39.9	9.20	4.34	389	0.717	1380	35	246	138	148	24.7	
Tr. 1-69	38.3	10.20	3.75	460	0.714	1010	35	213	104	140	15.4	
Tr. 1-74	42.0	7.78	5.40	320	0.653	947	34	230	131	113	8.6	
Sta. 2	41.9	8.03	5.22	319	0.556	586	37	273	122	117	12.4	
Sta. 3	35.6	12.70	2.80	449	0.856	1220	58	295	177	149	17.9	
Sta. 4	40.8	6.76	6.04	260	0.730	780	34	207	93	82	16.3	
Tr. 5- 1	35.5	11.90	2.98	444	0.856	930	55	275	164	98	12.0	
Tr. 5- 4	42.5	5.47	7.77	208	0.591	627	31	185	113	84	8.6	
Tr. 5- 7	38.8	9.52	4.08	347	0.727	727	39	204	146	131	11.9	
Tr. 5-10	38.8	9.74	3.98	360	0.676	747	38	195	130	112	10.2	
Sta. 6	40.5	7.31	5.54	245	0.613	749	37	205	108	122	12.3	
Sta. 7	44.2	5.16	8.57	204	0.545	578	29	179	89	87	13.2	8
Sta. 8	40.8	8.42	4.85	314	0.610	918	40	253	135	99	15.4	8
Tr. 8-11	35.0	11.30	3.10	369	0.805	1030	52	244	171	128	20.9	
Tr. 8-12	38.5	10.30	3.74	1040	1.350	5470	91	280	172	276	70.8	
Tr. 8-13	44.4	5.88	7.55	223	0.684	898	43	222	113	133	[illegible]	
Tr. 8-14	42.9	7.50	5.72	237	0.507	689	32	324	120	101	4.3	
Sta. 9	41.1	8.97	4.58	281	0.675	717	33	340	138	109	3.6	
Sta. 10	41.9	8.32	5.04	289	0.541	611	37	233	119	79	10.6	
Sta. 11	42.1	7.40	5.69	273	0.553	594	30	216	123	83	7.0	
Sta. 12	46.2	2.37	19.49	88	0.493	757	28	349	82	80	8.4	
Sta. 13	42.8	5.07	8.44	126	0.600	678	32	386	81	107	5.6	
Sta. 14	46.4	1.45	32.00	47	0.489	376	20	257	60	67	2.8	
Sta. 15	46.0	1.87	24.60	54	0.315	401	23	318	65	68	2.7	
Sta. 16	46.1	1.54	29.94	62	0.377	589	24	320	80	73	8.0	6
Sta. 17	44.6	2.98	14.97	72	0.403	480	25	317	94	88	2.4	
Sta. 18	47.3	1.95	24.26	84	0.482	595	23	334	57	73	3.7	
Sta. 19	43.5	4.29	10.14	110	[illegible]	636	33	471	73	99	2.5	
Sta. 20	49.8	1.49	33.42	45	0.310	504	34	349	71	69	[illegible]	
Sta. 21	43.6	3.65	11.95	115	0.550	1330	31	[illegible]	76	97	13.1	
Sta. 22	45.4	3.87	11.73	97	0.414	552	29	353	98	101	5.2	
Sta. 23	46.6	4.05	11.51	107	0.378	493	21	287	88	101	3.9	6
Sta. 24	41.5	7.00	5.93	207	0.426	571	28	276	85	128	7.9	
Tr. 24- 1	47.7	2.31	20.65	78	0.289	364	26	235	74	83	8.7	
							21	241	81	113	6.5	

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Sta. 22	45.4	3.87	11.73	97	0.414	552	[illegible]	[illegible]	88	101	3.9	
Sta. 23	46.6	4.55	11.51	107	0.378	493	21	287	88	101	3.9	
Sta. 24	41.5	7.00	5.93	307	0.426	571	28	276	85	128	7.9	
Tr. 24- 1	47.7	2.31	20.65	78	0.289	364	26	235	74	83	8.7	
Tr. 24- 5	42.6	6.34	6.72	194	0.537	639	21	241	81	113	6.5	
Tr. 24- 9	42.2	7.31	5.77	215	0.535	622	28	229	105	112	11.2	
Tr. 24-14	37.6	10.50	3.58	359	0.566	785	30	211	97	108	11.3	
Sta. 25	41.7	8.10	5.15	193	0.577	774	28	330	100	106	7.3	
Sta. 26	44.6	5.17	8.63	165	0.340	453	22	396	94	119	8.7	
Sta. 27	44.4	5.08	6.74	130	0.395	486	27	243	88	92	8.1	
Tr. 27- 1	41.8	7.06	5.92	303	0.523	761	28	264	87	112	8.5	
Tr. 27- 2	43.8	3.93	11.15	164	0.571	736	20	202	71	83	12.3	
Tr. 27- 3	47.0	2.05	22.93	67	0.342	463	20	208	65	86	8.4	
Tr. 27- 4	49.8	2.66	18.22	78	0.294	321	23	321	78	82	8.1	
Sta. 28	43.1	6.41	6.72	186	0.460	517	35	332	108	99	[illegible]	
Sta. 29	39.4	9.00	4.38	380	0.618	943	40	268	99	114	[illegible]	35
Sta. 30	44.5	5.34	8.33	191	0.476	459	24	252	110	92	8.3	8
Sta. 31	45.5	2.90	15.69	104	0.337	479	26	236	87	96	9.9	
Sta. 32	43.7	4.67	9.35	173	0.425	444	20	203	79	103	8.4	
Sta. 33	45.0	3.39	13.27	138	0.460	518	23	279	90	82	10.0	
Sta. 34	41.4	7.71	5.37	244	0.637	739	38	209	125	95	8.8	
Sta. 35	43.2	4.33	9.98	172	0.399	532	25	235	103	98	5.7	
Sta. 37	46.2	1.95	23.69	88	0.398	490	23	227	73	106	8.0	
Sta. 38	45.0	2.86	15.73	115	0.454	496	26	253	98	129	4.2	
Sta. 39	47.9	1.36	35.22	59	0.297	504	25	227	84	108	6.7	13
Sta. 40	41.2	6.07	6.79	619	1.010	1480	128	246	118	109	33.1	5
Sta. 41	42.7	5.90	7.24	157	0.479	507	22	222	87	98	5.4	
Sta. 42	40.7	7.90	5.15	256	0.728	844	27	233	140	151	18.8	
Sta. 43	44.6	3.98	11.21	102	0.592	422	24	228	96	77	2.4	
Sta. 44	38.8	9.38	4.14	263	0.694	819	25	378	140	131	4.7	
Sta. 45	43.3	6.56	6.60	175	0.591	537	35	261	120	104	4.0	
Sta. 46	43.1	5.15	8.35	177	0.576	570	25	204	93	109	14.3	
Sta. 47	41.7	7.40	5.64	227	0.563	589	32	215	105	101	5.8	
Sta. 48	41.7	5.97	6.98	218	0.617	538	27	195	98	102	8.9	10
Sta. 49	38.6	9.18	4.20	318	0.736	867	22	217	100	123	4.5	
Sta. 50	38.5	9.15	4.21	257	0.586	721	27	301	120	130	4.2	
MEAN 72 ANALYSES-	42.5	6.30	6.76	24	0.563	768	33	[illegible]	105	109		
MAX.	49.8	12.70	35.22	1040	1.350	5470	128	471	172	276		
MIN.	35.0	1.36	2.80	45	0.289	321	20	179	57	67		
MAX/MIN.	1.4	9.3		23.1	4.7	17.0	6.4	2.6	3.0	4.1		
STD. DEV.	3.17	2.92		163.2	0.1723	615.2	15.6	59.0	27.2	29.7		
Sta. 1*	40.9	8.93	4.58	434	0.623	1010	36	225	121	142		
Sta. 5*	38.9	9.16	4.25	340	0.713	758	41	215	138	106		
Sta. [illegible]	40.5	8.58	4.72	391	0.723	1470	47	260	140	129		
Sta. 24*	42.0	6.81	6.17	209	0.454	587	27	253	87	116		
Sta. 27*	45.0	4.50	10.00	142	0.414	528	25	233	82	91		
All 49 Stations*	43.1	5.65	7.62	200	0.538	669	31	273	101	102		

* averaged using Sta composite and TR analyses on per concretion basis.

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Application of the Kolmogorov-Smirnov test for normality of distribution indicated that all elements were either normally or log-normally distributed, except Cu which was distinctly log-normal. However the inclusion of anomalous sample TR 8-12 in another test yielded some high skew values (Appendix IVa).

Anomalous values, those in excess of two standard deviations from the mean, were recorded for the elements analyzed (Appendix IV). Among anomalous samples, TR 8-12 and Sta 40 stand out. The two samples had the highest insoluble residue content, 78% and 33% respectively, of all samples. In the case of TR 8-12 this was due to the nature of the oxide coating, present as an intergranular pervasion of semi-consolidated sediment from which it could not be separated for analysis. Sta 40 consisted of pieces of the oxides unusually highly contaminated by core material-chipped off and bagged in the field, unlike other specimens which were preserved whole. The high residue content along with anomalous values in K, Ca and Cu being a common factor x-ray diffraction tests were run on both (whole and residue) samples to determine whether clay minerals, as possible large adsorbents of the metals, made up a large fraction. As described elsewhere the method used failed to give any indications of concretion clay mineralogy, and the problem remains unsolved.

Element Interrelationship

A correlation matrix based on all 72 Shebandowan concretion analyses is given below. The computer program used generated variation diagrams between all variables which were examined to check the validity of the numerical correlation, but are not included in the thesis.

Table VII. Correlation coefficients for elements in 72 Shebandowan concretion analyses

	Mn	K	Ca	Mg	Cu	Zn	Ni	Co	Depth*
Fe	-0.93	-0.74	-0.82	-0.40	-0.43	0.18	-0.75	-0.56	-0.37
Mn		0.78	0.72	0.40	0.42	-0.19	0.82	0.61	0.34
K			0.86	0.79	0.73	-0.24	0.72	0.80	0.28
Ca				0.76	0.74	-0.16	0.73	0.68	0.46
Mg					0.64	0.01	0.49	0.79	0.15
Cu						-0.02	0.54	0.47	0.23
Zn							-0.12	-0.07	-0.33
Ni								0.62	-0.37
Co									0.13

* Average estimated station depth used for all traverse and composite station samples.

At the 99% significance level iron is negatively and manganese positively correlated with all elements but zinc. Chave and Mackenzie (1961) have suggested that in a group of chemical analyses of sediments, the highest correlation coefficients between element concentrations would be between elements occurring in the same mineral. They however indicated that fluctuation in the concentration of one major constituent could produce correlations between mineralogically unrelated elements. Applying these criteria to the Shebandowan concretions it is clear that the elements have little or no association with phases of iron which acts as the single overwhelming diluent. Furthermore, fluctuations in the concentration of iron could account for positive relationship between the other elements whether or not they are mineralogically related (Cronan and Thomas, 1972). For these reasons doubt is cast on such apparently strong co-variances as indicated among the group: Mn, Mg, Ca, K, Ni and Co. Zinc is singularly independent; its strongest positive correlation, significant only at the 94% level, is with iron. This slight correlation is undoubtedly weighted by the high concentrations of Zn in the U Upper L deposits which are iron-rich. This is the only area where Zn is consistently high, probably due to local sources of the element and not to coherence with iron-rich phases of the concretions. Zinc's negative correlation with depth (Fig. 4) is likewise due to its abundance in the shallow U Upper L stations, while iron's antipathy with depth extends throughout the Lakes (Fig. 4).

In Lake Ontario oxide coatings Cronan and Thomas (1972) found covariance between Mg, Ca and K and a lesser association between these elements and Fe; however, all these elements were negatively correlated with Mn, which was the most variable major constituent. Ni, Co and Zn showed convariance with Mn, suggesting association with the manganese phases, yet Cu did not correlate with either Mn or Fe, but with both Ni and Zn. Generally, Ni and Co follow Mn in the Swedish and Norwegian lake ores and the latter element is further associated with Norwegian Zn and Cu (Ljunggren, 1955a). However, no correlation obtains between Co or Ni and Mn in the Finnish or English crusts (Gorham and Swaine, 1965). In fact the correlation tends to be negative between Mn and Cu, and Ni and Cu in the English Lake District concretions.

The Ni-Cu-Mn coherence is nearly universal in the abyssal oceanic nodules, but it breaks down in some continental borderland deposits occurring at the lip of stagnant basins, where Mn chiefly accrues diagenetically, by upward diffusion through sediments (Cronan, 1972b). Zn and ~~Co~~ follow Mn in deep Atlantic nodules, but in the deep Pacific and Indian Oceans Co follows Fe. In the deep Atlantic, as in Lake Ontario, positive relationship was found among Mg, Ca and K but not between these and Fe or Mn.

Cronan (1969) has indicated that inter-element relationships can be partly explained in terms of partitions between the various phases of the nodules. In deep sea deposits the major phases are the manganese minerals birnessite and todorokite, the hydrated iron oxide minerals and the detrital silicates. Electron microprobe tests and bulk chemical analyses of different mineralogical varieties of nodules have shown Ni and Cu to be associated with todorokite (Burns and Fuerstenau 1966, and Cronan and Tooms 1969), where they are thought to complete successfully for lattice space with Mn. Among the captives of the hydrated FeO OH phases are V and Ti, while Co may be associated with either Mn or Fe phases. Cr, a common resistate constituent, belongs naturally with the detritals.

Despite restrictions imposed on interpretation of correlation coefficients of elements in the Shebandowan concretions, it seems plausible to assume that Mn is followed by Cu, Ni and possibly Co. While Zn normally follows Mn in ferromanganese oxide concretions such an association may be masked in Shebandowan Lakes by an apparent negative correlation due probably to zinc's abundance in U Upper basin. Ca, Mg and K follow Mn but this may be due to dilution by Fe. Brunskill et al. (1971) found higher concentration of these elements in interstitial sediment water than lake water of Experimental Lakes, suggesting these cations are being released by the fine (reactive) fractions of micas and feldspars in exchange for H ion to form kaolinite.

Since only ten assays of As have been obtained no significant correlation can be assumed with any other element. The highest individual value, 35 ppm, is however associated with a concretion sample having the low Mn/Fe ratio of 4.4.

Variation in the element content between deposits

Fig. 4 illustrates variation in elemental concentration and other parameters along the Lakes system. Anomalous variations stand out, as do positive and negative correlations between the elements. Less striking but evident is the negative correlation between mean basin depths and the Fe/Mn ratios of the concretions. Thus iron-richest deposits occur in the shallow U Upper and L Lower basins, while relatively Mn-rich concretions come from the deeper L Upper, M&L Middle and U Lower basins. As explained later this is probably due to effects of variation in geochemical environment with mean basin depth. Zinc is consistently rich in U Upper basin concretion deposits, its concentration levelling ~~off~~ in concretions down the watercourse. This suggests the presence of zinc sources in Upper Lake. Of the four Southwest Bay deposits, in the vicinity of Inco's Cu-Co-Ni orebodies, only Sta 42 and 44 samples yielded Co and Ni values about 1 standard deviation above average. Evidently the abundant bedrock source of these elements in this area does not ensure excessive supply to the concretions locally. Elsewhere throughout the Lakes system, positive correlation obtains generally between Mn, Ca, Mg, K, Ni, Cu and Co which are all negatively correlated with Fe.

Fig. 5b (right). Average i
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sequence of Table IX.

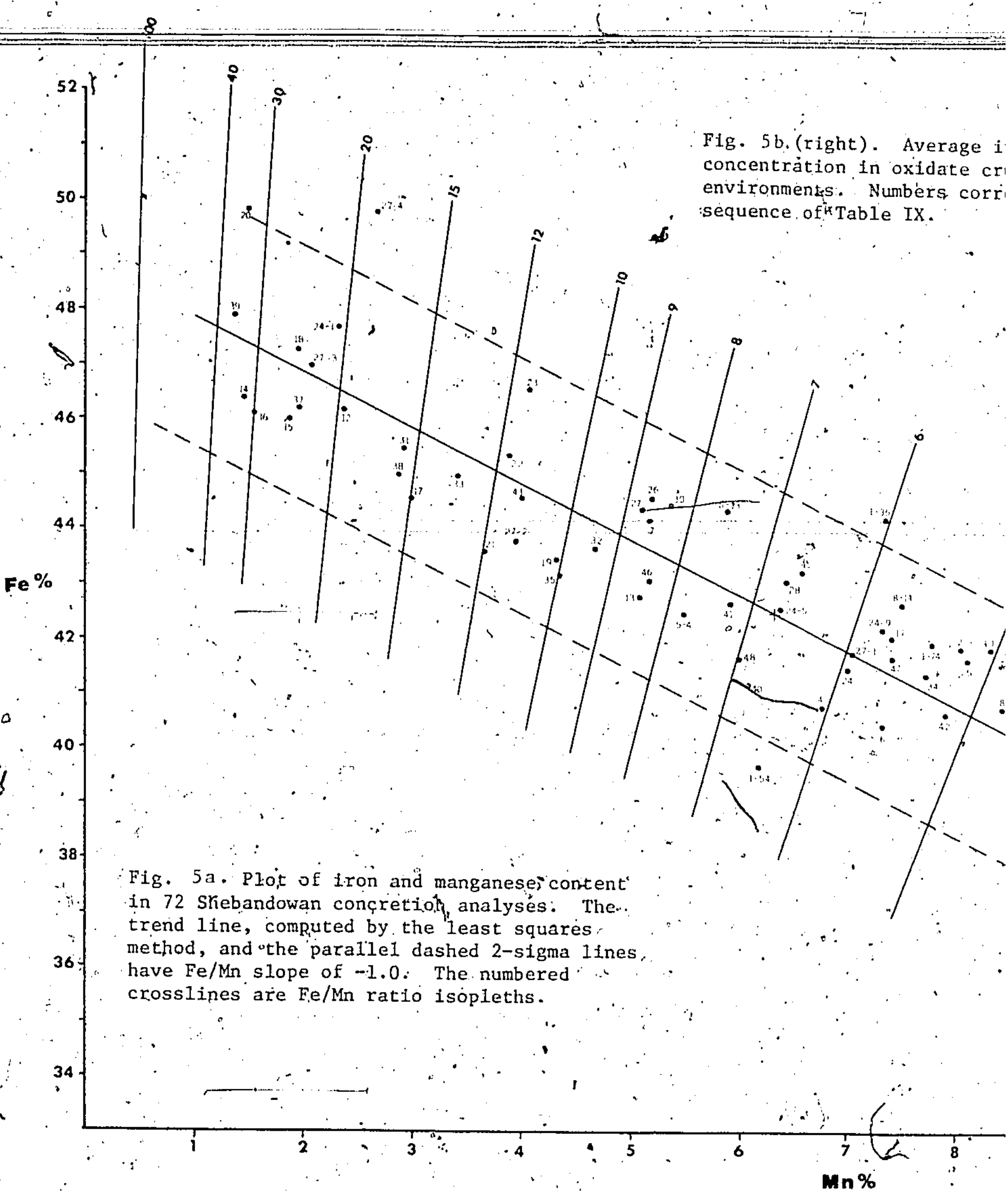

Fig. 5a. Plot of iron and manganese content in 72 Shebandowan concretion analyses. The trend line, computed by the least squares method, and the parallel dashed 2-sigma lines have Fe/Mn slope of -1.0. The numbered crosslines are Fe/Mn ratio isopleths.

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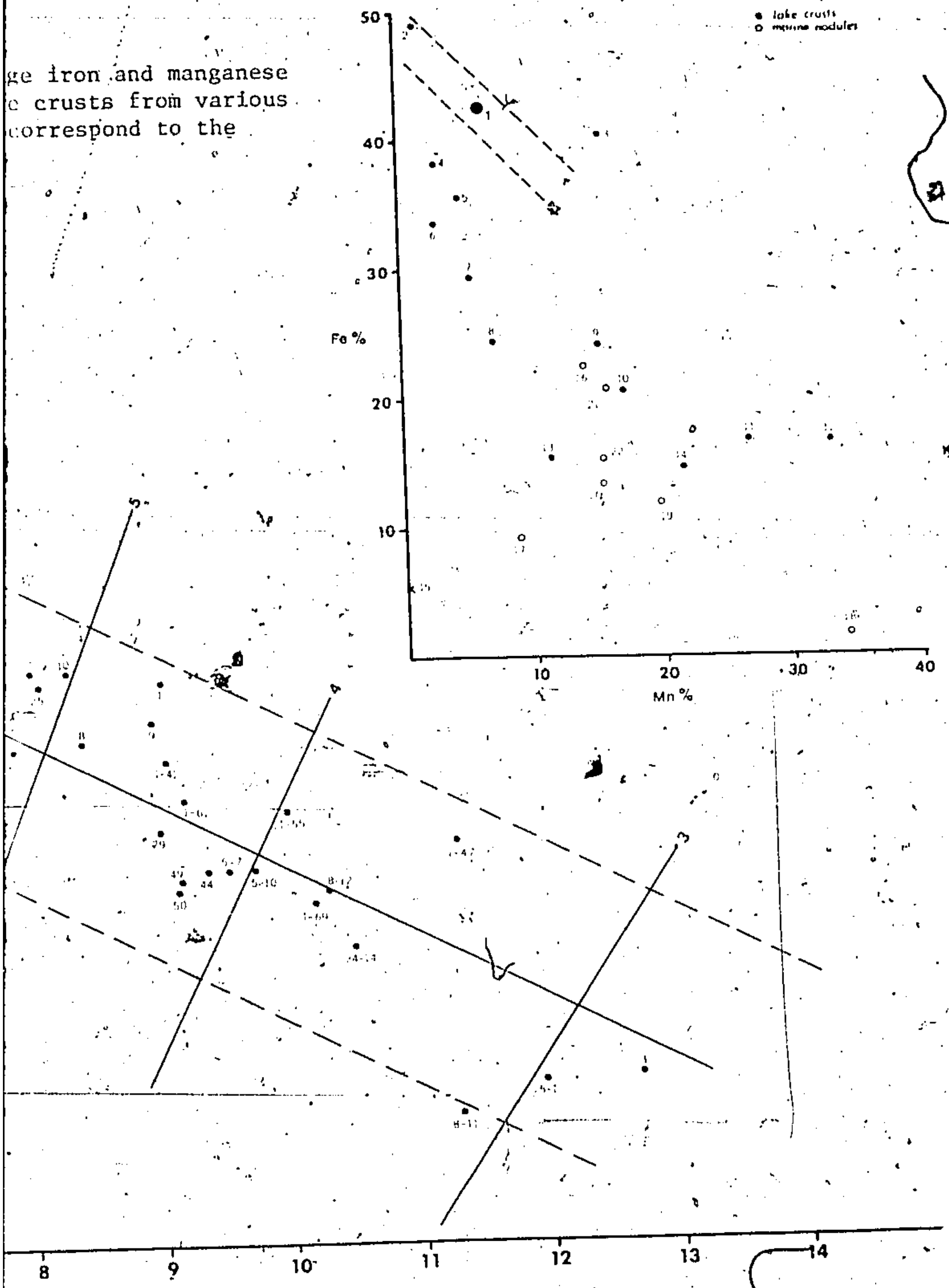

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Variation in the Element Content of Individual Deposits

Single concretion samples, collected at approximately equal intervals, over the entire lengths of each of 5 deposits, were analyzed to show elemental distribution at these stations. Analyses of four specimens, collected along a cross traverse in one of these deposits, were also made. The sequence and orientation of the traverse series is tabulated below.

