GYTTJA LAKE SEDIMENT EXPLORATION GEOCHEMICAL SURVEY OF EASTERN LAKE VERMILION-ELY AREA, ST. LOUIS AND LAKE COUNTIES, MINNESOTA

Minnesota Department of Natural Resources
Division of Minerals

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ABSTRACT

An organic-rich (gyttja) lake sediment geochemical survey was conducted over Lower Precambrian volcanic and associated rocks in northeastern Minnesota, for the purpose of determining the applicability of this method for evaluation of mineral resource potential and reconnaissance exploration. Two hundred and seventy samples were collected from 75 lakes over an area of 200 square miles (520 sq. km.).

A weak aqua regia leach on unignited gyttja produced the best contrast over background. Statistical analysis of the data indicates that trace element distributions are greatly dependent upon the limnological environment of each lake; trace elements tend to be concentrated in the organic and/or inorganic fractions of the gyttja; and, of all parameters considered, LOI (loss-on-ignition) is the best single indicator of limnological environment.

Due to the variations in lake environments and trace element accumulation in the gyttja, parameters other than the element concentrations were considered. However, the study indicated, even though a perfect datum for comparing lakes was not possible, the element concentrations for arsenic, cobalt, copper, nickel, lead, and zinc provided the best datum for comparing all 75 lakes.

Several significant anomalies were located by the survey. Anomalous copper was found in a lake near an interesting copper prospect. Copper, lead, titanium, and zinc appear to reflect bedrock composition; chromium, magnesium, and nickel reflect both bedrock composition and glacial dispersion.

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INTRODUCTION

Much of the Eastern Lake Vermilion-Ely area is underlain by Lower Precambrian metavolcanic and associated rocks. Although gold prospecting was done in this area as early as the mid-1800's and mining of Algoma type iron-formation began in 1884, intensive exploration for volcanogenic massive sulfide deposits did not commence until the late 1960's. The exploration for massive sulfide deposits has not resulted in the discovery of a mineable deposit, but significant showings have been located. The most prominent showing in the area is that of copper in an intermediate to mafic sequence of metavolcanic rocks.

The Division of Minerals of the Minnesota Department of Natural Resources has the responsibility for the administration of the approximate 10 million acres of state controlled mineral lands. This responsibility includes the administration of state mineral leases. To date, over 60,000 acres of state controlled mineral lands have been leased in the Lake Vermilion-Ely area. These leases were issued to six companies. Most of the leases, however, are now terminated.

It is also the responsibility of the Division of Minerals to assess the mineral potential of state controlled mineral lands. By 1974, the mining company exploration had diminished considerably in this area, but the Division of Minerals considered the geologic environment favorable for the occurrence of economic sulfide deposits. As a result, it was decided to conduct surveys to evaluate the mineral potential of state controlled mineral lands in this region.

The mining companies had conducted airborne electromagnetic and magnetic surveys. They followed up these surveys with ground geophysics and drilled some of the most promising conductors. Due to the extensive geophysical surveys that had been done, the Division of Minerals decided to attempt to utilize the chemical properties of the Quaternary deposits of the region as a means of generally delineating potential areas in combination with existing geologic and geophysical data.

The use of gyttja lake sediment as an exploration geochemical sample media has been reported (Coker and Nichol, 1975; Davenport et al., 1975; Timperley and Allan, 1974). Results from these surveys indicated that gyttja lake sediment is generally chemically representative of the drainage basin in which a lake is contained and does reflect known mineralization; however, analytical and interpretational methods varied between these surveys. Therefore, the Division of Minerals conducted a research program to develop analytical and interpretational methods applicable to portions of northern Minnesota.

The Division conducted a gyttja survey of 75 lakes, over an area of 200 square miles (520 square kilometers), during 1974-5 in the eastern Lake Vermilion-Ely area. The results of this survey are described in this report. Many graphs were prepared for this study which are not included in this report but are available for examination.

Since the completion of this survey, Hornbrook and Garrett (1976) have reported on a gyttja lake sediment survey conducted in Saskatchewan. For their survey, they arrived at essentially the same interpretational conclusions as described in the following report.

DESCRIPTION OF SURVEY AREA

Precambrian Geology

The general Lower Precambrian geology (after Morey, Green, Ojakangas, and Sims, 1970) of the Lake Vermilion-Ely area is shown on Figure 1. The general geology has been described by Morey et al., 1970; Sims, 1972a, b; and Sims and Morey, 1972. Sims (1973) has compiled the most detailed (1:48,000) bedrock geologic map available covering the entire survey area.

The Lake Vermilion-Ely area is composed of a complicated greenstone-granite complex. It consists of a metavolcanic-metasedimentary sequence, which is bordered on the south by the Giants Range Granite and on the north by the Vermilion Granite (Figure 1). The strike of the metavolcanic-metasedimentary sequence trends northeastward and is steeply dipping (Sims and Morey, 1972).

The Ely Greenstone (Figure 1) is the oldest known formation in the area. It consists predominately of pillowed or massive mafic lavas and synvolcanic diabase; with andesitic lavas and pyroclastic deposits; and lesser amounts of chert, banded iron-formation, and siliceous to carbonaceous tuff (Sims, 1972c; Sims and Morey, 1972). Algoma type banded iron-formations occur throughout the Ely Greenstone (Sims, 1972d). These iron deposits were mined near Ely (Sims, 1972e).

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* For this report, **gyttja** will be used to describe organic-rich lake sediments.

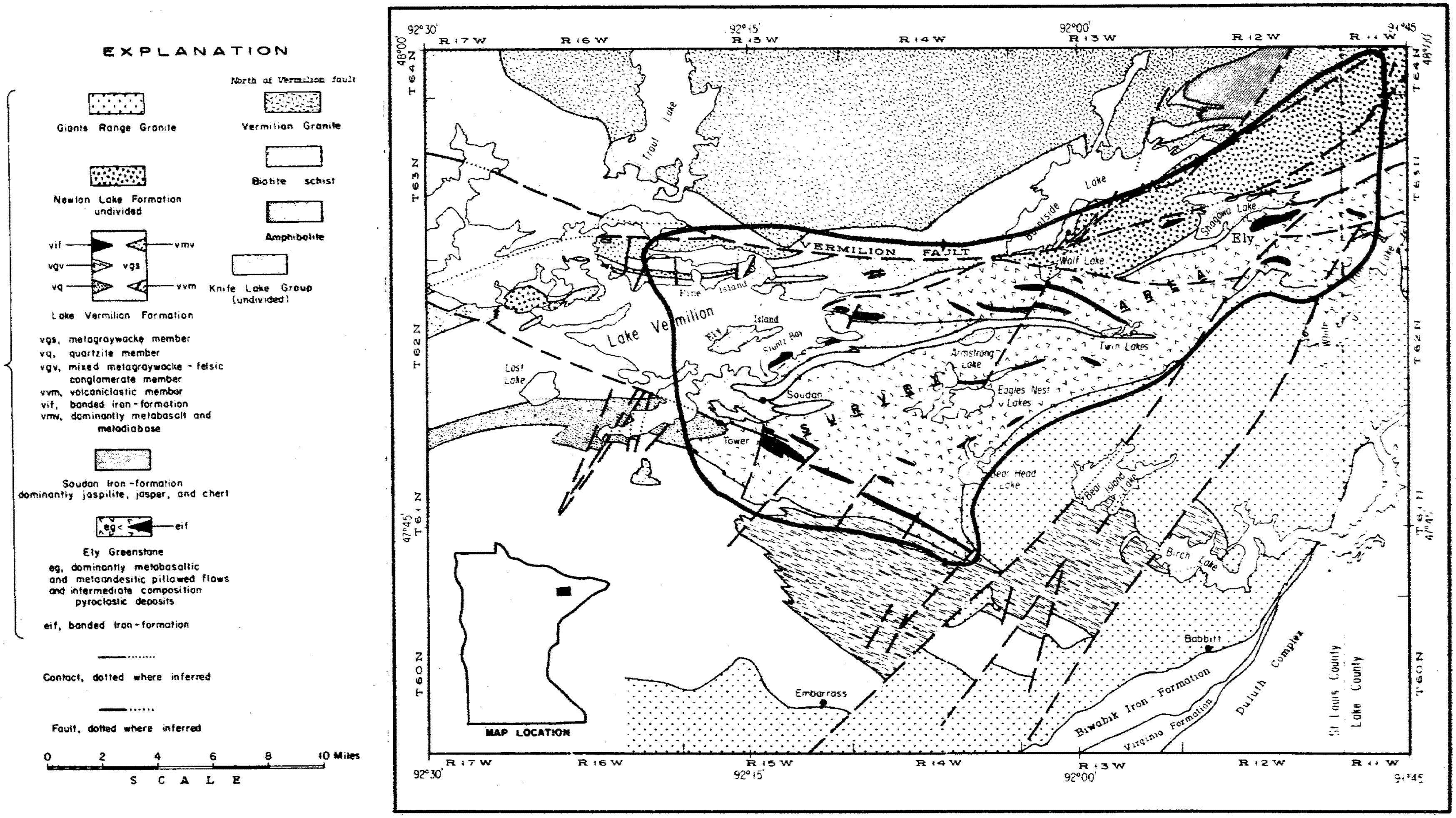

FIGURE 1: General Lower Precambrian geology of Lake Vermilion-Ely region, showing area of gyttja lake sediment exploration geochemical survey (Geology map from Morey, Green Ojakangas & Sims, 1970).

The Ely Greenstone is, in part, overlain stratigraphically by the Soudan (Algoma type) Iron-Formation (Figure 1) (Sims, 1972b). This iron-formation consists mainly of jaspillite, jasper, and chert, with varying amounts of magnetite and/or hematite (Sims, 1972d). Hematite deposits in this formation were mined at the town of Soudan (Figure 1) (Sims, 1972e).

The Soudan Iron-Formation and the Ely Greenstone are, in part, overlain stratigraphically by the Lake Vermilion Formation in the western portion of the area and the Knife Lake Group in the eastern portion of the area shown on Figure 1 (Sims, 1972b). Both the Lake Vermilion and Knife Lake Formations are composed dominantly of graywacke and other clastic rocks (Ojakangas, 1972). Lesser amounts of mafic and felsic lavas, conglomerate, dacitic tuff and agglomerate, banded iron-formation, and other rocks occur in both formations (Ojakangas, 1972; Sims, 1972c, d). The proportion of clastic rocks increases in both formations with distance from the apparent volcanic centers (Ojakangas, 1972).