Table VIII. Distribution of traverse samples (analyses in Table VI)

Station	Sample series	Axis sampled	Extension	Depth
1	Tr 1-36,41,47,54	short, 25ft	NW to SE	15-30 ft, increasing
1	Tr 1-55,61,69,74	long, 400ft	SW to NE	22± ft, isobathic
5	Tr 5-1,4,7,10	long, 700ft	NNE to SSW	20-30 ft, irregular
8	Tr 8-11,12,13,14	long, 50ft	WSW to ENE	40-10 ft, diminishing
24	Tr 24-1,5,9,14	long, 150ft	SW to NE	15-20 ft, isobathic
27	Tr 27-1,2,3,4	long, 100ft	SW to NE	15-20 ft, isobathic

Fig. 6 illustrates the relationship between iron and manganese content of concretions along the traverse series, and between traverse and the corresponding station composite averages. Compositional variation within each station comprises about half the variation or more for all analyses (Fig. 5). Strong unidirectional trends are shown at stations 24 and 27 along the SW to NE isobathic longitudinal traverses, with increases in the Fe/Mn ratios along this direction at the former and decreases at the

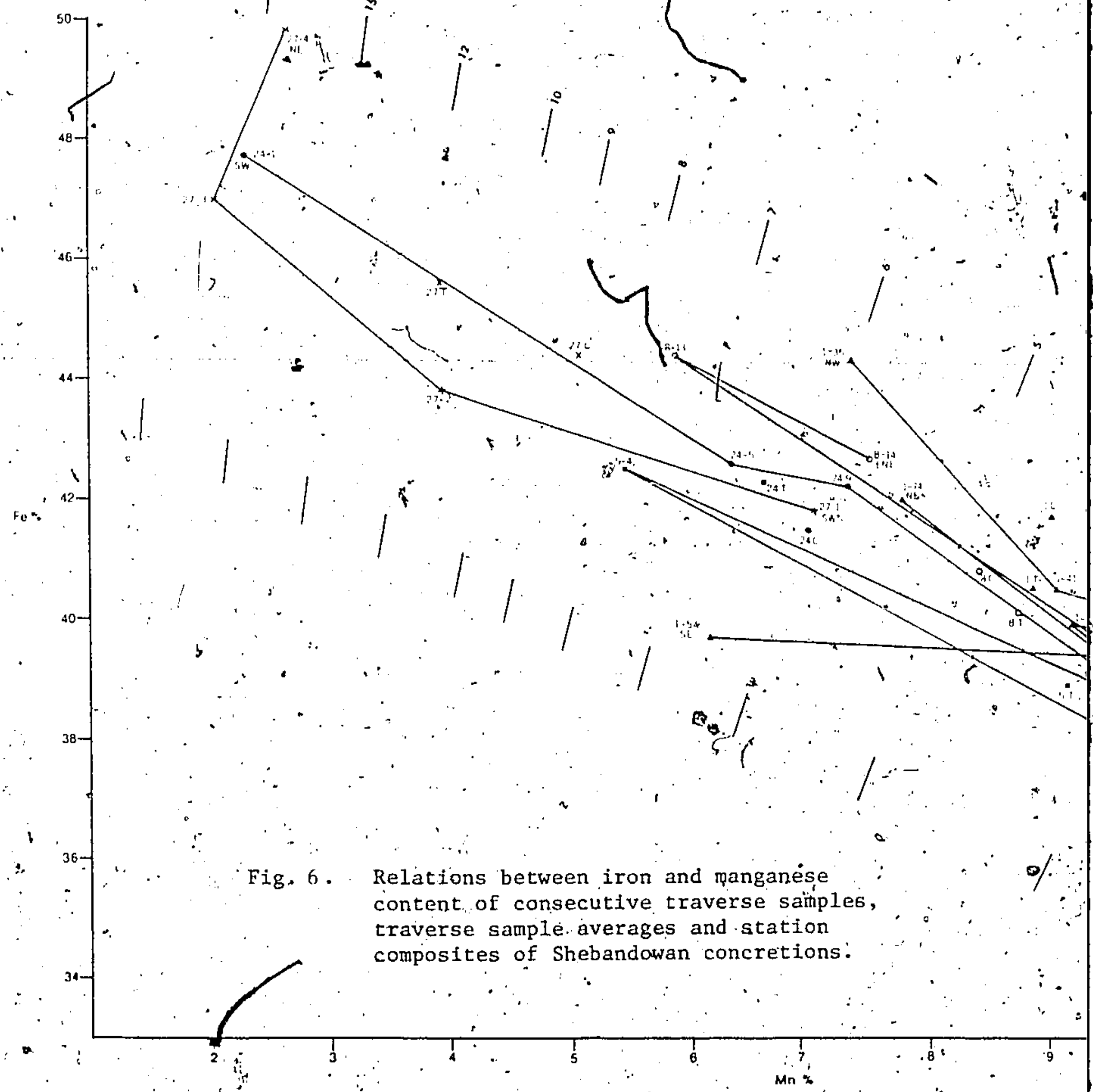

Fig. 6. Relations between iron and manganese content of consecutive traverse samples, traverse sample averages and station composites of Shebandowan concretions.

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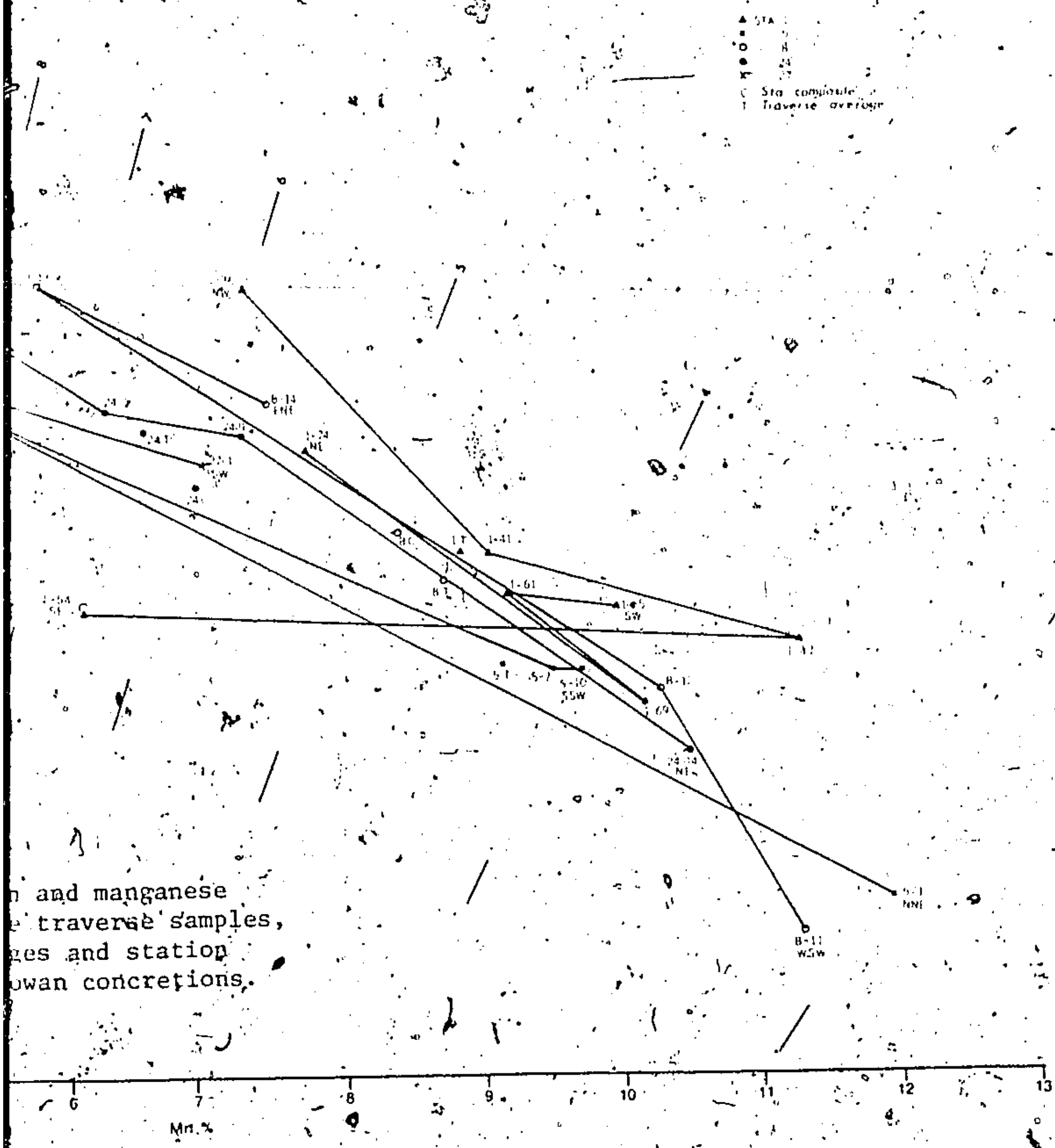

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latter station. Less marked trends are indicated at the other stations. In station 1 cross traverse the Fe/Mn ratios decrease with depth in the first three offshore samples, but the deepest sample has the highest Fe/Mn ratio. In station 8 this ratio decreases with depth between all consecutive samples, except the two nearshore samples. The significance of the Fe/Mn ratio trends is questionable in view that they persist only along two transects and that traverse averages agree rather closely with composite station averages (four grab concretions each). The latter observation suggests that the ratio trends may be fortuitous and that wide variations may be expected from any part of a deposit.

Wide variations within single deposits are also indicated for the other elements. The outstanding example is station 8 where Tr 8-12 showed the most anomalously high values on Mg, Ca, K, Ni and Co whereas other samples showed normal values. Again trends do not appear significant with regard to these elements.

Comparison with Fe-Mn concretion compositions from other environments

Average compositions of concretions from other lakes and marine environments are compared with those from Shebandowan in Table IX.

TABLE IX

Average Compositions of Fe-Mn oxide crusts from lacustrine and marine environments

	FeZ	MnZ	Fe/Mn	KZ	CaZ	MgZ	Cu ppm	Zn ppm	Ni ppm	Co ppm	As ppm	Pb ppm
1. Shebandowan Lakes - this report	42.5	6.3	6.8	0.02	0.56	0.08	33	260	105	109	10	n. d.
2. Lac à-la-Tortue, Que. (Béland 1961)	49.0	1.4	35.0	–	–	0.33	–	–	–	–	–	–
3. Mosque L., Ont. (Troup 1969)	40.2	15.7	2.6	–	–	–	10	250	95	135	–	24
4. Karelian-Finnish Ls. (Manheim 1965)	38.1	2.9	13.1	0.05	0.30	0.16	–	–	40	130	–	–
5. Swedish Ls. (Manheim 1965)	35.6	4.7	7.6	0.15	0.94	0.32	40	50	40	80	–	27
6. Lake George N.Y. (Schoettle et al. 1971)	33.5	3.6	9.4	–	–	–	1314	1177	702	220	–	–
7. L. Champlain, N.Y. (Schoettle et al. 1971)	29.5	5.4	5.5	–	–	–	60	240	–	230	–	–
8. L. Michigan (Rossman et al. 1969, Edgington et al. 1970)	24.[illegible]	7.0[illegible]	3.3	–	6.57	0.73	180	320	270	200	31-345	–
9. Oneida L., N.Y. (Dean 1970)	19.5-27.5	13.4-15.4	–	–	0.65-1.4	0.12-0.17	20-140	100-200	20-60	60-80	–	80-200
10. L. Ontario (Cronan et al. 1970)	20.6	17.0	1.2	0.24	3.1	2.2	363	1996	2385	643	–	1890
11. Ship Harbour L., N.S. (Troup 1969)	16.7	26.6	0.6	–	–	–	7	475	112	221	–	29
12. Grand L., N.S. (Troup 1969)	16.6	33.0	0.5	–	–	–	14	1665	296	196	–	26
13. English Lakes (Gorham et al. 1965, Troup 1969)	15.2	11.1	1.4	–	–	–	10	11000	20	40	–	–
14. Trout L. Wisc. (Twenhofel et al. 1945)	14.6	21.5	0.7	–	–	–	–	–	–	–	–	–
15. Earth's Crust (Taylor 1964)	5.63	0.095	59.3	2.09	4.15	2.33	0.0055	0.007	0.0875	0.0025	–	0.00125
16. Baltic Sea (Manheim 1965)	22.5	14.0	1.6	0.64	0.94	0.41	48	80	750	16[illegible]	–	38
17. White Sea (Manheim 1965)	9.2	8.8	1.0	0.58	1.72	0.90	–	–	–	–	–	–
18. Pacific Borderland off Baja California (Cronan 1972)	1.6	34.0	0.05	–	–	–	650	–	970	75	–	60
19. Pacific Ocean, (Cronan 1974, in press)	12.0	19.8	0.61	0.75	1.96	1.71	3920	680	6340	3350	–	846
20. Indian Ocean (Cronan 1974, in press)	13.3	15.1	0.88	–	3.16	–	2740	610	5070	2420	–	700
21. Atlantic Ocean (Cronan 1974, in press)	20.8	15.8	1.3	0.57	2.96	1.89	1160	840	3280	3180	–	1270
22. World Oceans (Cronan 1974, in press)	15.6	16.2	0.96	0.64	2.53	1.82	2561	710	4888	2987	–	867

A perusal of the table shows that in the oxide crust manganese and, even more so, the trace elements, copper, zinc, nickel, cobalt and lead, are greatly enriched relative to iron in the earth's crust (15). The enrichment varies with the crust environment, generally increasing from continental, through shallow marine, to deep sea occurrences.

The predominance of iron in the freshwater concretions and of manganese in the marine nodules is well known (Gorham and Swaine, 1965), although exceptions exist (Fig. 5b). This difference probably reflects the natural sequence of Fe precipitating before Mn from weathering solutions under oxidizing conditions (Krauskopf, 1957, 1967), so that down the aqueous profile between continental headwaters and deep oceanic basins, deposits tend to be relatively depleted in Fe and enriched in Mn. There are numerous known exceptions to this, whereby local conditions can bring about abnormally concentrated manganese deposits, as near water springs and in bogs (Sidwell, 1952), due to rapid presegregation of iron. Unusually high Mn/Fe ratios in near-continental marine nodule deposits (Fig. 5b-18) can also occur as a result of diagenetic remobilization of the manganese (Cronan and Tooms, 1969). As seen from Figure 3b, where the large dot marks the mean and the dotted lines bound all our concretions analyses, the Shebandowan crusts are of the iron-rich variety, even among the continental crusts.

The extensive association of Co, Ni, Cu and Zn with the hydrous oxides of Mn and Fe as principal controls on the fixation of the trace elements in soils and water has been widely recognized (Jenne, 1968). The mechanism is that of cation sorption and sorption capacities of the hydrated Mn and Fe oxides are comparable on a per weight basis with those of clays. Adsorption has been found to be strongly dependent on pH. The negative charge of the adsorbent increases with increasing pH value above its iso-electric point. Stumm and Morgan (1970) give the ranges 2-3 pH for zero point of charge of MnO_2 and 6-8 pH for ferric oxide; Collins and Buol (1970a) pinpointed the ZPC of ferric oxide at pH 5.1 in separate experiments. Sorption capacities for Ni (II), Zn (II) and Co (II) are slightly less than for Mn (II) which is sorbed to the extent of about 0.3 and 0.1 moles per mole of MnO_2 and Fe $(OH)_3$, respectively, at pH 7 (freshwater); but increase correspondingly to 1.0 and 0.3 at pH 8 (seawater) (Stumm and Morgan, 1970). The uptake of Mg (II) and Ca (II) by the sorption mechanism is considerably less. The figures quoted would indicate that in the slightly acid to neutral freshwater environment MnO_2 would be a considerably more efficient scavenger than Fe $(OH)_3$, as indeed is supported by correlation coefficients of Shebandowan crusts, discussed in the preceding section. In the more alkaline marine environment, however, the efficiency of sorption by the Fe-Mn oxides is substantially augmented and may be partly responsible for the generally strikingly greater abundance of Cu, Co, Ni, Zn and Pb in deep sea than lake crusts (Table IX).

There are nevertheless exceptions evident in the table. For instance, abundances of some of the trace elements in freshwater concretions of Lakes Ontario and George, approaching those in deep sea nodules, would require another explanation. According to Manheim (1965) minor element content in crusts is correlated negatively with their growth rates; the high growth rates in lake and shallow marine deposits are due to much higher concentrations of Fe and Mn in theirs than deep sea environments, together with lesser differences in concentration of the minor elements between all aqueous environments. The Lake George nodules have been dated at about 3300 B.P. (Schoettle and Friedman, 1971) an intermediate age between most lake and deep sea concretions. Similarly, intermediate age for the Lake Ontario oxide coatings has been proposed by Cronan and Thomas (1970) on the basis of known glacial history of Lake Ontario. By comparison, the relative sparseness of trace elements in the Shebandowan concretions is suggestive of their relative youth.

In many lakes the age of formation of concretions has been placed at between 5 and 100 years (Kindle 1935, Harris and Troup 1969). In a number of Swedish lakes, where lake concretions were mined for iron in medieval times, regeneration of new ore crops within 50 years had been reported (Mortimer, 1971). In the famous Canadian ore lake, Lac-à-La-Tortue, Quebec, mined intermittently during the 1860-1910 period, replenishment recurred in 5 to 10 year periods allowing a nearly continuous exploitation by moving dredging operations from one part of the lake to another (Ells 1898, Dresser and Denis 1949). Observations of oxide encrusted artifacts and buoys has also suggested a rapid growth rate in some lakes.

If contents of minor metals can be correlated with concretion growth rates, the average age of Shebandowan concretions would then be comparable with the 'younger' concretions from some North American and Fennoscandian lakes (Table IX). Needless to say this would only be a gross inference, for a host of factors undoubtedly accounts for differing growth rates, even in the same lake. For instance, a partial dissolution of concretions, or even lowering of pH insufficient for the dissolution, would be accompanied by desorption of the trace elements. Other factors such as the degree of complexing by organic substances and the influence of human activity around a lake are cited by Cronan and Thomas (1970) as possibly important in determining the uptake of elements by Fe-Mn oxide phases.

The content of As in Shebandowan concretions (average, 10 ppm) cannot be suitably compared with other Fe-Mn deposits because of the absence of comparative data. It is clearly less, however, than in Lake Michigan nodules (31-345 ppm), where the large concentration has been attributed to industrial sources, and in Black Sea Fe-Mn concentrations (500-1,000 ppm) (Edgington and Callender, 1970).

LAKE BOTTOM AND STREAM WATERS

Results of iron and manganese analyses of lake bottom and influent stream waters are given in Appendix III and plotted in Fig. 4. Determinations by atomic absorption following HNO_3 - HCl extraction were made by Bondar-Clegg & Co. Ltd. in Ottawa.

In general, the concentration of both elements was higher in the slow-moving and swampy streams than in those faster-flowing. Thus Swamp River and some of the marshy influents of Upper Lake carried values several times higher than rapid water of Kashabowie River and Greenwater Creek. Iron values ranged from 80 ppb in Greenwater Creek rapids (Sta 101) to 2000 ppb in the swampy and slow Burchell Road Creek (Sta 112), while manganese varied from 5 ppb in Greenwater Creek to 290 ppb in a swampy creek (Sta 109). The Fe/Mn ratios lay between 6 and 30.

Iron and manganese content of bottom lake waters was overall less than of the influents. Iron ranged from 90 to 910 ppb and manganese from 3 to 170 ppb, with Fe/Mn ratios between 5 to 55. Lowest and highest concentrations of both Fe and Mn occurred respectively in stations 34 and 8. There are no indications that Mn or Fe content or Fe/Mn ratio can be correlated with station depth, sub-basin, nearest influents, or concretion deposits. Values in bottom water sampled at the two barren stations were similar to those in water overlying the nearest concretion deposits possibly suggesting rapid mixing of the water.

The three water specimens taken near the surface at the lake system's outlet carried values similar to those in bottom waters.

As previously noted most of these analyses exceed by factors from 2 to 5 results obtained by contemporaneous sampling of Rasberry et al. (1971). This rather wide discrepancy can be possibly explained by differences in the analytic techniques used. However, differences between values obtained by the same technique are likely to be valid.

In the Swedish lakes and rivers, Ljunggren (1953) found higher Fe and Mn values, but could not correlate the Fe-Mn concentration in water with presence or absence of concretion deposits. Nor did the water's Fe/Mn ratio have bearing on the composition of associated Fe-Mn precipitates. Cronan and Thomas (1972) found very low bottom water Fe-Mn concentrations above the Lake Ontario oxide-coated sands, but interstitial water in the underlying sediments carried values higher by one to several orders of magnitude. The same relationship (without associated oxide deposits) was noted by Brunskill et al. (1971) in the Experimental Lakes.

Local and seasonal factors are likely the most important in regulating both income and redistribution of Fe and Mn in Shebandowan Lakes. The input by influents is largest in the spring and fall subject to regulation by the Upper Lake dams.

According to Gibbs (1973) the largest fraction of free Mn and Fe transported in the Yukon and Amazon rivers, which may not apply to the Shebandowan influents, is in metallic coatings (precipitates and co-precipitates) on suspended solids. About a third of the amount of Mn on coatings was reportedly found dissociated as Mn (II) or in complexes; the corresponding fraction for Fe was negligible. Both iron and manganese occurred substantially in suspended organic solids but negligibly as adsorbates on suspended material. In oxidized neutral waters, such as near surfaces of most lakes, any divalent Fe and Mn ions are readily oxidized and sedimented as insoluble Fe (III) forms and Mn (II, IV) oxides (Stumm and Morgan, 1970). The ferric precipitates, often colloidal in character, may be stabilized by organic bases.

While the deeper, thermally stratified Shebandowan sub-basins experience overall little oxygen depletion that could account for return of divalent Fe and Mn ions to hypolimnetic waters, such remobilization could take place locally. A second possibility is that in pockets of extensive, probably seasonal, sedimentation diagenetic remobilization of metals could occur, with transfer from profundal to littoral facies. In the first instance this would provide some diffusion of cations particularly Mn, into water overlying concretion sites, especially those at deeper stations. In the second case, supply to concretions would emanate from below, interstitially through the substrate. The latter scheme is illustrated in Fig. 8B.

SEDIMENTS

Twenty vertical sediment cores, 5 to 34 cm deep, were recovered at different concretion sites. Minus 80-mesh fractions of 30 samples, representing 2 to 5 cm core intervals, were analyzed for Fe, Mn, Cu, Ni and Co using the atomic absorption technique after HNO_3 - HCl extraction, by Bondar Clegg & Co. Ltd. Complete logs are found in Appendix II, while sections are shown in Fig. 4.

All cores are topped by up to 15 cm but on the average about 5 cm of yellow to brown gravelly to silty sand. Succeeding layers are made up of gray sand and/or massive to poorly banded gray silt or clay.

Four cores contained sections of an iron-rich reddish clay (about 7.5 YR 6/2 on Munsell Soil Color Charts (1954) when dry). This is undoubtedly the red Glacial Lake Kaministikwia clay described by Zoltai (1963, 1965a) and Keele (1924). The clay is massive, stiff and stoneless, although one section contains sandy grit horizons. The peculiar colour, evidently a lithological idiosyncrasy of the Keeweenawan provenance rocks near Thunder Bay, has permitted the tracing of this clay in the Lake Agassiz sediments as far west as the Rainy River area. At Finmark, in the Kaministikwia River valley, where the red clay has thickness of 20 feet or more, Keele (1924) obtained the following assay, in weight per cent: SiO_2 52.10, Al_2O_3 14.77, Fe_2O_3 7.79, CaO 5.62, MgO 5.34,

K_2O 2.45, Na_2O 1.88, L.O.I. 9.49. The presence of the red clay in cores of stations 24 and 26 extends the reach of Glacial Lake Kaministikwia west to include Upper Shebandowan Lake.

Almost invariably the highest Fe, Mn and base metal values are found in the top oxidized sediment and decrease downwards through the gray sediments. The red clay, assayed three times, is an exception, its content of the metals analyzed exceeding those of even the top cores, except in one instance. Average values of all cores assays are about 1.3% Fe, 300 ppm Mn, 20 ppm Cu, 20 ppm Ni, and 10 ppm Co.

The analyses support the visual evidence of yellow and brown discolouration that oxidation penetrates an average of 5 cm below the surface of sediments at concretion sites. Below that depth the colouring is in hues of gray, red clay excepted, with diminishing Fe and Mn values - indicative of reduction and possible remobilization of these elements. A progressive upward increase in the content of both metals is shown in the analyses of most cores. This is consistent with a mechanism of upward diagenetic migration of at least Mn ions within the sediments. That such a mechanism obtains is further suggested by increasing upward Mn/Fe ratios in all cores, consistent with the superior diagenetic mobility of Mn ions

(Shterenberg et al., 1970). The Mn/Fe ratio increase extends above from the sediments into concretions, a relationship considered diagnostic of diagenetic, as contrasted with hydrogenous, supply of Mn and Fe in marine nodules (Price and Calvert, 1970).

ORIGIN OF CONCRETIONS

The development of ferromanganese oxide deposits is a widespread Recent phenomenon within the exogenic cycle. Deposits of various forms occur on bedrock, in soil, in bogs, and on stream, lake, and shallow as well as deep marine bottoms.

The ultimate sources of iron and manganese are principally the pyroxenes, amphiboles, biotite, olivine and the accessory oxides of primary igneous rocks. Redistribution into derivative minerals follows recycling of the primary rocks by metamorphic and sedimentary processes. The Precambrian Shield rocks of the Shebandowan region consist of a mixture of igneous and sedimentary rocks which have undergone varying degrees of metamorphism.

Chemical weathering processes that liberate Fe and Mn from rocks at earth's surface include solution, hydrolysis, hydration and oxidation. According to Krauskopf (1957) the leaching rates of Fe (II) and Mn (II) are about the same from igneous rocks; thus on their release, these elements should maintain the same ratio (Fe/Mn=50/1) as in the fresh rock.

Despite the high incidence of bedrock exposure within the Shebandowan Lakes watershed, the fraction of material supplied by weathering of rocks is undoubtedly small compared to that from the weathering of overlying glacial drift. The

Wisconsin glaciers carried away most of the existing soil and rock mantle, in the area, additionally scraping away variable quantity of surface-bedrock material; and the mixture was redeposited down in the direction of their movement. Hence most of the drift and soil developed therein is allochtonous and much of it is even foreign to the watershed. Due to the great surface area of the poorly sorted drift and its permeable nature, it is far more reactive to leaching soil-water solutions than the bedrock.

As pointed out by Shakhov (1966) the development of podzolic profiles in unconsolidated Pleistocene rocks of the cool-temperate zone is a very rapid process in geological terms, bringing about a change from alkalic to acidic conditions within a few millenia. The concomitant release of iron and manganese to surface and groundwaters results in the impressively widespread ferromanganese deposits in swamps and lakes of the glaciated regions.

The cycles and relationship of iron and manganese in the exogenic environment have been widely covered, notably by Krauskopf (1957, 1967), Hem (1964, 1970), and Stumm and Morgan (1970). Among such factors as salinity, temperature, organic activity, pressure and autocatalysis, that determine fractionation and development of Fe and Mn oxide assemblages, the Eh and pH conditions are the most decisive in the low temperature and pressure environments obtaining at or near the surface of the earth. Upon their release from rocks as divalent ions, Fe and Mn respond similarly to Eh and pH conditions (Fig. 7) but iron is oxidized and precipitated at lower Eh-pH fields than manganese, activities being equal. Given persistent or repeated Eh-pH conditions down the watershed profile, whereby iron is removed from solution while manganese remained soluble, a residual enrichment in Mn with respect to Fe in water would result.

In the Shebandowan region the important initial separation of Fe and Mn, resulting in the latter's residual enrichment in groundwater, probably occurs in the podzolic profiles. The Mn/Fe ratio is conceivably further enriched in surface runoff and groundwater downstream through the selective removal of ferric oxide/hydroxide. The extent to which separation takes place is quite variable, according to local and seasonal Eh-pH conditions, governed by such factors as availability of decomposing organic matter, thickness of drift and drainage characteristics of soils, amount of rainfall, and so on. Local variations must account for the wide range of Fe and Mn values and ratios encountered in the Shebandowan Lakes' influents (Appendix III and Map 5).

The most common form of iron in solution is Fe (II) within the pH (5-9) and Eh (-0.10 to 0.20 mv) range of natural waters (Hem 1970). Ferrous complexes are formed by many

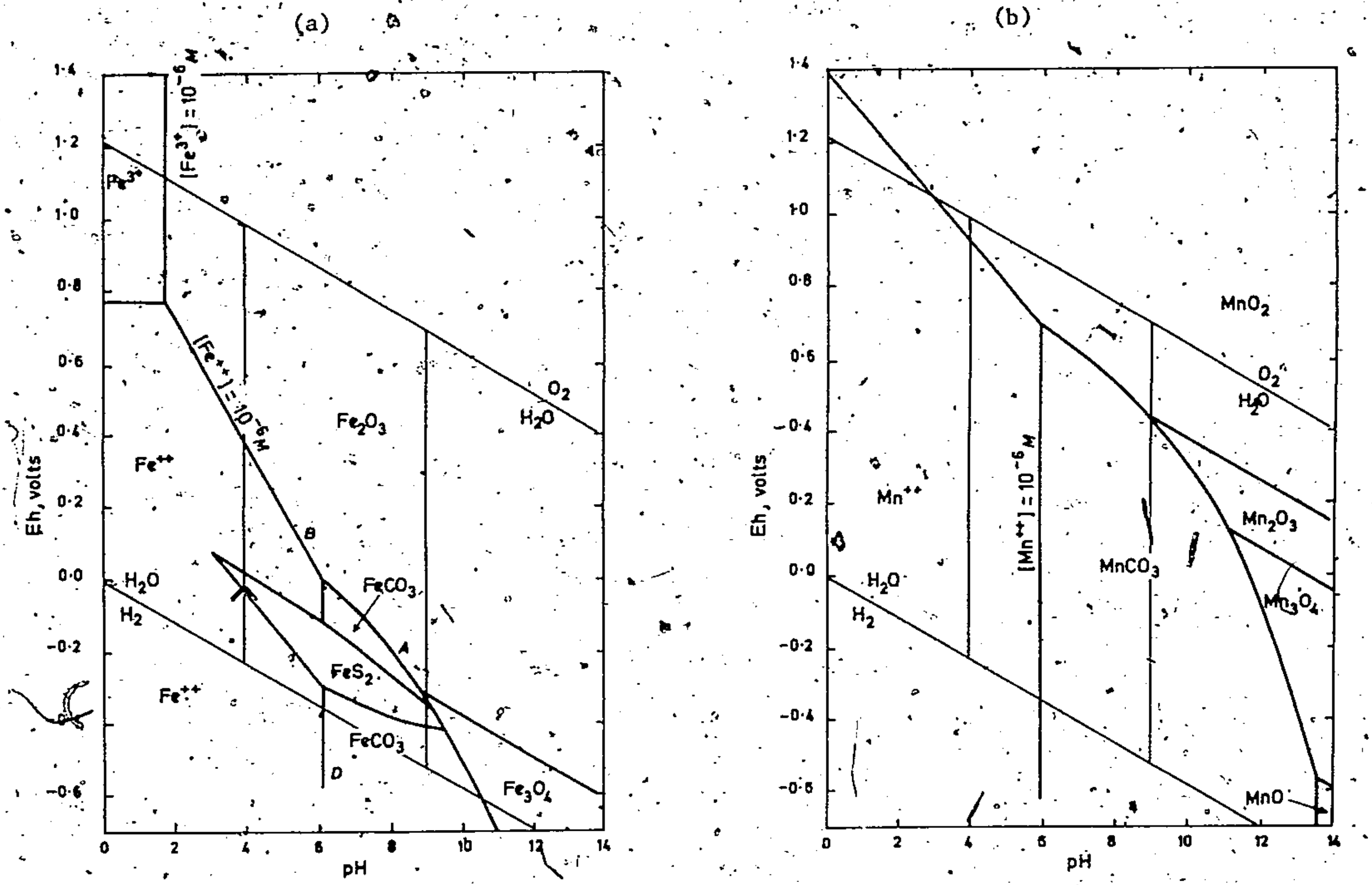


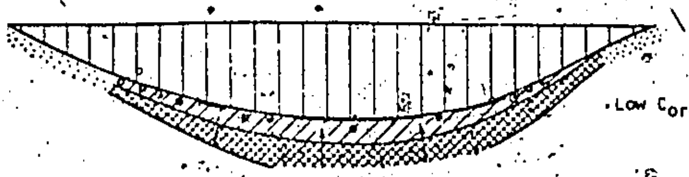
Fig. 7: Eh-pH diagrams showing stability fields of common iron (a) and manganese (b) minerals. Total activity of dissolved carbonate, 1M; of dissolved sulphur, 10^{-6}M; iron (a) and manganese (b), 10^{-6}M. (After Krauskopf, 1967).

organic molecules (Hem 1970) but they are stable in rather acid conditions and their nature is poorly known. According to Stumm and Morgan (1970) ferric ions have a stronger tendency to form complexes than ferrous or manganous ions. The Fe (III) complexes with orthophosphate, sulphate and many organic bases are better known. The Mn (III) form is not stable under normal conditions, while Mn (II) is relatively stable in solution requiring high pH rather than Eh for its oxidation. Mn (IV) has much lower potential for forming complexes than Fe (III), because of its great affinity for OH^-. This is evidenced by the much lower pH (2-3) of zero point of charge of MnO_2 than of ferric oxide (6-8) (Stumm and Morgan, 1970). Much of the iron and manganese may be transported in water as oxide hydrosols, often stabilized by organic matter and complexes.

The incoming runoff brings free Fe and Mn (1) in the form of oxide coatings; (2) in solution and organic complexes; (3) adsorbed on solids; and (4) incorporated in organic solids. The relative amount brought in by any of the four transport mechanisms will vary seasonally and locally. The largest water income in Shebandowan is in the spring from melting snow and in the fall from high precipitation. The proportion of the metals arriving in solution, as complexes and in organic solids will be higher in the swampy creeks, rich in humic content and low in pH, than in the better aerated rapid influents, richer in oxide-coated particles. On entering the lake most of the stream borne solid particles will settle on the bottom. Likewise, most of the dissolved material will be precipitated on coming in contact with the aerated lake water, particularly in the well oxygenated deeper Shebandowan sub-basins. As a result, relatively little dissolved Mn and especially Fe is probably held by Shebandowan Lakes waters as compared with more humic lakes, such as the Karelian Eningi-Lampi wherein 72-92% of total Mn and 30-48% total Fe are dissolved rather than suspended (Varentsov, 1972).

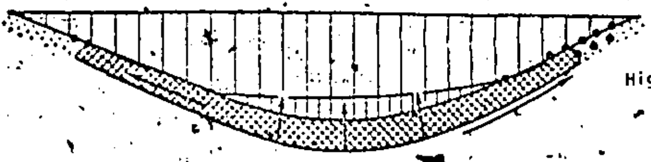
Various theories of origin of lake concretion deposits have been proposed which, with regard to supply of iron and manganese draw on hydrogenous and diagenetic sources.

Strakhov (1966) proposed a classification based entirely on diagenetic redistribution of Fe and Mn (Fig. 8). Accordingly, there is association between the content of organic matter in the lake sediments and the types of deposits formed. In oligotrophic lakes, which accumulate relatively little fresh organic matter, the incoming Fe (II) and Mn (II) are precipitated as oxides at the surface and drop to the bottom. Here they are reduced in the bottom silts and migrate up to the sediment-water interface, where they are reprecipitated on contact with oxygen-rich water. This oxidized layer serves as the incipient surface for the accumulation of ochre crust. With



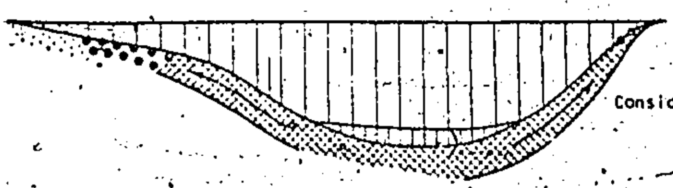
Low C_{org} content in silts (2-3%)

A - Monchosero group lakes



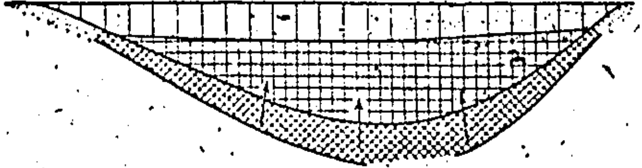
Higher C_{org} content in silts (3-5%)

B - Suystamon-Yarvi



Considerable C_{org} content in silts (6-7 %)

C - Pyjas-Yarvi



Sapropelic silts

D - Barren eutrophic lakes

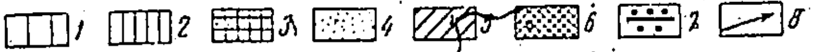


FIGURE 8. Types of lacustrine manganese accumulations

1 - oxygen-rich water

2 - bottom water, low in oxygen

3 - oxygen-free water

4 - sands

5 - brown silt (oxidation zone)

6 - gray to green-gray silts (reduction zone)

7 - ores

8 - direction of substance movement in diagenetic redistribution

(after Strakhov, 1966)

slightly increased trophism, oxygen deficiency develops in deep bottom water and the Mn (II) and Fe (II) ions migrate laterally and up through interpore space in sediments along potential gradients, depositing crusts above the low-oxygen water line and nodular to discoid concretions in or atop the oxidized sediments of the littoral zone. According to Strakhov, when a lake reaches the eutrophic stage all its sediments are reducing, preventing the formation of higher oxides. In support of Strakhov's diagenetic theory, Shterenberg et al., (1970) found steadily decreasing Fe/Mn ratios laterally and upwards in both nodules and sediments of Lake Punnus-Yarvi, the variation being attributed to the superior diagenetic mobility of Mn to that of Fe. Upward migration of Mn in interstitial water to Lake Michigan nodules was also postulated by Rossman and Callender (1968).

In keeping with Shakhov's theory, in the deeper Shebandowan basins, essentially lacking in oxygen stratification, concretion and crust-pavement deposits should occur in profundal sediments (Fig. 8A). The presence of such deposits could not be confirmed in our survey because of limitation in our depth reconnaissance capability. However, the littoral to sublittoral occurrence of the deposits along with the presence of apparently reducing (dark) silts, often observed just below concretion fields, suggest rather the presence of conditions illustrated in Fig. 8B.

Other proposed models of concretion formation usually combine diagenetic and hydrogenous sources of Fe and Mn (Ljunggren 1953, Troup 1969, Terasmae 1971, and Cronan and Thomas, 1972).

Troup (1969) elaborated a complex theory, requiring the concurrence of differential supply of Mn and Fe from a hypothetical, cyclically reducing hypolimnion, along with biotic mediation, to account for the presence of alternating Fe-Mn rich-poor microbanding of concretions in Grand Lake, N.S.. To explain this phenomenon, Gorham (in Harris and Troup 1970) suggested a simplified mechanism, whereby the chemical banding could be due to local effects by photosynthesizing plants of raising Eh-pH sufficiently to oxidize and precipitate excessive Mn in the summer. Both Ljunggren (1953) and Terasmae (1971) proposed that divalent Fe and Mn may be fed by groundwater to emerge directly at the oxidizing littoral shelf, precipitating as oxides about suitable nuclei. Cronan and Thomas (1972), finding supply of the major elements by upward diffusion incompatible with an impermeable substrate in part of Lake Ontario deposit, offered that a documented mechanism of upwelling water from the deep towards the shallow deposition site could transport Fe and Mn which would be deposited on crossing a high redox gradient zone.

The effect of biota as direct oxidizers of Fe and Mn has been widely asserted. Microorganisms such as *Metallogenium*, *Kusnezovia* and *Caulococcus* were reported to colonize directly Fe and Mn oxides in nodules of lakes in Russian Karelia (Perfilyev and Gabe, 1964). Other genera of microbes, notably *Sphaerotilus* (*Lepthothrix*), *Pedomicrobium*, *Siderococcus* and *Cephalosporium* are among some oxidizers of Mn reported responsible for deposition of MnO_2 in soils (e.g., Ivarson and Heringa 1972). Shterenberg et al. (1970) report micro-nodules built of colonies of the blue green algae, *Cloethrochia echinulata* in L. Punnus-Yarvi. Greenslate (1974) suggested, on the basis of an ultra-structural examination of 71 Pacific nodules, that several organisms are active in their construction. Both Kindle (1935) and Troup (1969) suggested that photosynthesis by algae may precipitate Fe and especially Mn by creating high pH-Eh microenvironments above the lake sediment-water interface. A similar effect by an aquatic bryophyte, *Marsupella aquatica*, rooted on brook stones, resulted in sheathing of the plant with MnO_2 (Ljunggren 1953). Despite the number of cases presenting evidence of biotic mediation, many writers (e.g. Krauskopf, 1957 and Stumm and Morgan, 1970) are skeptical about the role of organisms in the overall precipitation of the oxides. Manheim (1965) found more references in the literature to reducing than oxidizing effects by biota.

The mechanics of Shebandowan concretion formation are probably as follows. In those profundal areas of the sub-basins where sediment and organic material accumulate fairly rapidly, remobilization of the metals as cations is consequent on dissolution of the oxides/hydroxides resulting in their migration (Fig. 8B). On approach to the littoral and sub-littoral areas, largely maintained free of sediment accumulation, the Mn/Fe ratio gradually increases as Fe (II) is preferentially abstracted in sulphide or carbonate phases throughout the reducing zone, until under suitable Eh and pH conditions (Fig. 7) the Fe and Mn ions are oxidized and precipitated. Where pebbles of suitable size and shape act as plugs in the underlying substrate to oxidizing influences from above, the effective zero redox potential level is raised to the sediment-water interface. This results in a concentrated supply of ions from below, emerging into oxidizing water at the intersection of the prospective nucleus with sediment surface.

An initial coating is precipitated at the triple interface, as a film of FeOOH (Burns and Brown, 1972). At first Mn (II) is sorbed and probably occluded by the ferric oxyhydroxide, a considerable abstraction of Mn thus resulting even before Eh-pH fields of higher Mn oxides are reached (Collins and Buol, 1970a). With rising Eh-pH manganese will begin to precipitate as Mn (II, IV) oxides, due to chemosorption and autocatalytic oxidation of Mn (II) by the MnO_2

phase (Stumm and Morgan, 1970). The relative amounts of Fe and Mn going into concretions depend mainly on the activities of both and on Eh-pH conditions at deposition site. Seasonal variations may be brought about by cyclic bacterial activity or photosynthesising vegetation (E. Gorham: in Harris and Troup, 1970). The latter agency could be responsible for raising Eh-pH in the summer, to increase significantly the rate of autocatalytic oxidation of Mn, resulting in higher Mn/Fe ratio deposition than in winter time.[6] The mechanism would be workable in Shebandowan Lakes, where all concretion deposits presumably occur within the euphotic zone, and could account for the cryptic chemical banding observed in similar concretions from other lakes (Troup 1969; Harris and Troup 1970; Burns and Brown 1972).

The proportion of Fe and Mn derived from overlying water is unclear but probably less than that supplied by interstitial water. The morphology of radial concretion growth in the plane parallel to the interface would suggest a preponderance of supply from below (Manheim, 1965). However, the development of upward-pointing radial ridges, exemplified in the pulley and hatlike concretion morphologies, as well as the predominant upperside development of botryoidal structures, suggest significant contribution from the overlying water.

This is probably accomplished by sorption of any divalent Fe and Mn available. In view of the oxidizing nature of the water Mn (II), if at all present, would occur in high proportion to Fe (II); hence the possibility of Mn-enriched phases on concretion uppersides noted by Ljunggren (1953).

The correlation of the Fe/Mn ratios of Shebandowan concretion deposits with average associated sub-basin depths has already been noted. One explanation for this could be found in terms of morphometric factors affecting the efficiency of redistribution of Fe and Mn by the diagenetic process. Thus to deposits subtending the deeper basins, a more refined product of diagenetic segregation of these two elements would accrue in the form of higher Mn/Fe ratios, because of the longer average distance from point of origin to deposition site, than to the deposits in shallow basins. Alternatively, a higher degree of trophism in the shallow basins could conceivably prevent oxidation of some of the Mn (II) relative to that in deeper basins. But while there are indications that some oxygen deficiency obtains in Lower Lake, there are no confirming data of similar conditions occurring in the U Upper and U Middle basins. Besides, high Mn/Fe ratio concretions are known to occur even in shallow, oxygen-stratified, eutrophic lakes (Dean, 1970).

The iron-rich character of the Shebandowan deposits relative to others in the exogenic environment is likely due to the inefficiency of the existing geochemical processes to adequately pre-segregate iron. This is consistent with the view that Fe/Mn ratios in concretion and nodule deposits gradually decrease down the aquaeous profile from continental sources, through shallow marine, and into the deep sea environment (Krauskopf, 1957, 1967). Iron is in presumably too plentiful a supply in Shebandowan Lakes, located near the headwaters of a continental divide, to be efficiently separated from manganese even via the diagenetic process.

SUMMARY AND CONCLUSIONS

The results of the present investigations are summarized below.

1. Fifty ferromanganese concretion deposits of various sizes were found, at estimated depths of 6 to 40 feet, in each of a number of morphometrically distinct sub-basins of Shebandowan Lakes, a narrow system with a composite length of 30 miles.

2. The concretion supporting surface is either sand showing effects of oxidation to an average depth of 5 cm, or, rarely, schist rubble with little or no associated sand.

3. The concretions generally form at or just above the sand/water interface, developing concentrically in that plane around a nucleus. Composite Fe-Mn oxide accretionary material may, however in some instances, be several centimetres high parallel to the upright axis.