The Newton Lake Formation (Figure 1) conformably overlies at least a part of the Knife Lake Formation (Sims, 1972c). This formation consists mainly of andesitic and basaltic lavas and intrusive diabase, but also includes felsic-intermediate tuffs, agglomerates, and breccias, banded iron-formation, and several differentiated sill-like bodies of mafic to ultramafic composition (Green, 1972; Sims, 1972c, d).

The Giants Range Granite has been described by Sims and Viswanathan (1972) and the Vermilion Granite by Southwick (1972). Sims and Mudrey (1972a) propose that Biotite Schist and Amphibolite (Figure 1) north of the Vermilion Fault represent metamorphic equivalents of the volcanic-sedimentary sequence in the area.

In addition to the major granitic batholiths, small bodies of syenitic rock and related lamprophyres occur throughout the area (Sims and Mudrey, 1972b). These intrusive rocks are not shown on Figure 1.

In addition to the iron-formation previously mentioned, showings of chalcopyrite, sphalterite, galena, and gold have been located in outcrop and diamond drill core throughout the area (Files of Division of Minerals; Sims, 1972c, e). As mentioned in the Introduction, the recent exploration for volcanogenic massive sulfides has not resulted in the discovery of a mineable deposit. The most prominent showing in the area is located two miles west of Bear Head Lake near a smaller Skeleton Lake. Chalcopyrite, with traces of gold, was intersected by diamond drilling in a semi-massive to massive iron sulfide horizon which occurs conformably between mafic and intermediate volcanic rocks. Assays of this sulfide horizon yielded values up to 3.38% copper over several feet.

Quaternary Geology and Physiography

In general, the landscape consists of a variety of lakes, streams, swamps, conifer and hardwood forests (Boreal Forest type) with subordinate deciduous trees. The glacial deposits lie unconformably over the Lower Precambrian rocks in the area. Bedrock outcrops are generally abundant. The area has fairly rugged local topography, often exceeding 50 feet (15 meters). Lakes and swamps often occur between intervening bedrock outnrops. The elevation of the region is generally 1,300 to 1,600 feet (400 to 500 meters) above sea level. Because of low regional relief, the streams of the area are generally sluggish.

The distribution and geometry of the lakes is controlled by bedrock geologic structure, the effects of glacial gouging and glacial deposits. Of the 75 lakes surveyed in the region, 56 lakes are less than 1/4 square mile (0.65 square kilometers). Additional information on the lakes will be presented later in the report.