4. Observations of concretion specimens show a definite tendency to deviate from the general planar development, both up and down at the edges, resulting in a morphology of outwardly bifurcated radial section. These deviations are taken as being illustrative of the dual tendency to abstract material from both the substrate and the overlying water.

5. Partial re-solution, by contact with a reducing substrate from below and by periodically depressed Eh-pH conditions in the superjacent water above tends to mitigate deviation from the general planar concretion development. The changing conditions apparently affecting the upperside probably recur at irregular periods, possibly at the end of an unusually long winter when some oxygen depletion occurs under ice/snow cover. This would imply the existence of a precarious equilibrium between the Fe-Mn phases of concretions and the surrounding water.

6. Fracturing and consequent veining is a common feature of discoid concretions. The presence of oxide veins, standing in relief only outside the "active" surfaces is prime evidence for partial re-solution of concretion uppersides. Combined effects of re-solution and fracturing may result in eventual destruction of concretions.

7. Mushrooms and top-ring concretions are characterized by lack of downcurl and thick development of botryoides at the upper surfaces, thought to be due to relatively high-proportion of hydrogeneous Fe-Mn supply. Unlike normal concretions, described above, these do not show effects of upperside dissolution, possibly because of their occurrence in the shallowest, most oxidizing, parts of deposits.

8. X-ray diffraction analysis revealed the presence of goethite in three of four composite concretion samples studied. The presence of goethite in one of these samples was confirmed by Mössbauer spectroscopy, marking the first time that goethite was indicated by this method in a Fe-Mn concretion or nodule. No common manganese minerals were identified by X-ray diffraction patterns.

9. Bulk chemical analyses of acid-soluble portions of concretions from 49 stations gave an average of 43.1% Fe, 5.65% Mn, 0.53% Ca, 200 ppm K, 669 ppm Mg, 31 ppm Cu, 273 ppm Zn, 101 ppm Ni and 102 ppm Co. Although the Fe/Mn ratio was 6.7, variances of Fe and Mn were similar. Analyses of 10 composites for As gave an average whole-sample content of 10 ppm.

10. A correlation matrix indicated significant positive relationships between all elements and Mn in concretions, except Zn which was independent and Fe which showed strong negative correlation with the others. In spite of doubts incurred by iron's effects as diluent, it is thought that Ni, Cu and probably Co follow Mn. Zn normally follows Mn, but the association is masked by the apparent preferred occurrences of Zn in Upper Lake, probably due to the vicinity of a source there.

11. Compositional variation within each deposit was about half the total variation between all the Shebandowan deposits. No significant trends were indicated by analyses of samples taken at regular intervals along transects of deposits.

12. The iron-rich nature of Shebandowan deposits is typical of lake deposits and probably explained by iron's tendency to oxidize before manganese, which becomes consequently concentrated in deposits farther down the aquatic profile. The low content of minor elements probably reflects a relatively rapid rate of concretion formation and the low pH of lacustrine relative to marine environments.

13. The compositions of bottom lake and influent waters are similar, ranging from 80 to 2,000 ppb Fe and 3 to 290 ppb Mn, with Fe/Mn ratios from 5 to 55. There is no correlation between Fe-Mn water content and station depth, sub-basin, influents, or concretion deposits. The composition of water appears to be particularly liable to seasonal and local variation; hence meaningful conclusions could be drawn only after regular sampling and analysis from stations throughout the year.

14. Acid-soluble fraction analyses of 30 sediment core samples indicate upward increase in a Fe and Mn content of most cores and Mn/Fe ratio increase in all cores. This

suggests a diagenetic upward mobilization of the elements where Mn is more mobile than Fe.

15. Four sediment cores contained horizons of a distinctive red clay, deposited in Glacial Lake Kaministikwia. The discovery of this clay in two Upper Lake station extends westward several miles the previously established limits of the Glacial Lake.

16. In considering sources of iron and manganese to Shebandowan Lakes, the fraction of material released by weathering is probably far greater from the permeable glacially transported material than from bedrock. Important initial segregation of iron and manganese and the latter's consequent enrichment occur in soils developed in drift.

17. A considerable fraction of material supplied to concretions is derived by lateral and upward remobilization of Mn and Fe from profundal to littoral sediments. Probably a subordinate amount is obtained directly from the overlying water.

18. Initial precipitation of Fe $(OH)_3$ on a nucleus is followed by sorption of Mn (II). With suitable ensuing increase in pH-Eh, mixed Fe-Mn oxides are deposited after Mn (II) is oxidized to Mn (IV) and precipitated as MnO_2, which may contain a substantial fraction of Mn (II) autocalytically sorbed.

19. The somewhat higher Mn content in deposits occurring at the lip of the deeper sub-basins may be due to a higher Mn/Fe ratio diagenetic product, on account of the greater distance between the profundal muds and concretion substrate than in shallower basins. Otherwise, the effect of some oxygen depletion in the more trophic shallow basins may deprive some Mn (II) of an opportunity to become oxidized; in some cases Mn could only be present as divalent ions sorbed in the ferric oxide phases.

PLATE IV

Central portion of the underside of a concretion from Station 1, magnified 5 times. Note the lack of a palpable nucleus, heavy ridging, and botryoides—best developed in the lower and left parts of the picture. The white spiculed growth is a sponge, while the attached light-toned hemispheres are colonies of a fungus of the genus Aposphaeria (kindly identified by Dr. K.A. Pirozynski, Mycology Section, Biosystematics Research Institute, Ottawa), which normally thrive on organic material. The fungi, whose diameters appear to be coincidentally similar to those of the Fe-Mn botryoides, are now hollow, devoid of spores, except for a few specimens which contain unidentified translucent prismatic crystals. The presence of such apparently well oxygenated underside, with well preserved primary oxidate structures, rich in organic matter and biotic growths, is very rare and found only in a few concretions. It is evident that this part of the specimen could not develop in contact with a reducing substrate.

APPENDICES

APPENDIX I

Log of Shebandowan concretion deposits

Station - Basin*	Location Relative To Landmark	Deposit Size (ft) and Orientation	Estimated depth (ft)	Bottom Type
1-MU	S side large I. in Threemile Bay	400 ENE x 25	15-30	rock-gravel-sand
2-UM	W tip, Teapot I.	15 diam.	30	sandy
3-MM	SE side, Teapot I.	100 NE x 15	35-40	pebbly-sandy
4-MM	NE tip, Little Bare I.	10-long crevice in rock	40	silty sand
5-MM	between Little and Big Bare Is.	700 NNE x 10-70	20-35	sandy
6-MM	off N point, The Narrows	35 diam.	25-30	sandy
7-1 MM	100' SE of Big Bare I.	50 ENE x 25	25-30	sandy
7-2 MM	off WSW point Big Bare I.	small	10-15	pebbly-sandy
7-3 MM	W of above	undetermined	15	sandy
8 MM	off W point, Kabaigon I.	50 WSW x 10	10-40	rock-gravel-sand
9 MM	75' W of tiny I.	small	6-10	boulders, pebble
10 MM	SW of above I.	40 E x 10	30-35	sand
11 MM	off NW point, Pine I.	several patches	20	pebbles-sand
12 UU	off NE point, I.	20 x 10	15	rocky, above mud
13 UU	off SW tip, I.	very small	30	pebbly-sandy
14 UU	SE side, 'Windbreak' I.	very small	30	rocky, above mud
15 UU	S of SW end I.	small	15	pebbly, above mu
16 UU	along SW side Slate I.	300 long	20	schist debris, ab
17 UU	SE side, small I.	small	15-20	very rocky
18 UU	off E point, I.	very small	15	rocky-pebbly
19 UU	off NE point, I.	2 concs. only	15	rocky-pebbly
20 UU	70' SW of SW I. tip	small	10-15	rocky-pebbly
21 UU	40' off SW I. tip	small	15-20	rocky-pebbly
22aUU	30' off SW I. tip	very small	15-20	slaty, above mu
22bUU	30' S of E end, same I.	very small	15-20	slaty, above mu
23aUU	25' S off NE point	very small	15	schist debris
23bUU	50' NE off same point	very small	15	schist debris
23cUU	30' N off same point	one conc. only	15	schist
24 MU	along SE side, near SW end of I.	150 ENE x 10	15-20	sand off boulde
25 MU	35' S of small I.	15 x 15	15	rocky, above
26aMU	15' SW of SW tip of I.	small	10-15	sandy off boulc
26bMU	20' S of point, SW of same I.	small	10-15	sandy off boulc
27 MU	W end deposit begins 50' SW of I.	100 NE x 20	15-20	sandy-pebbly
28 LU	50' S of S end of I.	10 x 20	15	sand some vege
29 LU	S of SW tip of Boyes I.	30 EW x 15	25-30	rock rubble, lit
30aLU	S side of I.	small	15	pebbly-sandy
30bLU	40' E of 30a	small	15	pebbly-sandy
31 UM	75' S of point, E side Narrows	small	35	slaty
32 UM	100' S of SW end of I.	35 NE x 20'	25	pebbly-sandy
33 MM	300' S of E tip of I.	very small	10-15	rocky rubble
34 MM	75' NE of N tip of I.	60 x 20	35	pebbly-sandy
35 LL	50' W of Burnt I.	small	15	rubble
36 LL	N side of Jammer I.	small	10	pebbly-sandy
37-LL	40' W of W point, Cache I.	very small	19	rocky, very lit
38-LL	80' N of W point of small I.	very small	15	rocky, very lit
39-LL	40' W of island.	60 NE x 10	6-10	rocky, rubble
40-UL	30' N of Potato I.	small	20	rubble
41-UL	40' S of I. across from #2 Shaft	small	15-20	rubbly-sandy
42 UL	100' NW of I. with ventillation raise	undetermined	35-40	rubbly-sandy
43 UL	100' E of Discovery Point (#1 Shaft)	small	35-40	rubbly-sandy
44aUL	60' SW of W end of I.	small	20	rubbly
44b-UL	40' S of same I.	small	20	rubbly
45-UL	100' SE of I.	25 NE x 10	20	rubbly
46-UL	125' W of Yacht I.	30 E x 10	25	rubble-sand
47-LM	120' SW of SW end of I.	40 x 15	20	rubble-sand
48-LM	80' S of W end of I.	40 E x 10	20	sandy
49-LM	120' SW of I.	very small	12-15	rocky
50-LM	50' W of small I.	very small	10	rocky

* U-Upper; M-Middle; L-Lower;
first letter designates Lake section; second letter designates Lake

1 of

	Concretions		
	Concentration	Dominant Type	Remarks
	high	all kinds	emergent weeds; 'mossy' growths on some concs; concretions cemented together in places
	medium	discs, rings	
	medium	discs, top rings	
	f. high	discs	
	f. high	discs	submerged ridge on line with Is
	medium	discs	
	medium	discs	'moss' on some concs.
	sparse	discs, top rings	
	sparse	discs	
	medium	discs, top rings, slags	field plunges steeply WSW; 'moss' on some concs.
	sparse	mushrooms, top rings	'moss' on some concs.
	medium	discs	'moss' on some concs.
	medium	discs	
	sparse	incipient rings	
	very sparse	incipient rings	
	very sparse	incipient rings	
	very sparse	mushrooms, rings	
mud	very sparse	weak rings	some upperside 'moss'
	very sparse	weak mushrooms, rings	
	sparse	incipient rings	some 'mossy' uppersides
		weak rings	
	sparse	mushrooms, rings	some crust on boulders
	sparse	mushrooms, rings	
	very sparse	weak rings	
	very sparse	weak rings	
	very sparse	rings	
	very sparse	rings	
		ring	
	high	discs, rings, mushrooms	
	sparse	mushrooms, rings	
	sparse	mushrooms, rings	
s	sparse	mushrooms, rings	
	high	discs, mushrooms	emergent grasses below deposit; some concs. buried by ¼ - ½ in. sand.
tion	medium	discs, rings, mushrooms	
c sand	medium	mushrooms, rings	
	sparse	mushrooms, rings	
	sparse	mushrooms, rings	
	sparse	discs	'perfect' discs - no concavities
	medium	discs, rings	
	very sparse	rings	
	high	discs, rings, mushrooms	
	sparse	mushrooms, rings	
	sparse	mushrooms, rings	only Sta. where concs. not grabbed
sand	sparse	rings, top rings	
sand	sparse	rings, top rings	
	high	thick, multidecker rings	
	sparse	mainly rings	
	medium	mainly rings	
	high	discs, rings	local coalescence; covered by veneer of fine sediment (from raise?)
	f. high	rings	
	medium	rings	
	medium	rings	
	medium	rings, mushrooms	some bottom vegetation.
	medium	discs, rings	
	f. high	discs, rings	some concs. totally buried in sand.
	f. high	discs, rings	some concs. slightly buried
	very sparse	mushrooms, rings	
	very sparse	mushrooms, rings	

2 of 2

APPENDIX II

SEDIMENT CORE LOGS

Core 1 (7.5 cm) Sta 1

0-2 cm grey-brownish sand
2-7.5 cm grey-silty clay

Core 2 (10.5 cm) Sta 2

0-2 cm grey-brown gravelly sand
2-10.5 cm grey clay

Core 3 (15 cm) Sta 3

0-4 cm yellow-brown gravelly sand
4-15 cm grey gravelly sand grading down to sand

Core 4 (4.5 cm) Sta 4

0-4.5 cm dark brown gravel grading down to yellow-brown gravelly sand

Core 5 (5 cm) Sta 5

0-5 cm dark brown-grey gravelly sand grading to greyish sand

	Analyses (ppm)					
Interval	Mn	Fe	Cu	Ni	Co	Fe/Mn
0-2 cm	280	13,000	10	12	8	46
0-4 cm	430	19,500	28	24	11	45
0-4 cm	800	17,000	8	14	8	21
10-14 cm	182	12,000	12	16	7	71
0-4.5 cm	14,000	74,000	26	34	26	5
0-5 cm	250	13,000	14	18	8	52

APPENDIX II (cont'd)

SEDIMENT CORE LOGS

			Analyses (ppm)					
		Interval	Mn	Fe	Cu	Ni	Co	Fe/Mn
Core 6 (22 cm) Sta 6								
0-2 cm	gravel and grey clay	0-4 cm	350	14,600	63	16	8	42
2-22 cm	grey clay							
Core 7 (12 cm) Sta 7								
0-6 cm	brown sand grading to silty sand	0-4 cm	320	13,000	8	8	4	41
6-12 cm	grey clay	7-11 cm	138	13,000	18	16	8	94
Core 8 (18 cm) Sta 8								
0-2 cm	yellowish silty clay	0-4 cm	450	13,000	20	17	9	29
2-18 cm	grey clay with irregular silty and gritty horizons							
Core 10 (14 cm) Sta 10								
0-10 cm	yellow-brown gravelly sand	0-4 cm	900	9,400	9	9	6	10
10-14	grey sand							
Core 11 (14 cm) Sta 11								
0-7 cm	yellow-brown gravelly sand	0-4 cm	320	14,000	13	16	7	44
7-22 cm	grey gravelly sand							

APPENDIX II (cont'd)

SEDIMENT CORE LOGS

		Interval	Mn	Fe	Cu	Ni	Co	Fe/Mn
			Analyses (ppm)					
Core 24 (29.5 cm) Sta 24								
0-2 cm	yellow-brown sand	0-3 cm	600	12,000	6	8	6	20
2-14 cm	grey-silty clay	12-16 cm	550	34,600	65	54	24	63
14-29.5 cm	light Indian red clay; calcareous-HCl positive	23-27 cm	1,250	60,000	90	70	28	48
Core 26 (34 cm) Sta 26								
0-6 cm	yellow-grey gravelly-sand	0-5 cm	300	19,500	24	20	10	65
6-7 cm	light Indian red clay							
7-34 cm	grey silty sand with odd laminae of coarse sand	29-33 cm	133	13,500	22	19	8	102
Core 28 (5 cm) Sta 28								
0-5 cm	yellow-brown gravelly sand	0-5 cm	400	17,000	10	14	8	43
Core 30 (5 cm) Sta 30								
0-5 cm	yellow-brown slightly gravelly sand	0-5 cm	220	22,000	12	24	11	100
Core 32 (24 cm) Sta 32								
0-15 cm	brown slightly gravelly sand grading down to brown sand	0-4 cm	420	39,500	14	11	9	94
		9-13 cm	144	14,000	16	21	11	97
15-24 cm	grey silty sand	19-23 cm	70	8,000	10	12	6	114

APPENDIX II (cont'd)

SEDIMENT CORE LOGS

		Interval	Mn	Fe	Cu	Ni	Co	Fe/Mn
			Analyses (ppm)					
Core 34 (10 cm) Sta 34								
0-2 cm	yellow-grey sand	0-2 cm	550	11,000	8	12	6	20
2 cm-10 cm	grey silt and clay	6-10 cm	122	12,000	16	6	8	98
Core 41 (8 cm) Sta 41								
0-7 cm	yellow-brown slightly gravelly sand	0-4 cm	90	6,700	6	12	8	74
7-8 cm	dark grey slightly gravelly sand							
Core 46 (7 cm) Sta 46								
0-3 cm	yellow-brown gravelly sand	0-3 cm	250	10,000	8	14	7	40
3-6 cm	light Indian red clay							
Core 47 (28 cm) Sta 47								
0-6.5 cm	yellow-brown gravelly sand	0-4 cm	280	13,000	14	20	12	46
65-28 cm	light Indian red silty clay interfingered with grey silty sand; red clay calcareous-HCl positive	23-27 cm	460	32,000	65	45	20	70

APPENDIX II (cont'd)

SEDIMENT CORE LOGS

Core 48 (34 cm) Sta 48

0-4.5 cm	yellow-grey slightly gravelly sand
4.5-34 cm	grey sand occ. streaked with yellow-grey

	Analyses (ppm)					
Interval	Mn	Fe	Cu	Ni	Co	Fe/Mn
0-5 cm	150	9,000	8	10	6	60
29-33 cm	82	10,600	14	16	7	129

APPENDIX III.

Shebandowan lake and stream water sample (1970) analyses (AA following HNO_3 - HCl extraction -, by Bondar-Clegg & Co. Ltd., Ottawa).

Sample No.	Mn ppb	Fe ppb	Sample No.	Mn ppb	Fe ppb
Station 1	9	165	Station 39	12	215
2	12	160	40	4	115
3	85	710	41	4	105
4	4	112	100	90	700
5	12	145	101	5	80
6	15	150	102	28	220
7	20	190	103	25	190
8	170	910	104	7	130
11	40	295	105	43	520
12	32	155	106	20	440
18	10	265	107	20	330
20	15	145	108	68	485
22	11	100	109	290	1,800
24	72	725	110	52	820
26	18	200	111	7	210
27	7	110	112	145	2,000
28	7	90	113	142	490
29	45	300	114	30	300
30	5	100	115	33	950
31	15	155	116	5	260
32	12	155	117	28	420
34	3	165	118	6	135
35	4	90	119	6	155
37	6	120	120	3	95
38	5	127			

APPENDIX IV

Appendix IVa. Mean Analyses of Shebandowan Concretions Calculated by 4 Methods

Sample		Fe%	Mn%	K (ppm)	Ca%	Mg (ppm)	Cu (ppm)	Zn (ppm)	Ni (ppm)	Co (ppm)	Depth (ft)
Mean	72*	42.5	6.30	242	0.563	768	33	261	105	109	21
	71*	42.6	6.24	231	0.552	702	32	260	104	106	21
	69*	42.7	6.15	222	0.550	688	31	262	104	105	
	49*	43.1	5.65	199	0.536	658	31	273	100	102	21
Standard Deviation	72	3.17	2.92	163	0.172	615	15.6	59.0	27.2	29.7	
	71	3.15	2.90	134	0.146	251	14.1	59.3	26.2	22.1	–
	69	3.27	2.88	127	0.150	244	14.3	59.8	26.8	21.5	
	49	2.80	2.71	118	0.143	232	15.8	64.0	24.1	20.1	
Skew	72	−0.08	0.03	1.85	1.37	6.23	3.94	1.11	0.62	2.49	0.64
	71	−0.11	0.05	0.72	0.34	1.09	4.62	1.12	0.57	0.32	0.66
	69	−0.05	0.11	0.78	0.41	1.24	4.62	1.10	0.66	0.31	–
	49	−0.15	0.17	0.15	0.71	1.64	4.71	0.85	0.67	0.37	0.62

*72 – all 72 analyses.
71 – 71 analyses; anomalous Tr 8-12 omitted.
69 – 138 (69 replicate) analyses; Excluded: Sta 1 and Tr. 1-55 for which replicates lacking, and anomalous Tr. 8-12.
49 – 49 stations; all analyses for each station first averaged on per concretion basis; Tr 8-12 excluded in averaging Station 8.

Appendix IVb. Table of Anomalous Samples (Values in excess of 2 or 3 Standard Deviations for 72 Analyses)

Sample		Fe%	Mn%	K	Ca	Mg	Cu	Zn	Ni	Co
Sta	3	-2	+2						+2	
Tr	5-1	-2							+2	
Tr	8-11	-2							+2	
Tr	8-12			+3	+3	+3	+3	+2	+2	+3
Sta	13							+3		
Sta	19									
Sta	20	+2						+2		
Sta	26									
Tr	27-4	+2					+3			
Sta	40			+2	+2					

DIVISION			BACILLARIOPHYTA											CHRYSOPHYTA		PYRROPHYTA			CRYPTOPHYTA			CYANOPHYTA			
DATE	STATION	DEPTH / GENUS	ASTERIONELLA	CYMBELLA	FRAGILARIA	MELOSIRA	NAVICULA	NITZSCHIA	PINNULARIA	STEPHANODISCUS	SYNEDRA	TABELLARIA	UNIDENTIFIED	DINOBRYON	OPHIOCYTIUM	CERATIUM	GLENODINIUM			CRYPTOMONAS		ANABAENA	APHANOCAPSA GROUP	CHROOCOCCUS GROUP	OSCILLATORIA
15 JULY 1970	A	3'-0"								■	■			■						■			■	■	
		10'-0"								■	■			■						■				■	
	B	3'-0"	■							■	■			■						■		■	■	■	
		15'-0"								■		■	■	■						■			■	■	
	C	3'-0"								■		■		■		■				■		■	■	■	
		15'-0"								■		■		■						■			■		
	D	3'-0"								■		■		■	■					■			■	■	■
		15'-0"								■	■	■		■						■			■	■	
	E	3'-0"								■				■		■						■	■		
		15'-0"	■							■		■		■						■		■	■	■	
	F	3'-0"								■		■		■						■		■		■	
		15'-0"	■		■					■				■		■				■		■	■	■	
11 AUGUST 1970	A	3'-0"					■			■	■			■						■					
		10'-0"			■		■	■		■	■	■		■						■		■	■		
	B	3'-0"	■				■				■									■		■	■		
		15'-0"	■		■					■	■	■								■		■			
	C	3'-0"								■		■								■		■			■
		15'-0"	■		■	■				■	■	■		■		■				■		■	■	■	
	D	3'-0"	■							■										■		■	■	■	■
		15'-0"	■		■					■		■	■							■			■	■	■
	E	3'-0"			■	■				■	■			■		■				■		■		■	■
		15'-0"	■	■	■	■				■	■	■		■						■			■	■	
	F	3'-0"	■		■					■		■		■						■		■	■	■	
		15'-0"	■				■			■	■	■	■	■						■		■		■	■
15 SEPTEMBER 1970	A	3'-0"	■		■	■			■	■	■	■		■		■				■		■	■	■	■
		10'-0"	■	■	■	■	■		■	■	■	■		■		■				■		■	■	■	■
	B	3'-0"	■		■	■					■	■		■						■		■	■	■	■
		15'-0"	■		■		■		■	■	■	■		■		■				■		■	■	■	■
	C	3'-0"	■	■	■	■	■			■	■	■		■		■				■		■	■	■	■
		15'-0"	■		■	■			■	■	■	■		■		■				■		■	■	■	■
	D	3'-0"	■		■					■	■	■		■						■		■	■	■	■
		15'-0"	■		■	■			■	■	■	■		■		■				■		■	■	■	■
	E	3'-0"	■		■	■				■	■	■		■		■				■		■	■	■	■
		15'-0"	■	■	■	■			■	■	■	■		■		■				■		■	■	■	■
	F	3'-0"	■		■	■			■	■	■	■		■								■	■	■	■
		15'-0"	■		■	■			■	■	■	■		■						■		■	■	■	■

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LAKE SHEBANDOWA-
PHYTOPLANKTON SURVEY

CHLOROPHYTA														EUGLENO-PHYTA			DIVISION		
COSMARIUM	CRUCIGENIA	EUASTRUM	? GONIUM	NEPHROCYTIUM	PANDORINA	PEDIASTRUM	SCENEDESMUS	SPHAERO-ZOSINA	SPONDYL-OSIUM	STAURASTRUM	TETRAEDON	XANTHIDIUM	UNIDENTIFIED		EUGLENA		GENUS / DEPTH	STATION	DATE
																	3'-0"	A	15 JULY 1970
							■						■				10'-0"		
	■				■								■				3'-0"	B	
																	15'-0"		
	■				■												3'-0"	C	
													■				15'-0"		
																	3'-0"	D	
					■												15'-0"		
																	3'-0"	E	
																	15'-0"		
																	3'-0"	F	
													■				15'-0"		
																	3'-0"	A	11 AUGUST 1970
													■		■		10'-0"		
													■				3'-0"	B	
					■										■		15'-0"		
													■				3'-0"	C	
										■							15'-0"		
															■		3'-0"	D	
■																	15'-0"		
■													■				3'-0"	E	
															■		15'-0"		
																	3'-0"	F	
■										■					■		15'-0"		
■					■							■	■		■		3'-0"	A	15 SEPTEMBER 1970
■					■	■				■		■	■		■		10'-0"		
■					■			■		■			■				3'-0"	B	
					■		■			■			■		■		15'-0		
				■	■							■	■		■		3'-0"	C	
■					■								■		■		15'-0"		
■					■					■		■	■		■		3'-0"	D	
■					■							■	■		■		15'-0"		
■					■								■		■		3'-0"	E	
■												■	■		■		15'-0"		
■					■					■			■		■		3'-0"	F	
■					■								■		■		15'-0"		

■ ORGANISMS PRESENT ONL SMALL NUMBERS.

■ ORGANISMS MAKING UP 10% OF THE POPULATIO REPRESENTING THE DOM-GENERA.

APPENDIX V

REPRODUCED FROM RASBERRY ET AL

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APPENDIX VI

Water chemistry at two Shebandowan concretion stations, July 13, 1970. Readings (unpublished) by R.A. Ryder.

STATION 1

Barometric pressure 29.58 in TDS 56 mg/l

Depth (m)	Temp. (°C)	O_2 (mg/l)	pH	Turb. (JTU)	Color (HU)
0	22.0	9.0	7.3	0.7	15.0
1	22.0				
2	22.0				
3	22.0				
4	21.5				
4.5		9.0	7.2		15.0
5	19.5				
6	19.0				
7	18.0				
7.2	18.0	9.0	7.1	1.7	15.0

STATION 5

Barometric pressure 29.58 in TDS 32 mg/l

Depth (m)	Temp. (°C)	O_2 (mg/l)	pH	Turb. (JTU)	Color (HU)
0	23.5	8.0	7.2	---	---
1	23.0				
2	22.0				
3	20.0				
4	19.0				
5	18.0				
6	17.0				
7	14.0	8.0	6.6	1.2	30.0
8	9.0	8.0	6.5	1.5	30.0
8.5	9.0				

APPENDIX VII

LOCATION OF CONCRETION (1-50) AND WATER SAMPLE (100-120) STATIONS.

(Determinations from Ont. Lands and Forests 1": ¼mi. base maps)

STA	LATITUDE	LONGITUDE	STA	LATITUDE	LONGITUDE
1 from	48°38.96'	90°24.31'	34	48°38.20'	90°14.80'
to	39.00'	24.21'	35	36.53'	11.43'
2	39.03'	20.15'	36	36.42'	10.52'
3	39.06'	20.08'	37	36.96'	07.71'
4	38.81'	15.73'	38	36.77'	06.26'
5TR from	38.66'	15.86'	39	37.20'	03.82'
to	38.78'	15.76'	40	35.74'	13.45'
6	37.26'	13.72'	41	35.91'	14.60'
7-1	38.60'	15.88'	42	35.87'	15.46'
7-2	38.60'	15.90'	43	35.98'	16.01'
7-3	38.60'	15.92'	44a	35.74'	15.49'
8	39.18'	19.46'	b	35.72'	15.46'
9	39.84'	19.11'	45	36.83'	13.99'
10	39.83'	19.10'	46	36.28'	14.11'
11	38.76'	16.79'	47	37.65'	13.32'
12	35.08'	31.32'	48	37.60'	13.06'
13	35.70'	31.02'	49	38.23'	13.02'
14	35.65'	30.53'	50	37.98'	12.67'
15	35.94'	30.44'			
16 from	35.92'	30.20'	100	35.53'	17.24'
to	35.97'	30.10'	101	36.52'	28.22'
17	35.98'	29.80'	102	34.74'	31.40'
18	36.47'	30.02'	103	34.69'	31.49'
19	36.40'	28.85'	104	38.37'	21.83'
20	36.63	28.90'	105	34.24'	32.87'
21	37.05'	28.67'	106	35.65'	31.70"
22a	37.67'	27.99'	107	38.08'	10.68'
b	37.67'	27.92'	108	40.37'	17.64'
23a	37.58'	28.02'	109	38.63'	26.59'
b	37.60'	28.02'	110	36.74'	30.94'
c	37.60'	28.04'	111	39.34'	25.06'
24	37.71'	27.21'	112	37.23'	30.00'
25	38.02'	26.25'	113	39.96'	20.62'
26a	38.68'	25.21'	114	39.10'	14.93'
b	38.66'	25.26'	115	38.12'	05.77'
27 from	38.56'	25.12'	116	37.21'	03.58'
to	38.56'	25.17'	117 (roughly)	36.2'	04.4'
28	38.13'	24.30'	118	37.20'	03.64'
29	37.59	23.11'	119	37.22'	03.69'
30a	38.13'	22.20'	120	36.90'	09.67'
b	38.14'	22.17'			
31	38.52'	21.76'			
32	38.93'	20.91'			
33	39.03'	18.39'			

APPENDIX VIII

Precision and accuracy of analyses

Owing to technical difficulties it was not possible to monitor or check the level of precision and accuracy in commercial analyses made for this thesis. Similarly, not enough is known concerning analytical methods employed and the precision and accuracy attained for data from publications and other sources, used for comparison with the basic thesis data. Any conclusions about the absolute concentrations of elements, particularly in trace quantities, and any comparisons of these must accordingly be guarded.

REFERENCES

Aarnio, B.,

1917: Järvimalmit eräissä Pusulan, Pyhäjärven, Lopen, Somerniemen ja Tammelan järvissä: Geotekn. Tied no. 20.

Aarnio, B.,

1918: Om sjömalmerna i några sjöar i Pusula, Loppis, Somerniemi och Tammela socknar: Geol. Komm. i Finland Geotekn. Medd., no. 20, p.77.

Armstrong, F.A.J., and Schindler, D.W.,

1971: Preliminary chemical characterization of waters in the Experimental Lakes Area, northwestern Ontario: J. Fish. Res. Bd., Canada, v.28, no. 1, p.171-187.

Austria, V.B.,

1970: The Cu, Pb, Zn, Mn and Mo content of stream and spring sediments, southwestern New Brunswick: Rept. of Invest. No. 11, Min. Res. Br., Dept. Nat. Res., Prov. New Bruns.

Beals, H.L.,

1966: Manganese - iron concretions in Nova Scotia Lakes: Maritime Sediments, v.2, p.70-72.

Béland, J.,

1961: Shawinigan Area: Que. Dept. Nat. Res., Geol. Rept. 97, p. 54.

Bell, J.W.,

1908: Quebec: in Mines Branch, Summ. Rept., 1907-1908, p. 19.

Bonatti, E., Kraemer, T., and Rydell, H.,

1972: Classification of submarine iron - manganese deposits: in D.R. Horn, (Ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs., I.D.O.E., p. 149-166.

Brunskill, G.J., Povoledo, D., Graham, B.W., and Stainton, M.P.,

1971: Chemistry of surface sediments of sixteen lakes in the Experimental Lakes Area, northwestern Ontario: J. Fish, Res. Bd., Can., v.28, no. 1, p.277-294.

Brunskill, G.J., and Schindler, D.W.,

1971: Geography and Bathymetry of selected lake basins, Experimental Lakes Area, northwestern Ontario: J. Fish, Res. Bd. Can., v.28, no. 1, p. 139-155.

Burns, R.G., and Brown, B.A.,

1972: Nucleation and mineralogical controls on the composition of manganese modules: in D.R. Horn, (Ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs., I.D.O.E., p. 51-62.

Burns, R.G., and Fuerstenau, D.W.,
1966: Electron-probe determination of inter-element relationship in manganese nodules: Am. Mineralogist, v.51, p.895-902.

Callender, E.,
1968: Manganese: the discovery of a new mineral resource in the Great Lakes: Limnos, v.1, no.4, p.22-25.

Carpenter, R., Johnson, H.P., and Twiss, R.S.,
1972: Thermomagnetic behaviour of manganese nodules: J. Geoph. Res., v.77, no. 36, p.7163-7174.

Carpenter, R., and Wakeham, S.G.,
1973: Mössbauer studies of marine and fresh water manganese nodules: Chem. Geol., v.11, no. 2, p.109-116.

Chave, K.E., and Mackenzie, F.T.,
1961: A statistical technique applied to the geochemistry of pelagic muds: Jour. Geology, v.69, p.572-582.

Collins, J.F., and Buol, S.W.,
1970a: Effects of fluctuations in the Eh-pH environment on iron and/or manganese equilibria: Soil Science, v.110, no. 2, p.111-118.

Collins, J.F., and Buol, S.W.,

1970b: Patterns of iron and manganese precipitation under specified Eh-pH conditions: Soil Science, v.110, no. 3, p.157-162.

Cronan, D.S.,

1969: Inter-element associations in some pelagic deposits: Chem. Geol., v.5, p. 99-106.

Cronan, D.S., and Thomas, R.L.,

1970: Ferromanganese concretions in Lake Ontario: Can. J. Earth. Sci., v.7, p.1346-1349.

Cronan, D.S., and Thomas, R.L.,

1972: Geochemistry of ferromanganese oxide concretions and associated deposits in Lake Ontario: Geol. Soc. Amer., Bull., v.83, no. 5, p.1493-1501.

Cronan, D.S.,

1972: Regional geochemistry of ferromanganese nodules in the world ocean: in D.R. Horn, (Ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs., I.D.O.E. p.19-30.

Cronan, D.S., and Tooms, J.S.,

1969: The geochemistry of manganese nodules and associated pelagic deposits from the Pacific and Indian Oceans: Deep-Sea Res., v.16, p.335-359.

Dean, W.E.,

1970a: Fe-Mn oxidate crusts in Oneida Lake, New York: Conf. Great Lakes Res. Proc., no. 13, pt. 1, p.217-226.

Dresser, J.A., and Denis, T.C.,

1949: Geology of Quebec, v.3, Economic Geology: Que. Dept. Mines, Geol. Report., 20.

Edgington, D.N., and Callender, E.,

1970: Minor element geochemistry of Lake Michigan ferromanganese nodules: Earth Plan. Sc. Let., v.8, p. 97-100.

Ells, R.W.,

1898: Geology of the Three Rivers map sheet: Geol. Surv. Can. Ann. Rept., v.XI, pt. J, p.59-61.

Folk, R.L.,

1961: Petrology of sedimentary rocks: Hemphill's, p.154.

Forsyth, J.B., Hedley, J.G., and Johnson, C.E.,

1968: The magnetic structure and hyperfine field of goethite (α-FeOOH): Phys. C. (Proc. Phys. Soc.), Ser. 2, v.1, p.179-187.

Gager, H.M.,

1968: Mössbauer spectra of deep-sea iron-manganese nodules: Nature, v.220, p.1021-1023.

Garrett, R.G.,

1969: The determination of sampling and analytical errors in exploration geochemistry: Econ. Geol., v.64, no. 5, p.568-569.

Garrett, R.G.,

1973: The determination of sampling and analytical errors in exploration geochemistry - a reply: Econ. Geol., v.64, no. 2, p.282-283.

Gibbs, R.J.,

1973: Mechanism of trace metal transportation in rivers: Science, v.180, p.71-73.

Giblin, P.E.,

1964: Burchell Lake Area: Ont. Dept. Mines, Geol. Rept. 19, p.39, 1 map.

v.d. Giessen, A.A.,

1967: Magnetic properties of ultra-fine iron (III) oxide-hydrate particles prepared from iron (III) oxide-hydrate gels: J. Phys. Chem. Solids, v.28, p.343-346.

Glasby, G.P.,

1972: The geochemistry of manganese nodules from the northwest Indian Ocean: in D.R. Horn, (Ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs., I.D.O.E., p.93-104.

Gorham, E.,

1958: The Physical limmology of Northern Britain: Limmol & Oceanog., v.3, no. 1, p.40-50.

Gorham, E., and Swaine, D.J.,

1965: The influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments: Limmol and Oceanog., v.10, no. 2, p.268-279.

Greenslate, J.,

1974: Microorganisms participate in the construction of manganese nodules: Nature, v.247 (in press).

Greeson, P.E.,

1971: Limnology of Oneida Lake with emphasis on factors contributing to algal blooms: U.S. Geol. Sur., open-file rept., Albany, N.Y.

Hanson, G.,

1932: Manganese deposits of Canada: Geol. Surv. Can., Econ. Geol. Ser., no. 12, Ottawa, p.120.

Harris, R.C., and Troup, A.G.,

1969: Freshwater ferromanganese concretions: chemistry and internal structure: Science, v.166, no. 3905, p.604-606.

Harris, R.C., and Troup, A.G.,

1970: Chemistry and origin of freshwater ferromanganese concretions: Limnol. Oceanogr., v.15, no. 5, p.102-712.

Hayes, F.R., Reid, B.L., and Cameron, M.L.,

1958: Lake water and sediment: II. Oxidation - reduction relations at the mud-water interface: Limmol. and Oceanog., v.3, no. 3, p.308-317.

Hem, J.D., and Cropper, W.H.,

1959: Survey of ferrous-ferric chemical equilibrium and redox potential: U.S.G.S. Water Supply Paper 1459 - A, p.31.

Hem, J.D., and Skougstad, M.W.,

1960: Coprecipitation effects in solutions containing ferrous, ferric, and cupric ions: U.S.G.S. Water Supply Paper 1459 - E, p.95-110.

Hem, J.D.,

1963: Chemical equilibria and rates of manganese oxidation: U.S.G.S. Water Supply Paper 1667 - A, p.74.

Hem, J.D.,

1964: Deposition and solution of manganese oxides: U.S.G.S. Water Supply Paper 1667 - B, p.42.

Hem, J.D.,

1965: Reduction and complexing of manganese by gallic acids: U.S.G.S. Water Supply Paper 1667 - D, p.28.

Hem, J.D.,

1970: Study and interpretation of the chemical characteristics of natural water: U.S.G.S. Water Supply Paper 1473, p.363.

Herzenberg, C.L.,

1969: Mössbauer spectrometry as an instrumental technique for determinative mineralogy: In I.J. Gruverman (Ed.), Mössbauer effect methodology, v.5, p.209-230.

Herzenberg, C.L., and Riley, D.L.,

1969: Interpretation of the Mössbauer spectra of marine iron-manganese nodules: Nature, v.224, p.259-260.

Hills, G.A., and Morwick, F.F.,

1944: Reconnaissance soil survey of parts of northwestern Ontario: Rept. no. 8, Ont. Soil Survey; Exper. Farms Service, Domin. Dept. Agric. and Ont. Agric. College.

Hodgkinson, J.M.,

1968: Geology of the Kashabowie Area: Ont. Dept. Mines, Geol. Rept. 53, p.35, 2 maps.

Horn, D.R., Horn, B.M., and Delach, M.N.,

1972: Distribution of ferromanganese deposits in the world ocean: in D.R. Horn (Ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs.; I.D.O.E., p.9-18.

Hough, J.L.,

1958: Geology of the Great Lakes: Univ. Illinois Press, p.313.

Howard, H.H., and Chisholm, S.W.,

1972: Manganese budget of a eutrophic lake (abstract): In Northeastern Section, 7th Annual Meeting, Geol. So. Am. Abstr., v.4, no. 1, p.22.

Hrynkiewicz, A.Z., Sawicka, B.D., and Sawicki, J.A.,

1970: The Mössbauer effect in the Pacific Ocean Fe-Mn nodules: Phys. Stat. Sol. (a) 3, p. 1039-1045.

Hutchinson, G.E.,

1957: A treatise in limnology. Vol. 1. Geography, physics and chemistry: John Wiley & Sons, New York, p.1010.

Ivarson, K.C., and Heringa, P.K.,

1972: Oxidation of manganese by microorganisms in manganese deposits of Newfoundland soil: Can. J. Soil Sci., v.52, p.401-416.

Jenne, E.A.,

1968: Controls of Mn, Fe, Co, Ni, Cu and Zn in concentrations in soils and water: the significant role of hydrous Mn and Fe oxides: In: Trace inorganics in water; Amer. Chem. Soc., Advances in Chem. Series 73, p.337-387.

Johnson, C.E., and Glasby, G.P.,

1969: Mössbauer effect determination of particle size in micro-crystalline iron-manganese nodules: Nature, v.222, p.376-377.

Johnson, D.G.,

1969: Ferromanganese concretions in Lake Champlain: M.S. Thesis, Vermont Univ., Burlington, p.96.

Keele, J.,

1924: Preliminary report on the clay and shale deposits of Ontario: Geol. Surv. Can., Mem. 142, p.125-129.

Kindle, E.M.,

1932: Lacustrine concretions of manganese: Am. J. Sc., v.24, p.496-504.

Kindle, E.M.,

1935: Manganese concretions in Nova Scotia lakes: Roy. Soc. Can. Trans., sect. V, p.163-180.

Kindle, E.M.,

1936: The occurrence of lake bottom manganese deposits in Canadian lakes: Econ. Geol., v.31, no. 7, p.755-760.

Van der Kraan, A.M., and Van Loeff, J.J.,

1966: Superparamagnetism in submicroscopic α-FeOOH particles observed by the Mossbauer effect: Phys. Letters, v.20, no. 6, p.614-616.

Krauskopf, K.B.,

1956: Factors controlling the concentrations of thirteen rare metals in sea-water: Geochim. et Cosmochim. Acta, v.9, p.1-32B.

Krauskopf, K.B.,

1957: Separation of manganese from iron in sedimentary processes: Geochim. et Cosmochim. Acta, v.12, p.61-84.

Krauskopf, K.B.,

1967: Introduction to geochemistry: McGraw-Hill, Inc, p.721.

Kuznetsov, S.J.,

1968: Recent studies on the role of microorganisms in the cycling of substances in lakes: Limnol. and Oceanog., v.13, no. 2, p.211-224.

Lerman, A., and Brunskill, G.J.,

1971: Migration of major constituents from lake sediments into lake water and its bearing on lake water composition: Limnol. and Oceanog. v.16, no.6, p.890.

Ljunggren, P.,

1953: Some data concerning the formation of manganiferous and ferriferous bog ores: Geol. Fören. Stockholm Förhandl., bd. 75, h. 2, p.277-297.

Ljunggren, P.,

1955a: Geochemistry and radioactivity of some Mn and Fe bog ores: Geol. Fören. Stockholm Förhandl., bd. 77, h. 1, p.33-43.

Ljunggren, P.,

1955b: Differential thermal analysis and X-ray examination of Fe and Mn bog ores: Geol. Förhandl., bd. 77, h. 2, p.135-147.

Lumsden, T.W., Bland, R., and Whitehead, R.,

1970: Report for 1969 on the water quality monitoring programme in the Lake Shebandowan area of Ontario: James F. MacLaren Ltd., Environ. Sc. Div., Toronto, p.27.

Mackereth, F.J.H.,

1966: Some chemical observations on post-glacial lake sediments: Phil. Trans. Roy. Soc. London, Ser. B, 250, p.165-213.

Manheim, F.T.,

1970: The diffusion of ions in unconsolidated sediments: Earth Planet, Sci. Lett., v.9, p.307-309.

Manheim, F.T.,

1965: Manganese-iron accumulations in the shallow marine environment: Symposium on Marine Geochemistry, Occ. Publ. no. 3 - 1965, Narrangansett Marine Laboratory, Univ. Rhode Island, p.217-276.

McInnes, W.,

1899: The geology of the area covered by the Seine River and Shebandowan map sheets, comprising portions of Rainy River and Thunder Bay Districts, Ontario: Geol. Surv. Can., Ann. Rept., v.X, pt. H, p.13-65.

McMahon, J.W.,

1969: The annual and diurnal variation in the vertical distribution of acid - soluble ferrous and total iron in a small dimictic lake: Limnol. and Oceanog., v.14, no. 3, p.357-367.

Mero, J.L.,

1972: Potential economic value of ocean-floor manganese nodule deposits: in D.R. Horn, (Ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs., I.D.O.E., p.191-204.

Moore, E.J.,

1910: The occurrence and origin of some bog iron deposits of Thunder Bay, Ontario: Econ. Geol., v.5, p.528-537.

Moore, E.S.,

1910: Bog iron on English River: 18th Ann. Rept. of Ont. Bur. Mines, part 1, p.180-195.

Morgan, J.J., and Stummn, W.,

1965: The role of multivalent metal oxides in limnological transformations, as exemplified by iron and manganese: In O. Jaag (Ed.) Proc. 2nd Intern. Conf. Water Pollution, Res. v.1, Pergammon Press, New York, p.103-131.

Morgenstein, M.,

1972: Manganese accretion at the sediment-water interface at 400 to 2,000 meters depth, Hawaiian Archipelago: in D.R. Horn, (Ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs., I.D.O.E., p.131-138.

Morin, J.A.,

1973: Geology of the Lower Shebandowan Lake Area, District of Thunder Bay: Ont. Div. Mines, Geol. Rept. 110, 45p.

Mortimer, C.H.,

1941: 1942 The exchange of dissolved substances between mud and water: J. Ecol. v.29, p.280-329; v.30, p.147-201.