The last glaciation of this region, described by Wright (1972), took place during the Wisconsin Stage. The last glacier to advance over the entire Lake Vermilion-Ely area is called the Rainy Lobe. This lobe advanced in a southwesterly direction. The Rainy Lobe consisted of two phases of glaciation: 1) the St. Croix Phase which advanced over the entire Lake Vermilion-Ely area, and 2) the Vermilion Phase which advanced to the terminal moraine named the Vermilion Moraine (Figure 2). The Vermilion Moraine appears to truncate an east-west trending recessional moraine of the St. Croix Phase in the southern portion of the area (Figure 2). Therefore, the till north of the Vermilion Moraine may have resulted from the Vermilion Phase and that south from the St. Croix Phase of the Rainy Lobe Glacier.

The till and end moraines in this area lie unconformably over the Lower Precambrian rocks. The thickness of the till seldom exceeds 100 feet. The till and end moraines are generally a silty-sandy, coarse gravel (Matsch). Both the angularity and lithology of the clasts in the till and end moraines indicate local derivation (Matsch). The till south of the Vermilion Moraine appears to contain less gravel and has been transported a greater distance than that to the north.

Examination of the ice-contact deposits in this area (Figure 2) indicates that these deposits are generally locally derived based on the angularity and lithology of the clasts (Matsch). In addition, the ice-contact deposits are poorly sorted. Winter, et al. (1973) reports that eskers are abundant in the ice-contact deposits.

The local derivation and high permeability of the glacial deposits in the Lake Vermilion-Ely area suggest that these deposits should reflect the chemical composition of the underlying bedrock and also permit the