Mortimer, C.H.,

1971: Chemical exchanges between sediments and water in the Great Lakes - speculations on probable regulatory mechanisms: Limnol. and Oceanog., v.16, no. 2, p.387-404.

Naplekova, N.N., et al.,

1970: Manganese fixation by cellulose - decomposing microorganisms: Soviet Soil Sci., v.2, p.41-48.

Naumann, E.,

1922: Södra och mellersta Sveriges sjö-och myrmalmer: Sveriges Geol. Unders., v.13 (1919), no. 6, Ser. C, no. 297, p.194.

Naumann, E.,

1930: Die Binnengewässer, Vol. IX: In Einführung in die Bodenkunde der Seen (A. Thienemann, ed.) E. Schweizerbartische Verlagsbuchhandlung, Stuttgart, p.126.

Oborn, E., and Hem, J.D.,

1962: Some effect of the larger types of aquatic vegetation on iron content of water: U.S.G.S. Water Supply Paper 1459 - I, p.237-268.

Perifilyev, B.V., and Gabe, D.F.,

1961: The capillary method for studies of micro-organisms. (in Russian): USSR Acad. Sci. Press, Moscow - Leningrad.

Perifilyev, B.V., and Gabe, D.F.,

1964: Investigation of manganese and iron bacteria in bottom sediments: USSR Acad. Sci., Moscow.

Phillips, D.W., and McCulloch, J.A.W.,

1972: The climate of the Great Lakes Basin: Climatol. Stud. no. 20, Environment Canada.

Ponnamperuma, F.N., Tianco, E.M., and Loy, T.,

1967: Redox equilibria in flooded soils: I. The iron hydroxide systems: Soil Sci., v.103, no. 6, p.374-382.

Ponnamperuma, F.N., Loy, T., and Tianco, E.M.,

1969: Redox equilibria in flooded soils: II. The manganese oxide systems: Soil Sci., v.108, no. 1, p.48-57.

Presant, E.W.,

1971: Geochemistry of iron, manganese, lead, copper, zinc, arsenic, antimony, silver, tin, and cadmium in the soils of the Bathurst area, New Brunswick: Geol. Surv. Can., Bull. 174, p.93.

Prest, V.K.,

1969: Retreat of Wisconsin and Recent ice in North America: Geol. Surv. Can., Map 1257A.

Price, N.B., and Calvert, S.E.,

1970: Compositional variation in Pacific Ocean ferromanganese nodules and its relationship to sediment accumulation rates: Marine Geol., v.9, p.145-171.

Raab, W.,

1972: Physical and chemical features of Pacific deep sea manganese nodules and their implication to the genesis of nodules: in D.R. Horn, (ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs., I.D.O.E., p. 31-50.

Rasberry, J.M., Bland, R., and Whitehead, R.,

1971: Report for 1970 on the water quality monitoring programme in the Lake Shebandowan area of Ontario: James F. MacLaren Ltd., Environm. Sc. Div., Toronto, p.34.

Rossiter, M.J., and Hodgson, A.E.M.,

1965: A Mössbauer study of ferric oxy-hydroxide: J. Inorg. Nucl. Chem., v.27, p.63-71.

Rossman, R., and Callender, E.,

1968: Manganese Nodules in Lake Michigan: Science, v.162, no. 3858, p.1123-1124.

Rossman, R., and Callender, E.,

1969: Geochemistry of Lake Michigan manganese nodules: 17th Conf. Great Lakes Res., Proc., p.306-316.

Ruttner, F.,

1953: Fundamentals of limnology: Univ. Toronto Press.

Ryder, R.A.,
1965: A method for estimating the potential fish production of north-temperate lakes: Trans. Amer. Fisheries Soc., v.94, no. 3, p.214-218.

Sapozhnikov, D.G., (ed.),
1970: Manganese deposits of the Soviet Union: Israel program for scientific translation, Jerusalem, p.522.

Savage, W.S.,
1936: Solution, transportation and precipitation of manganese: Econ. Geol., v.31, no. 3, p.278-297.

Schoettle, M., and Friedman, G.M.,
1971: Fresh water iron-manganese nodules in Lake George, New York: Geol. Soc. Am., Bull., v.82, p.101-110.

Shaw, D.M., Reilly, G.A., Muysson, J.R., Pattenden, G.E., and Campbell, F.E.,
1967: An estimate of the chemical composition of the Canadian Precambrian Shield: Can. J. Earth Sci. 4, p.829-853.

Shegelski, R.J.,
1971: The general stratigraphy and the iron and manganese beds of Thunder Bay: B.Sc. Thesis, Lakehead Univ., p.83.

Shinjo, T.,

1966: Mossbauer effect in antiferromagnetic fine particles: J. Phys. Soc. Japan, v.21, no. 5, p.917-922.

Shterenberg, L.E., Stravinskaya, E.A., and Uranova, O.V.,

1970: Basic processes controlling ore-formation in the lakes of the northern forest zone (based on Lake Punnus - Yarvi): Lithol. and Min. Res., no. 1, p.21-33.

Sidwell, K.O.,

1952: Manganese ore occurrences in New Brunswick: N.B. Res. Dev. Board, Fredericton, N.B.

Siuta, J., and Motowicka-Terelak, T.,

1969: The origin and systematics of ferruginous precipitates in Quarternary formations and in present day soils: Biul. Peryglac., no. 18, p.209-257.

Sorem, R.K., and Foster, A.R.,

1972: Internal structure of manganese nodules and implications in beneficiation: in D.R. Horn, (Ed.): Ferromanganese Deposits on the Ocean Floor; Lamont - Doherty Geol. Obs., I.D.O.E., p.167-182.

Strakhov, N.M.,

1966: Types of manganese accumulation in present-day basins: their significance in understanding of manganese mineralization: Internat. Geol. Rev., v.8, no. 10, p.1172-1196.

Strakhov, N.M.,

1968: Geokhimya osadochnogo margantsovorudnego processa: Nauka, p.495.

Stumm, W., and Morgan, J.J.,

1970: Aquatic chemistry: Wiley Interscience.

Tanton, T.L.,

1938a: Shebandowan Lake, Ontario: Geol. Surv. Can., Map 338A. Scale 1" :1 mi.

Tanton, T.L.,

1938b: Quetico sheet (east half), Ontario: Geol. Surv. Can., Map 432A, Scale 1" : 4 mi.

Taylor, S.R.,

1964: Abundance of chemical elements in the continental crust: a new table: Geochim. et Cosmochim. Acta, v.28, p.1273-1285.

Terasmae, J.,

1971: Notes on lacustrine manganese-iron concretions: Geol. Surv. Can., Paper 70-69, p.13.

Troup, A.G.,

1969: Geochemical investigation of ferromanganese concretions from three Canadian lakes: M.S. Thesis, McMaster Univ., p.76.

Twenhofel, H., McKelvey, V.E., Nelson, H.F., and Feray, D.E.,

1945: Sediments of Trout Lake, Wisconsin: Bull. Geol. Soc. Am., v.56, p.1099-1142.

Varentsov, I.M.,

1972: On the main aspects of formation of ferromanganese ores in Recent basins: 24th Intern. Geol. Cong., Sect. 4, Min. Dep., p.395-403.

Wanless, R.K.,

1970: Isotopic age map of Canada: Geol. Surv. Can., Map 1256A.

Wolfe, W.J.,

1973: Geochemical exploration in Archean metavolcanic-metasedimentary belts of the Puskaskwa region, Ontario: CIM Bull., v.66, p.75-83.

Yamamoto, N.,

1968a: The magnetic properties of the synthetic iron oxyhydrates: Bull. Inst. Chem. Res., Kyoto Univ., v.46, no. 6, p.275-282.

Yamamoto, N.,

1968b: The particle size dependence of the Néel temperature of α-FeOOH fine particles: Bull. Inst. Chem. Res., Kyoto Univ., v.46, no. 6, p.283-288.

Zapffe, C.,

1931: Deposition of manganese: Econ. Geol., v.26, p.799-832.

Zoltai, S.C.,

1963: Glacial features of the Canadian Lakehead area: Can. Geographer, v.7, no. 3, p.101-115.

Zoltai, S.C.,

1965a: Glacial features of the Quetico-Nipigon area, Ontario: Can. J. Earth Sc., v.2, no. 4, p.247-269.

Zoltai, S.C.,

1965b: Thunder Bay, surficial Geology: Ont. Dept. Lands & Forests, Map S - 265; Sc. 1" : 8 mi.

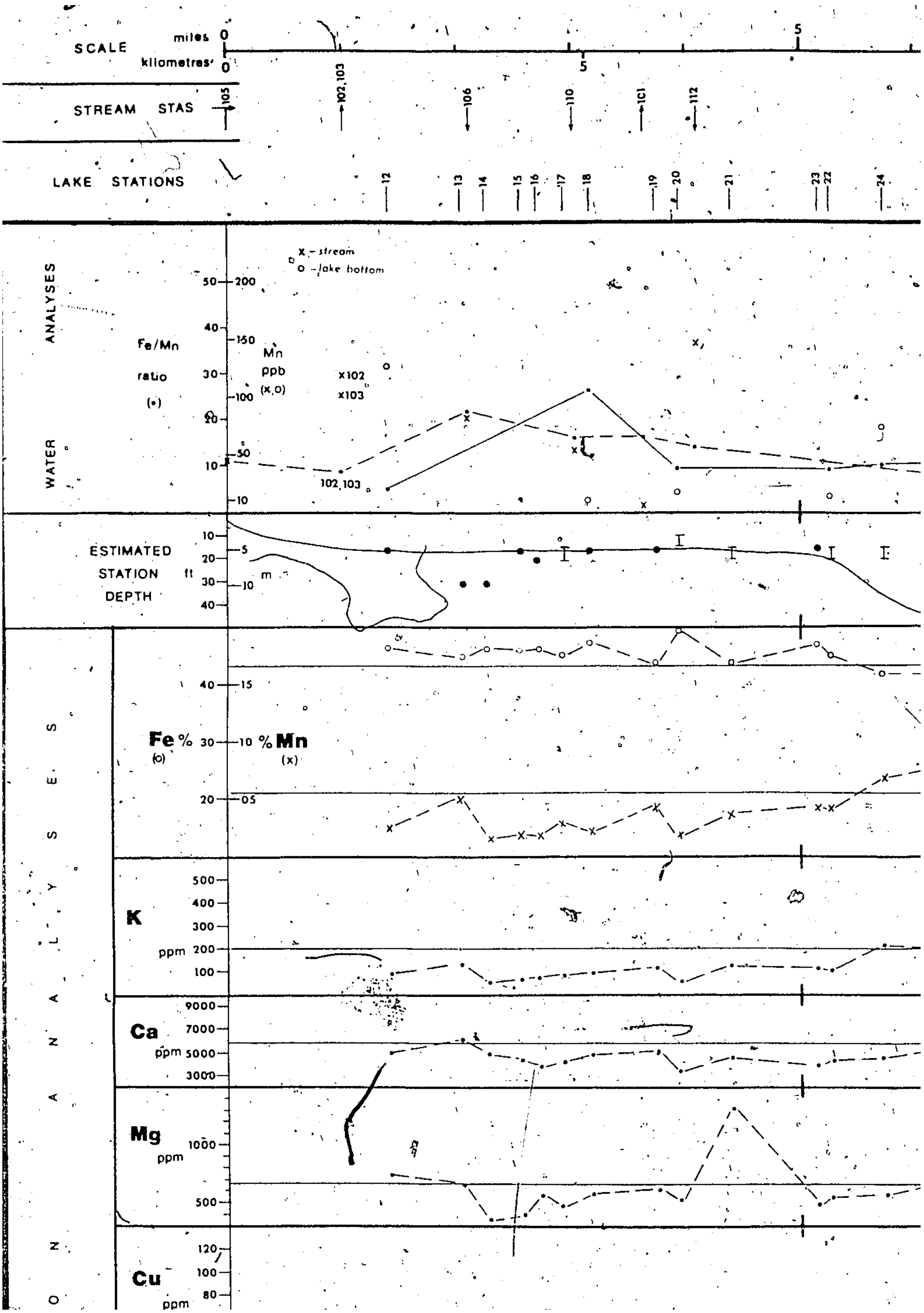
Zoltai, S.C.,

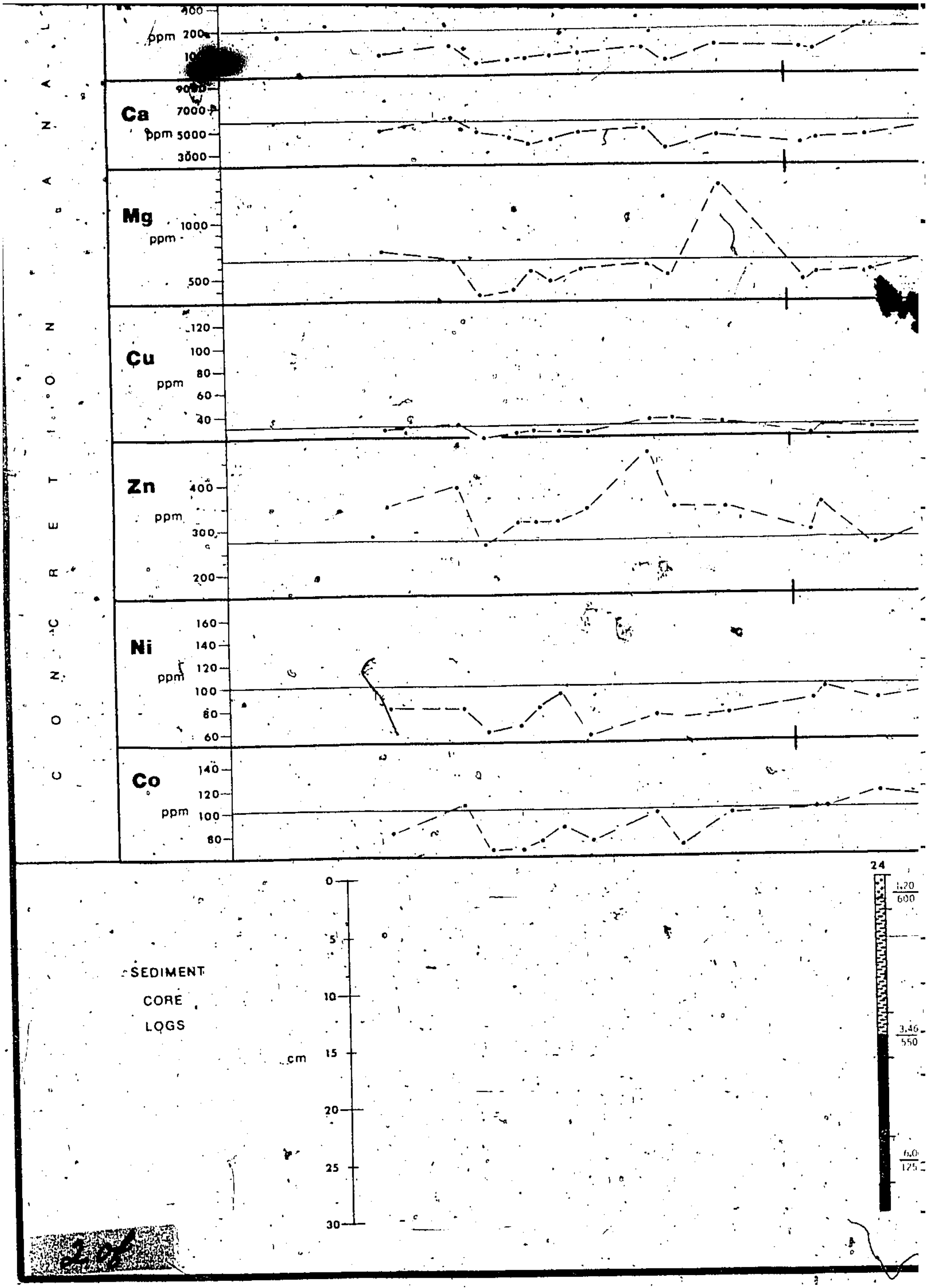
1965c: Forest sites of site regions 5S and 4S, northwestern Ontario: Ont. Dept. Lands & Forests Res. Rept. 65, p.1-121.

ABSTRACT

Littoral ferromanganese concretions have been collected from 50 localities in Shebandowan Lakes, Ontario, a multi-basin complex 30 miles long. The average composition of the concretions: 43.1% Fe, 5.65% Mn, 0.538% Ca, 200 ppm K, 669 ppm Mg, 31 ppm Cu, 273 ppm Zn, 101 ppm Ni and 102 ppm Co, is similar to that of concretions from other North American and Fennoscandian lakes. X-ray diffraction and Mössbauer spectroscopic methods detected the presence of goethite and other unidentified ferric oxyhydroxide minerals. Observation of the growth habits of hundreds of concretions show that they form at the sand-water interface by concentric accretion in that plane, with a tendency to deviate in both up and down directions at the edges, possibly illustrative of a dual source of elements. Partial re-solution of bottom and top concretion surfaces is likely responsible for maintaining the overall flat growth. Sediment cores at concretion sites have upwardly increasing Mn and Fe contents and Mn/Fe ratios, implying a diagenetic accrual of these metals to concretions by transport from profundal to littoral sediments. A hydrogenous component of the metals' accrual is indicated by the presence of upfolded edges on common discoid concretions and of upperside botryoidal growth, the latter best observed on mushroom-type morphologies. Somewhat higher Mn/Fe ratios in concretions of deposits sub-

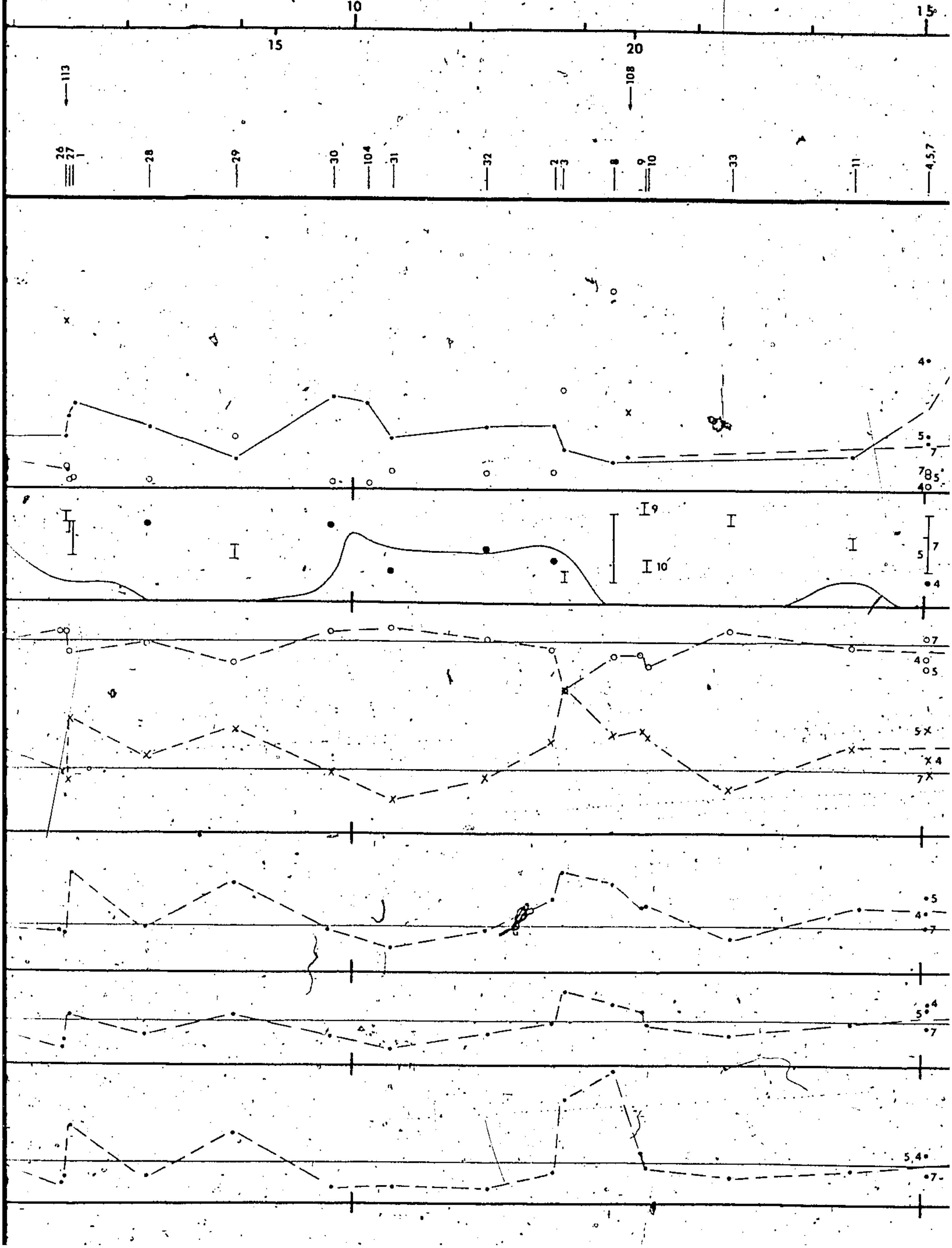
tending the deeper basins is probably explicable by diagenetic segregation of Mn and Fe over a longer distance than in shallower basins.

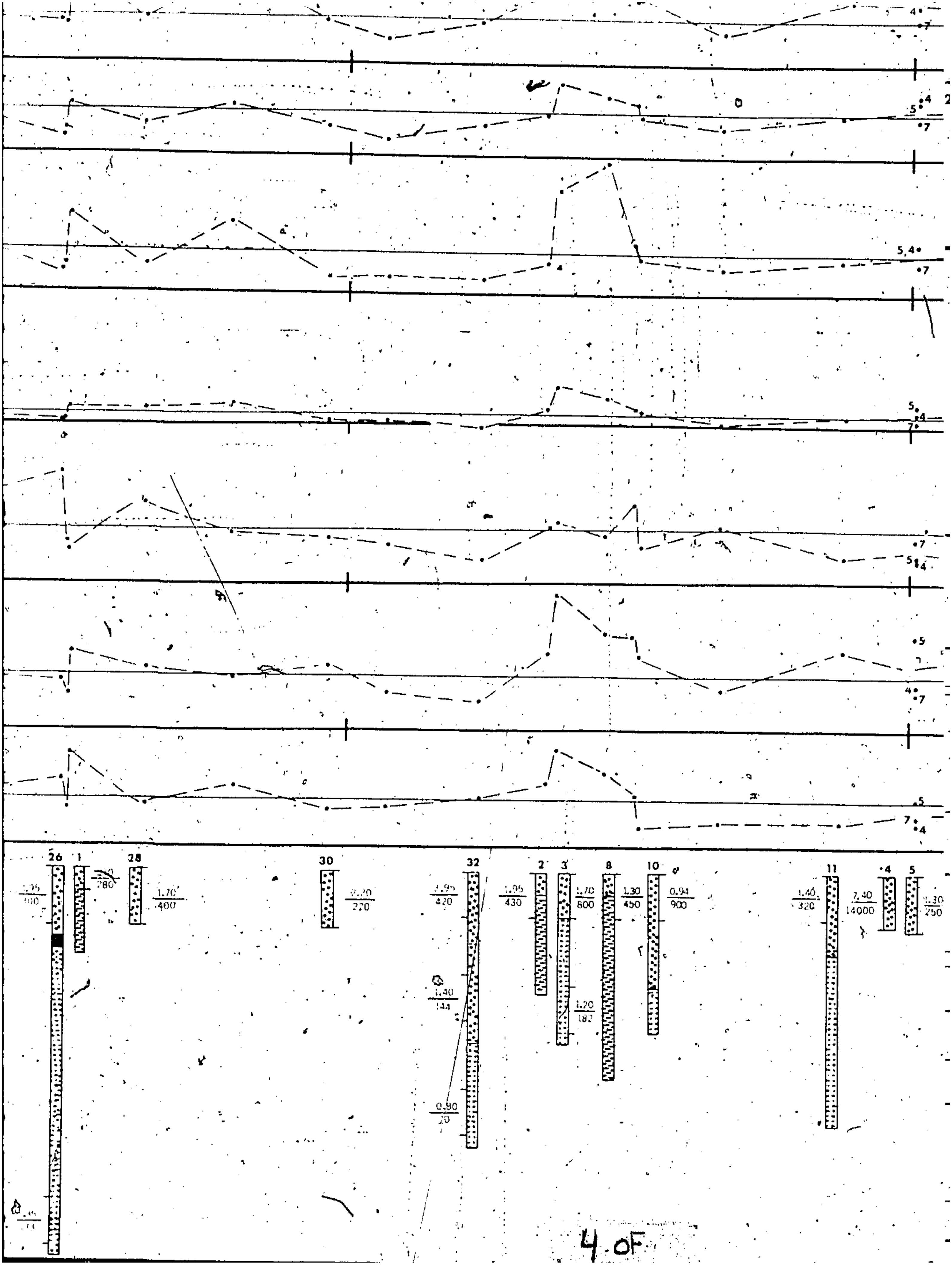

SCALE
miles 0
5
kilometres 0
5
STREAM STAS
105
102,103
106
110
101
112
LAKE STATIONS
12
13
14
15
16
17
18
19
20
21
23
22
24
WATER ANALYSES
x - stream
o - lake bottom
Fe/Mn ratio (•)
Mn ppb (x,o)
50
40
30
20
10
200
150
100
50
10
x102
x103
102,103
ESTIMATED STATION DEPTH
ft
m
10
20
30
40
5
10
ANALYSES
O N
Fe% (o)
%Mn (x)
40
30
20
15
10
05
K ppm
500
400
300
200
100
Ca ppm
9000
7000
5000
3000
Mg ppm
1000
500
Cu ppm
120
100
80


C O N C R E T I O N   A N A L
400
ppm 200
10
9000
Ca
7000
ppm 5000
3000
Mg
1000
ppm
500
120
Cu
100
80
ppm
60
40
Zn
400
ppm
300
200
160
Ni
140
120
ppm
100
80
60
Co
140
120
ppm
100
80
SEDIMENT
CORE
LOGS
0
5
10
cm
15
20
25
30
24
1.20
600
3.46
550
6.0
125

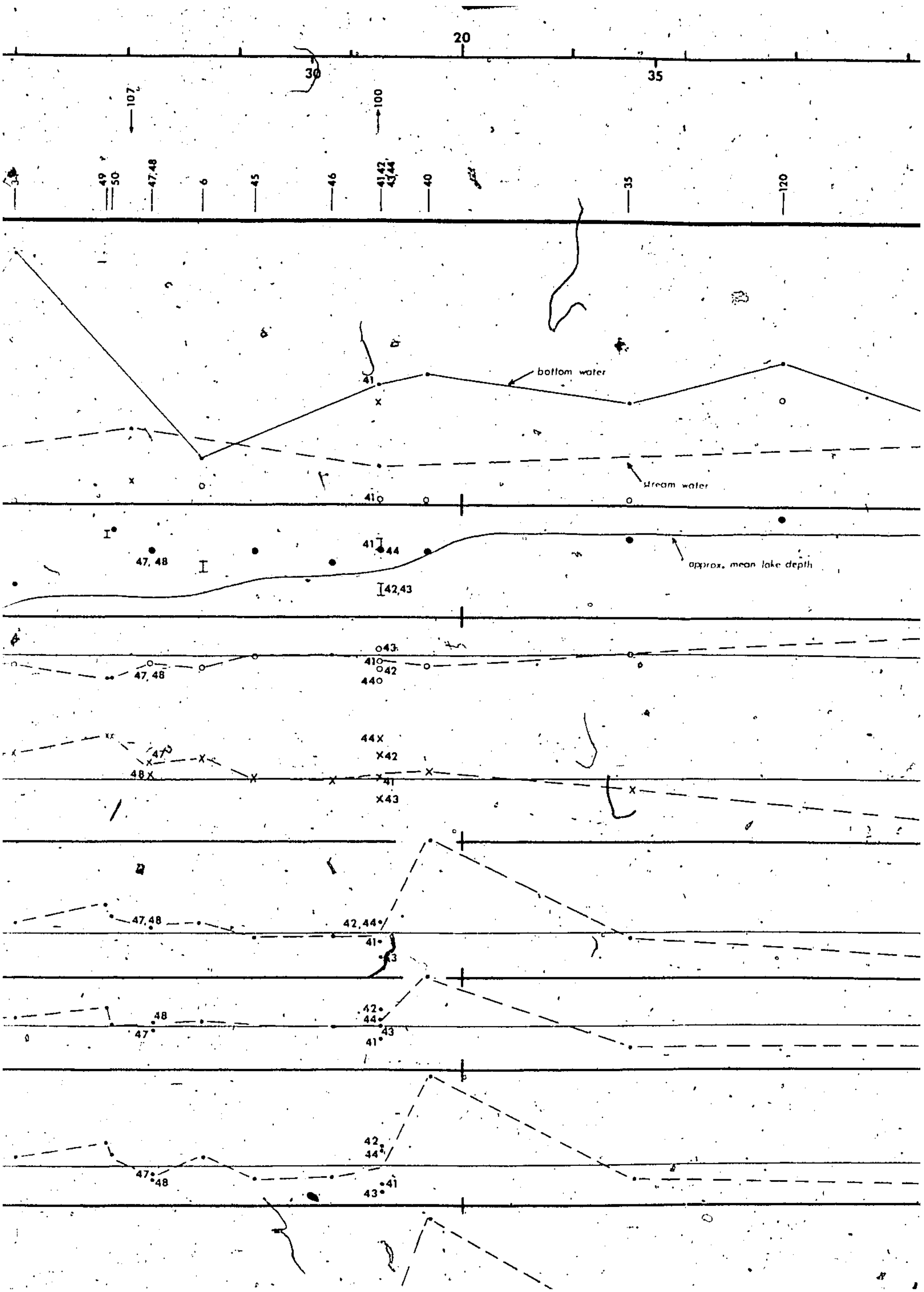
2 of

3 of

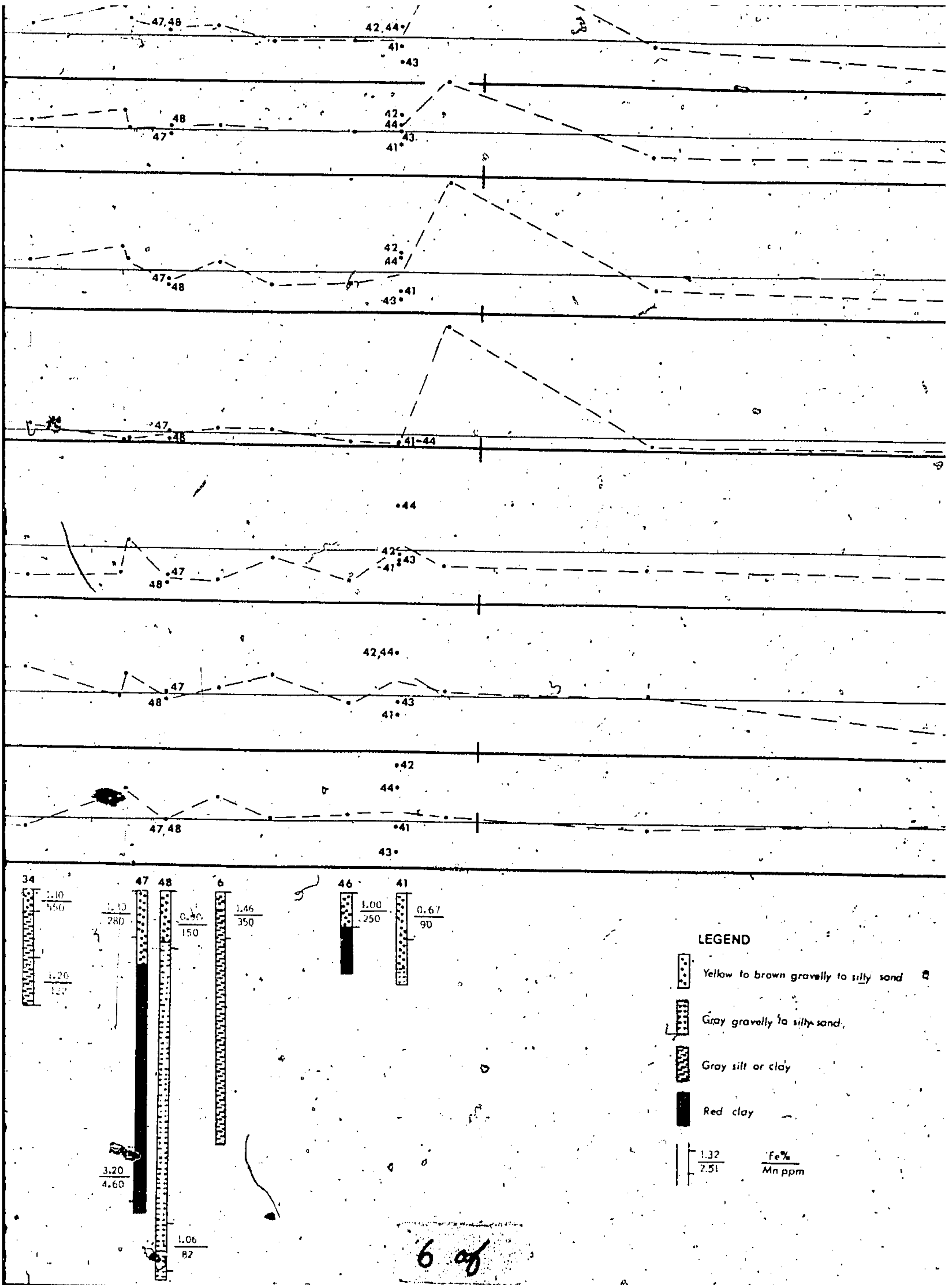

10
15
15
20
113
108
26
27
1
28
29
30
104
31
32
2
3
8
9
10
33
11
4,5,7
4
5
7
7
8
5
4
9
10
7
5
4
7
4
5
5
4
7
5
4
7
5
4
7
5,4
7

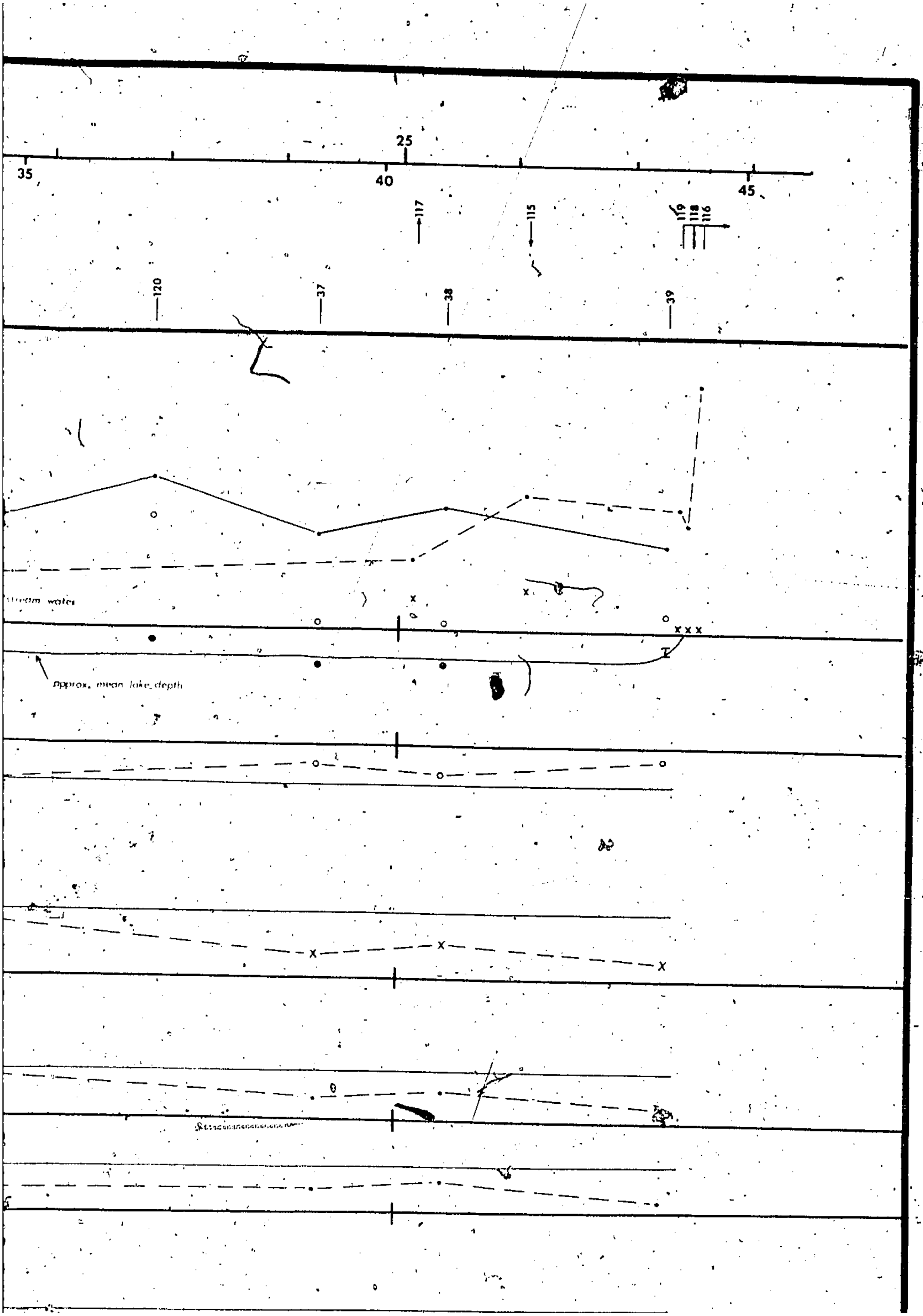

4
7
5
4
2
7
5,4
7
5
4
7
7
5
4
5
4
7
5
7
4
26
1
28
30
32
2
3
8
10
11
4
5
1,95/900
780
1,70/400
2,20/220
3,95/420
1,40/144
0,80/20
1,95/430
1,70/800
1,20/182
1,30/450
0,94/900
1,40/320
7,40/14000
1,30/250

4.OF



20
30
35
107
100
34
49
50
47,48
6
45
46
41,42,43,44
40
35
120
bottom water
stream water
41
approx. mean lake depth
47, 48
41
44
42,43
43
41
42
44
47, 48
44
42
41
43
47
48
47,48
42,44
41
43
48
47
42
44
43
41
42
44
47
48
41
43


47,48
42,44
41
43
48
47
42
44
43
41
42
44
47
48
41
43
47
48
41-44
44
42
41
43
47
48
42,44
47
48
43
41
42
44
47,48
41
43
34
1.10
550
1.20
122
47
1.30
280
3.20
4.60
48
0.90
150
1.06
82
6
1.46
350
46
1.00
250
41
0.67
90
LEGEND
Yellow to brown gravelly to silty sand
Gray gravelly to silty sand
Gray silt or clay
Red clay
1.32
2.51
Fe%
Mn ppm


25
35
40
45
117
115
119
118
116
120
37
38
39
stream water
approx. mean lake depth

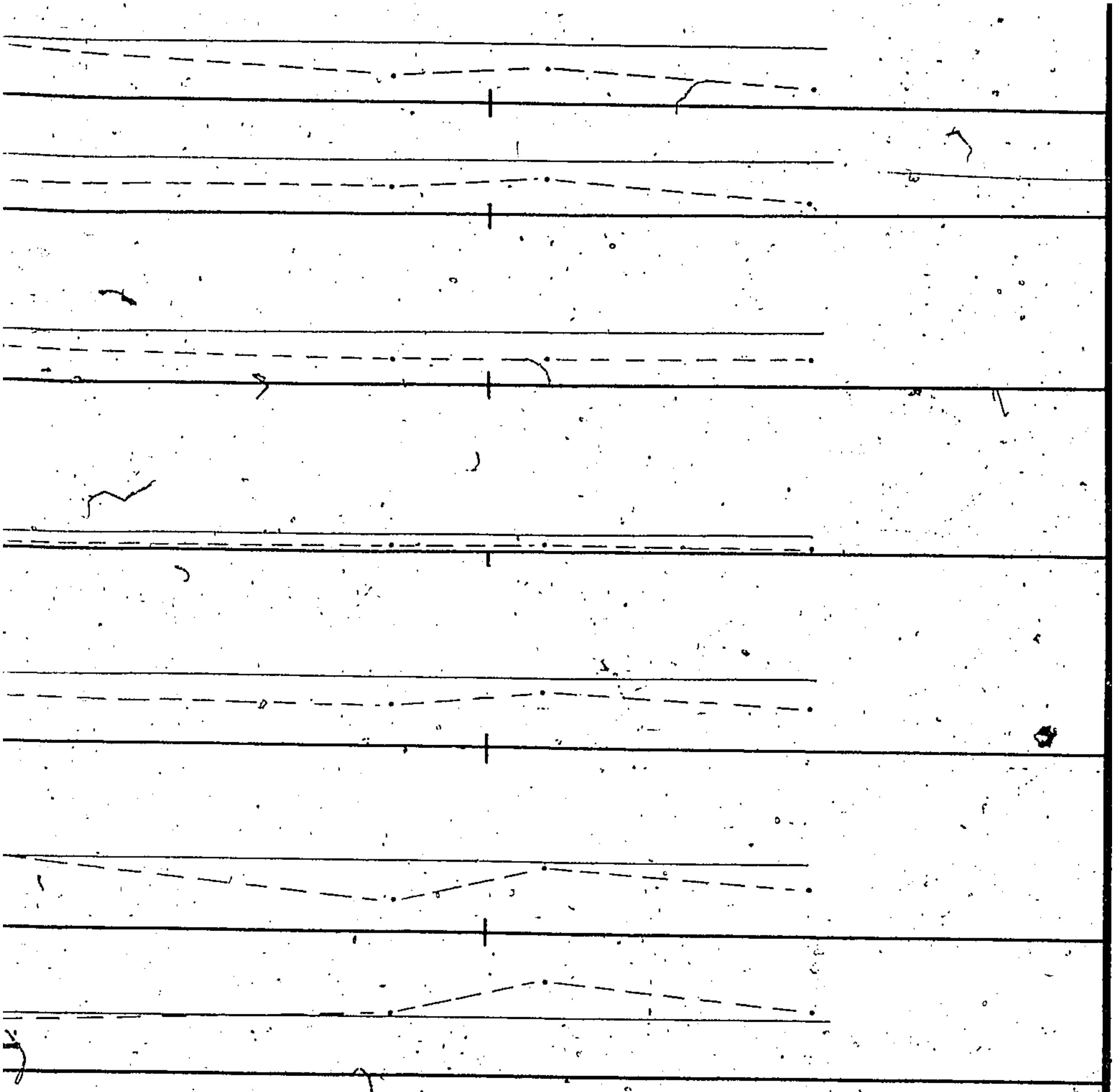
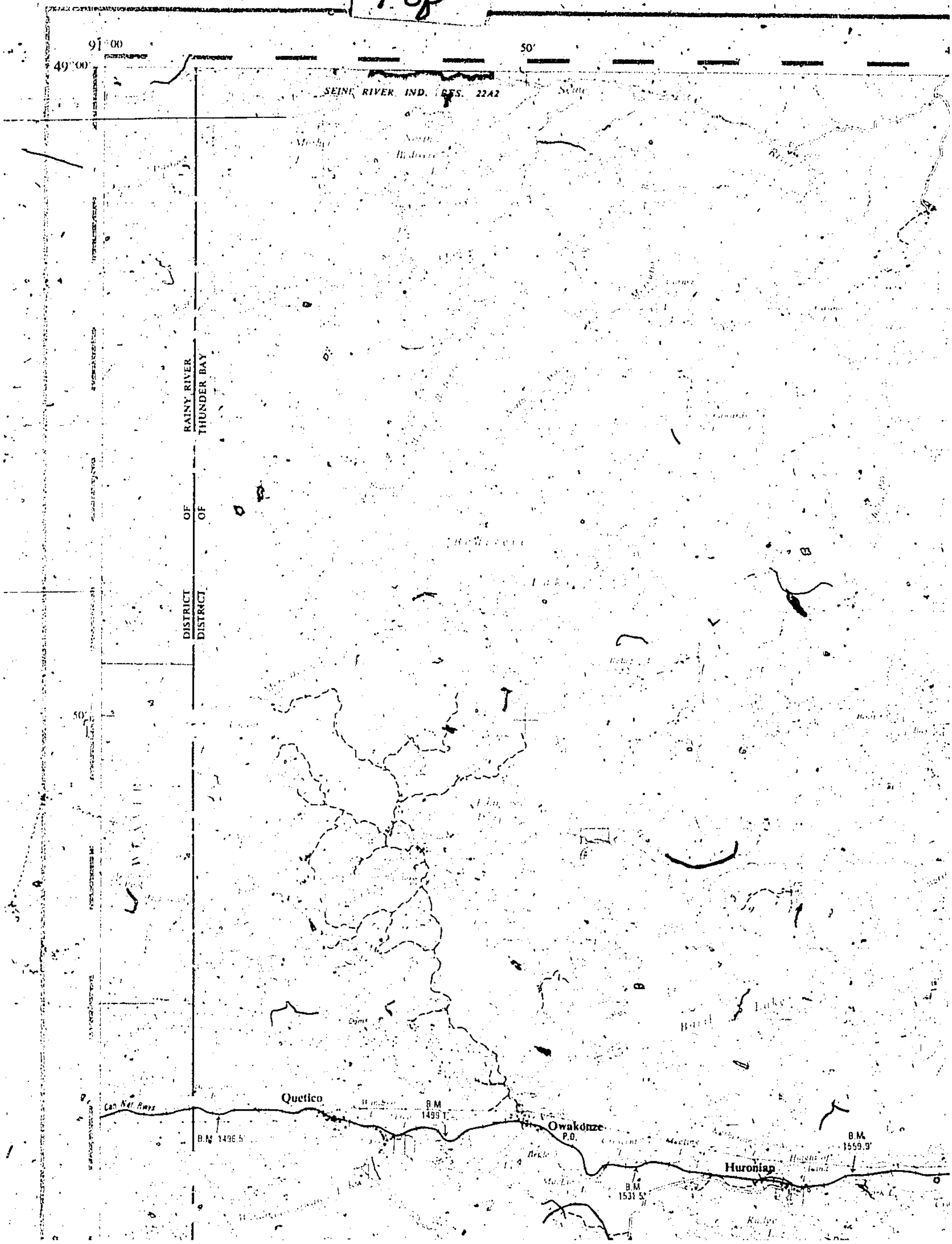
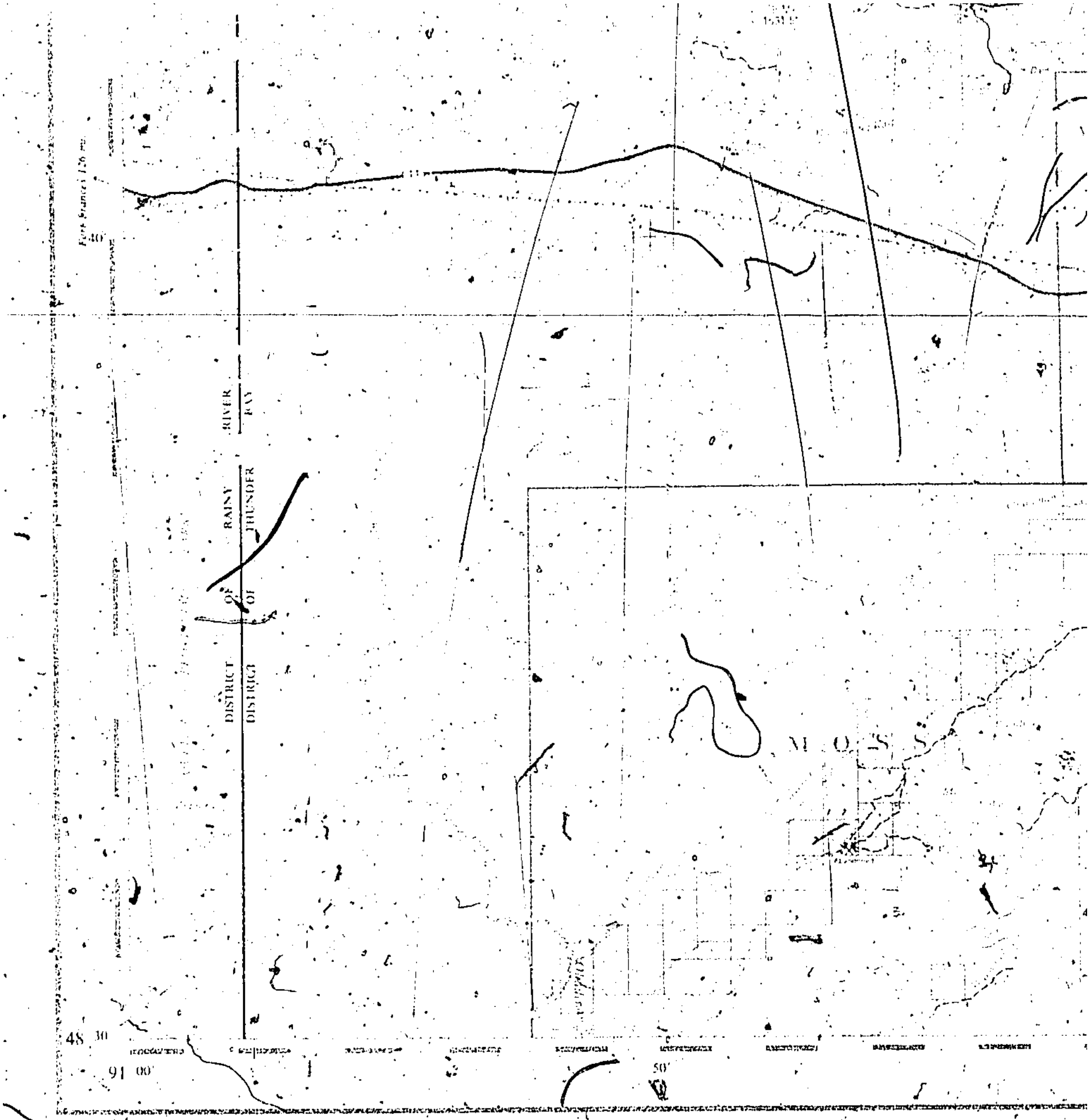


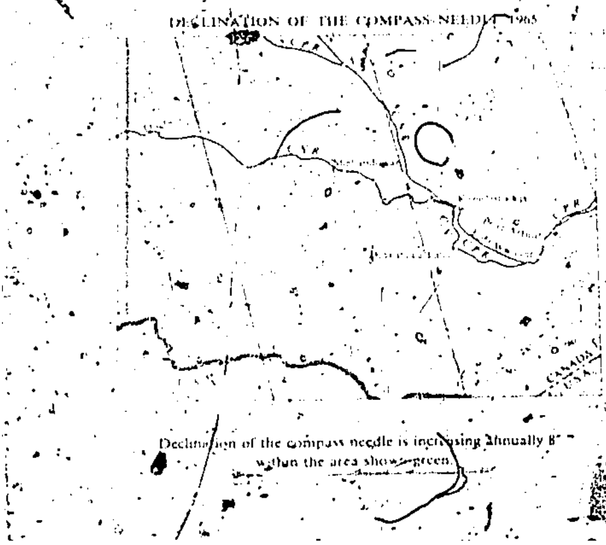
Figure 4, Variation in the composition of concretions, sediments and waters along Shebandowan Lakes. The data are plotted at offsets to a schematic axial line, commencing at the southwest end of Upper Lake (left) and ending at the Lower Lake outlet (right). Concretion analyses: all traverse and composite analyses have been weighted for each station on per concretion basis.

PROVINCIAL SERIES

1 of







DECLINATION OF THE COMPASS NEEDLE 1965

Declination of the compass needle is increasing annually 8' within the area shown green.

Ontario Forestry Resources Inventory Maps compiled from air photographs flown in 1962 were used for the base of this map. Revised to 1969

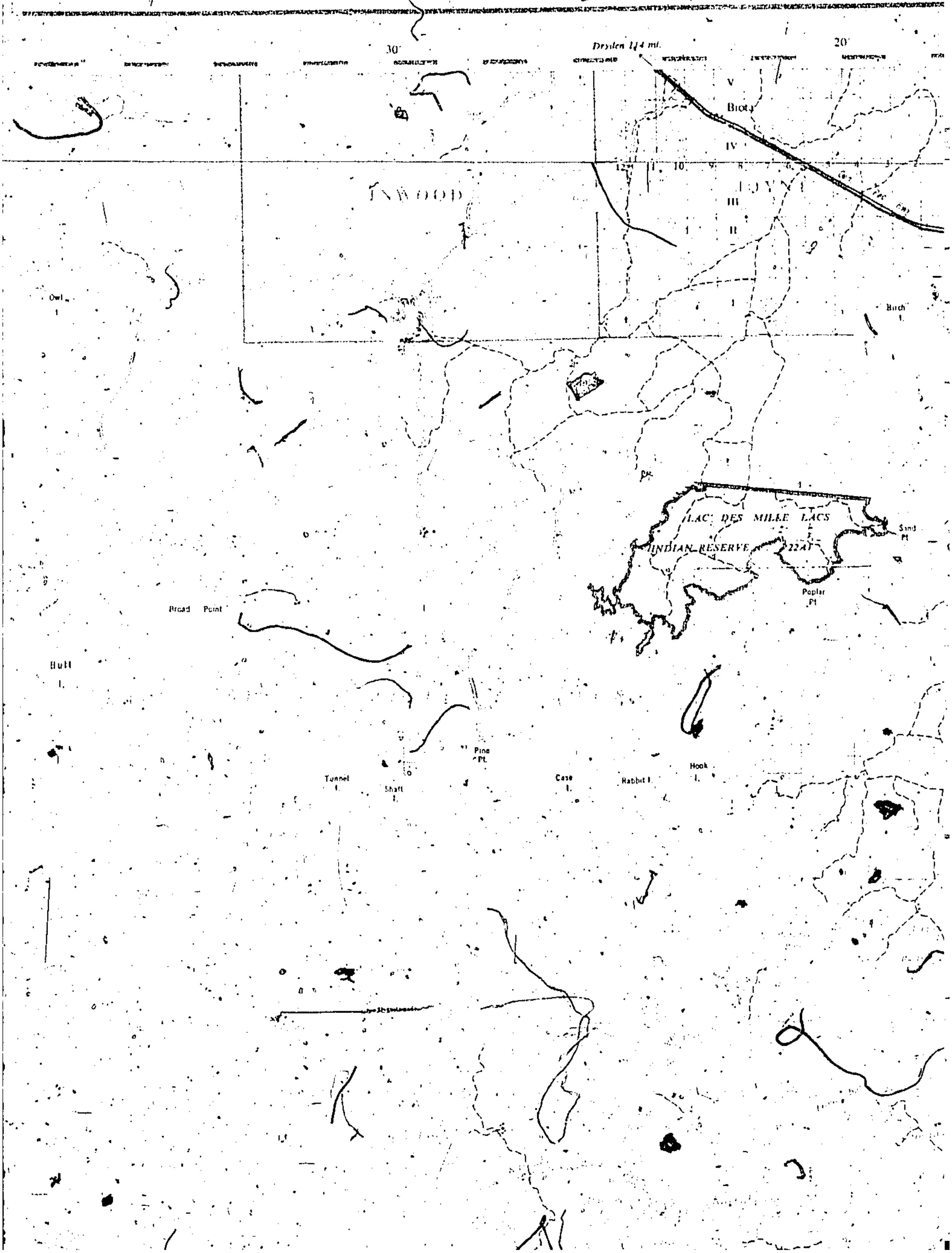
Transverse Mercator Projection

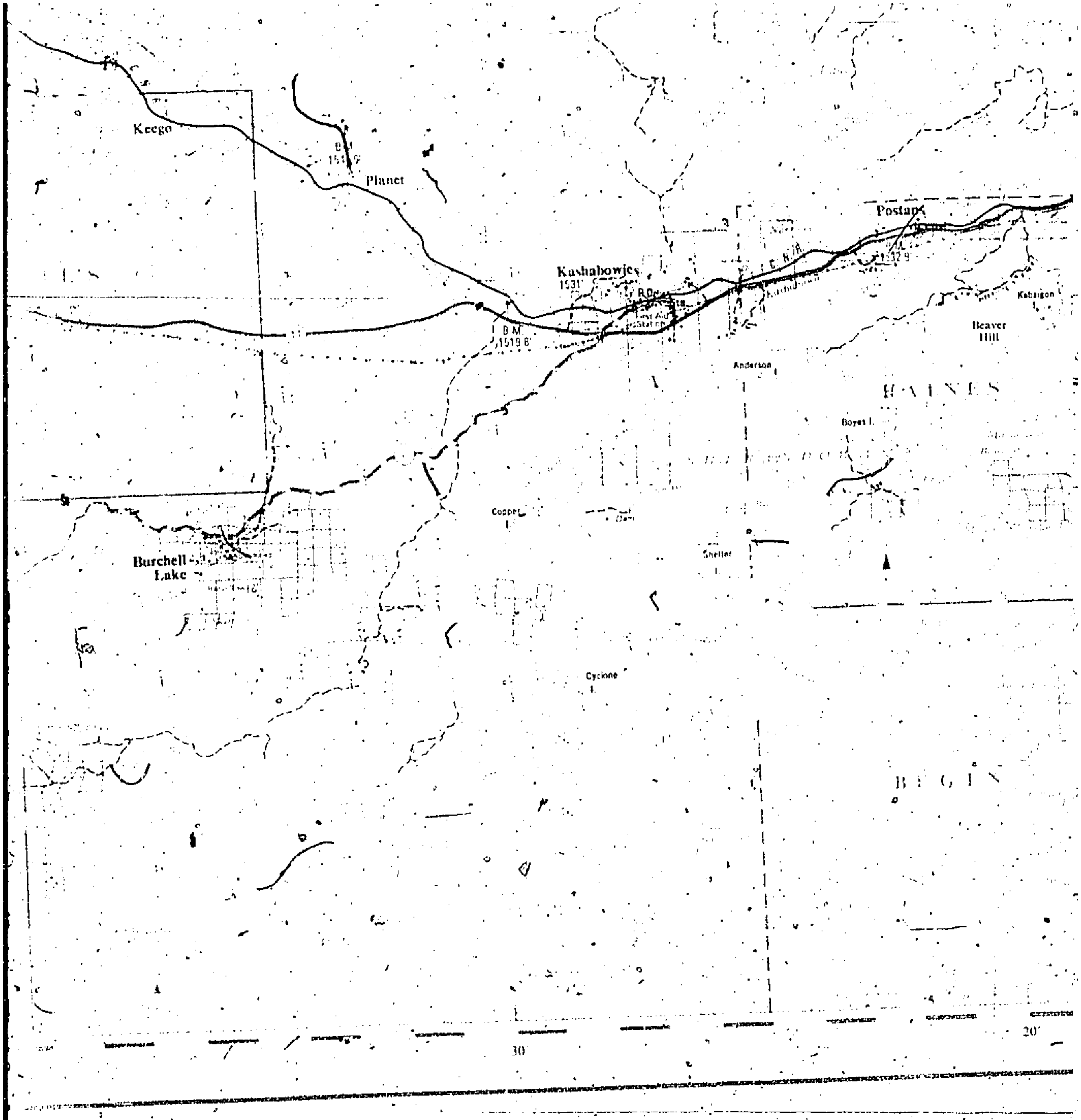
King's Highway (surfaced)
Secondary Highway (surfaced)
All weather road (surfaced)
Dry weather road (unsurfaced)
Trail or portage
Railway — Sta.
International boundary
Provincial boundary
County or District boundary
Township boundary — Surveyed — Unsurveyed
Municipal boundary
Park boundary
Reserve boundary
Building
Post Office — P.O

PROVINCE OF ONTARIO

DEPARTMENT OF LANDS AND FORESTS

3 of





LAC DES MILLE LACS

ONTARIO

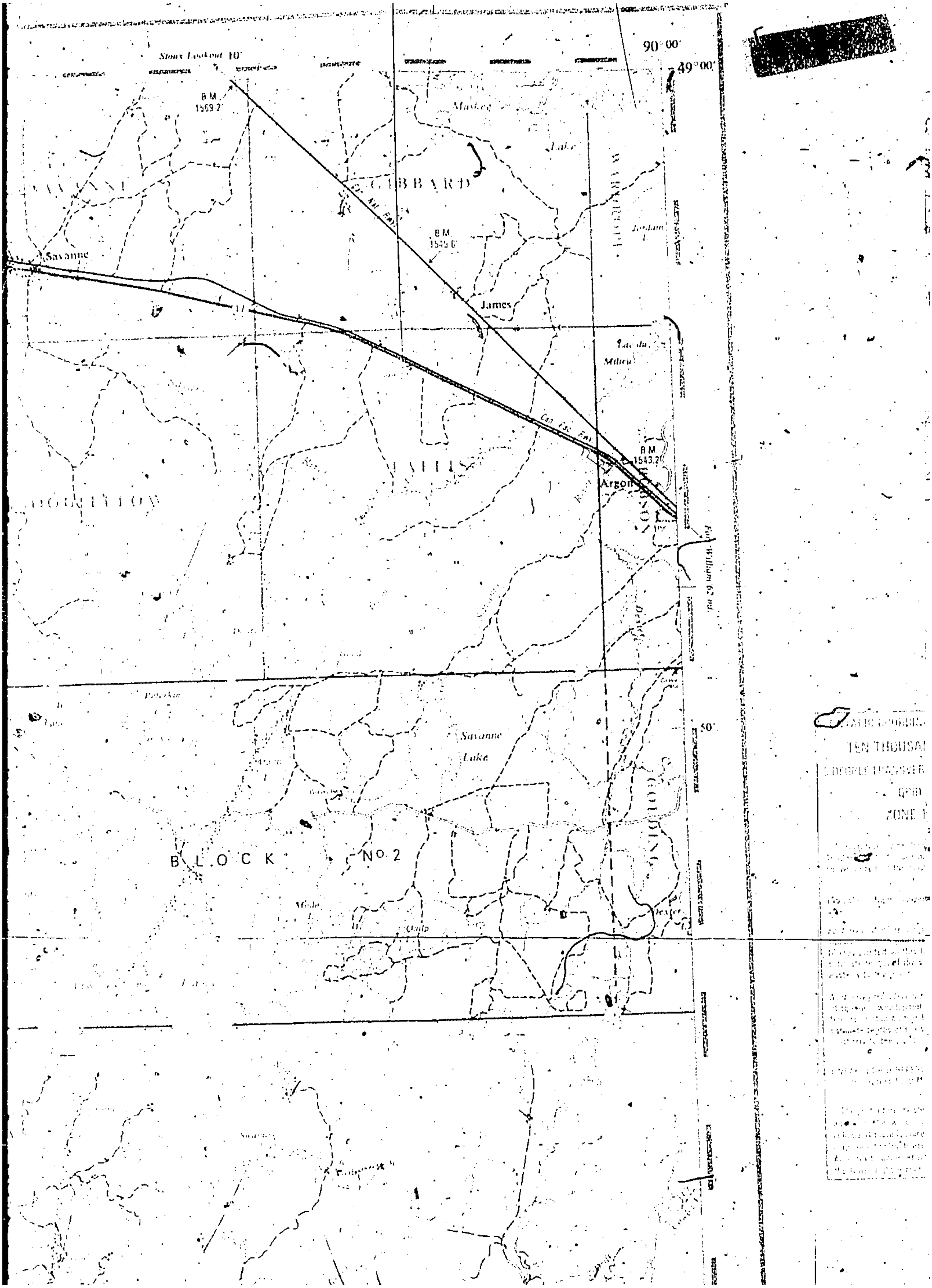
Scale 1:126,720 or 1 Inch to 2 Miles

Miles 2 1 0 2 4 6 8 10 Miles

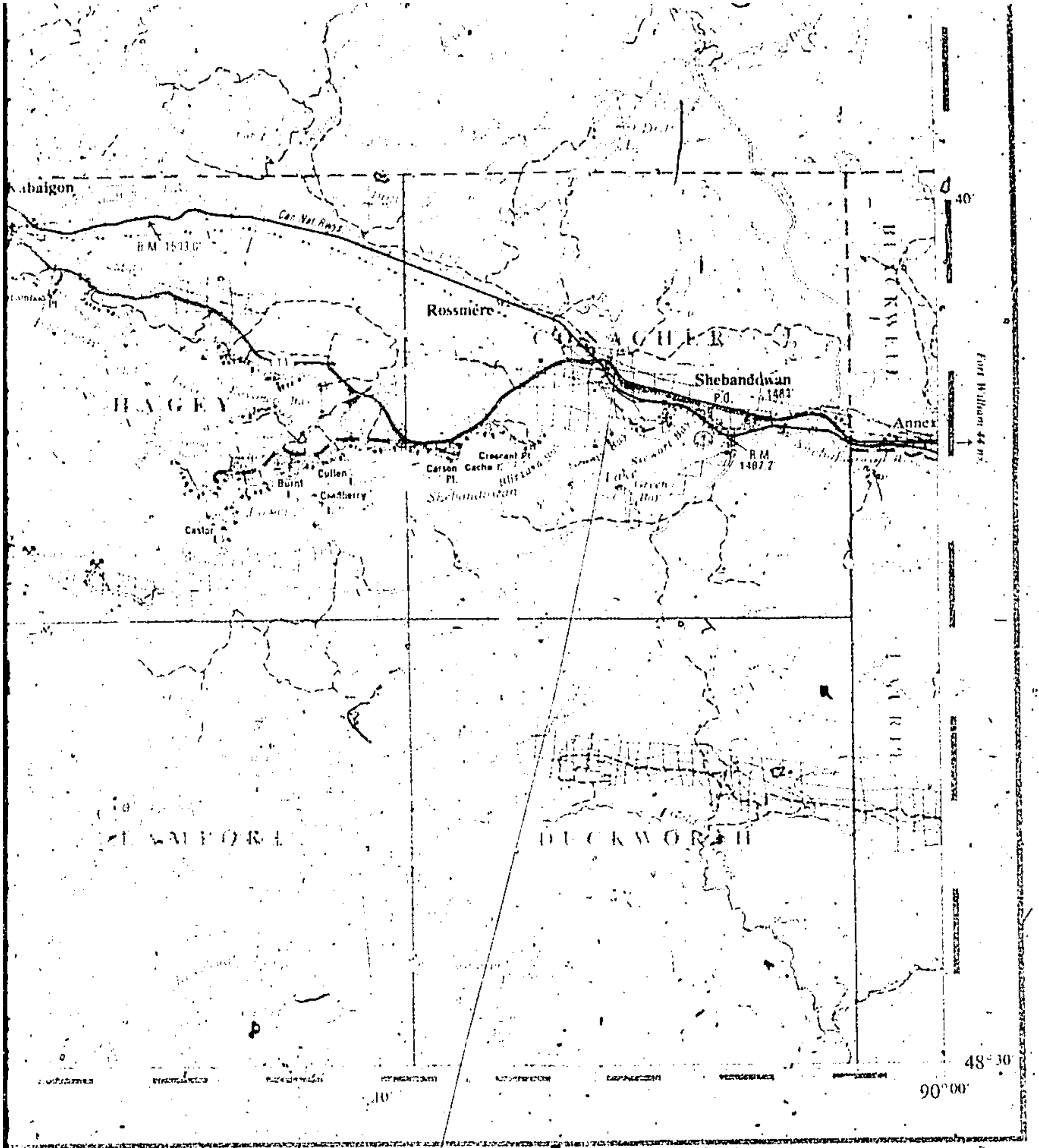
Kilometres 2 1 0 2 4 6 8 10 12 14 16 Kilometres

For Department of Lands and Forests administrative purposes, the area covered by this map is within the Districts of Port Arthur and Fort Frances with District Foresters' Offices located at Port Arthur and Fort Frances.

4 OF


Sioux Lookout 10'
90°00'
49°00'
B.M. 1569.2'
Muskeg
Lake
GIBBARD
Jordan L.
B.M. 1545.6'
Savanne
James
Lac du Milieu
B.M. 1543.2'
Argon
Fort William 62 mi.
Savanne
Lake
BLOCK No 2
Dexter
50'
TEN THOUSAN
ZONE

[redacted]



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Department of Lan
Parliament Building
Toronto, Ontario.

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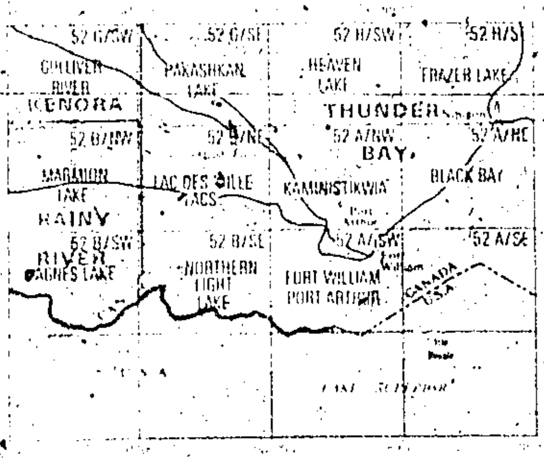

Index to adjoining maps of the 1 Inch to 2 miles series

FIRST EDITI