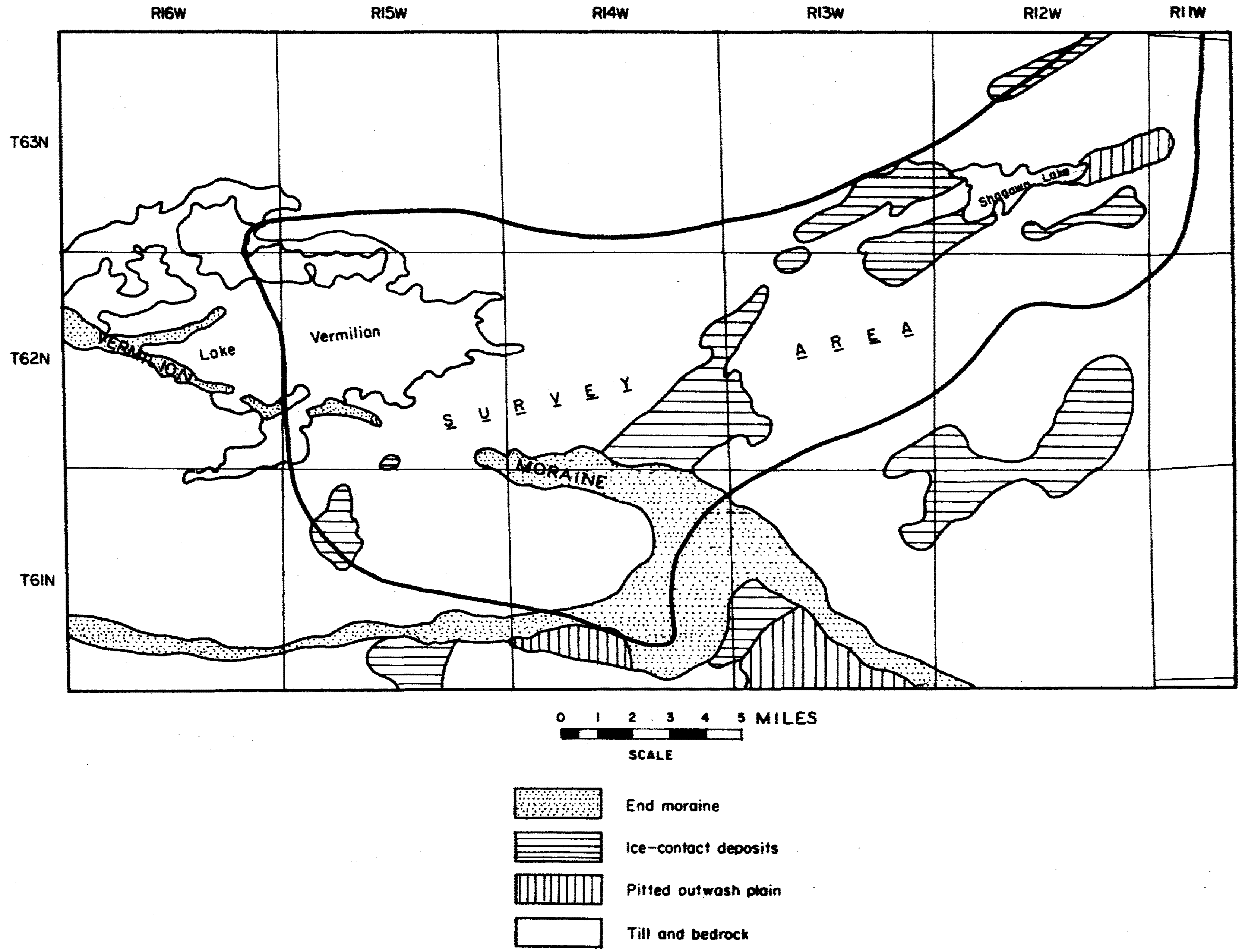

FIGURE 2: General glacial geology of the Lake Vermilion-Ely area (Adapted from map by Winter, Cotter & Young, 1973).

chemical migration of mobile elements in the surface and groundwaters.

Climate

The climate of the region is of continental type with occasional periods of prolonged heat during the summer and frequent outbreaks of polar air during the winter. The following mean monthly temperatures for the region were obtained from Kuehnast: January mean maximum 15°F (−9°C) and mean minimum −6°F (−21°C); July mean maximum 78°F (26°C) and mean minimum 54°F (12°C). Mean annual precipitation is 28 inches (71cm) per year (Kuehnast).

PREVIOUS SURVEYS

As early as 1956, Schmidt reported the reflection of mineralization in lake sediments in New Brunswick and Quebec. However, it was not until the 1970's that reports on the use of lake sediment as a geochemical exploration sample media frequently appeared in the literature. Use of lake sediment as a geochemical reconnaissance method, however, was applied by mining and exploration companies prior to this time.

Recently, several accounts have been reported on the use of lake center organic-rich sediments. Coker and Nichol (1975) have reported that in the southern Canadian Shield of Ontario, orientation surveys over known zinc-copper and nickel orebodies have indicated that lake center organic-rich sediment does reflect mineralization, but due to the various dispersion processes of trace elements into the lakes, element concentrations had to be normalized with manganese. In the Daniel's Harbour area of Newfoundland, lake center organic-rich samples reflected known zinc mineralization; however, a strong relationship was identified between zinc, iron, and LOI (Davenport, Hornbrook, and Butler, 1975). Residuals derived from multilinear regression of zinc with iron and LOI better defined zinc mineralization than did the zinc concentrations. In the Nechako Plateau, British Columbia, Hoffman and Fletcher (1976) report that lake center organic-rich sediments, based only on the metal concentrations, did reflect lithology and known copper, molybdenum, and lead mineralization. For an organic-rich lake sediment survey conducted in Saskatchewan, Hornbrook and Garrett (1976) concluded that the iron, manganese, and organic content does not appear to play a dominating role as scavengers in producing false anomalies. As a result, statistical treatment of the data did not offer improvement over the element concentrations.

Timperley and Allan (1974) have presented a model describing metal dispersion and accumulation in lakes. This model depicts mechanical transport of anomalous metal into lakes via stream sediment and other sediments entering into the lake from the drainage basin, and chemical migration by stream water, surface runoff, and groundwater. The accumulation of anomalous metal in the organic-rich lake sediment has been suggested to result mainly by metal-organic complexing, coprecipitation with iron and manganese, sorption by clay minerals, lattice held metal in primary silicates, and sulfide formation (Coker and Nichol, 1975; Timperley and Allan, 1974; Davenport, Hornbrook, and Butler, 1975; Nichol, Coker, Jackson, and Klassen, 1976). The chemical processes by which metals accumulate in the organic-rich lake sediments is greatly dependent upon the limnological environment. The chemical nature of the lake water can vary greatly between lakes (Coker and Nichol, 1975; Nichol, Coker, Jackson, and Klassen, 1976). Dissolved oxygen content of bottom waters has a large effect on coprecipitation of metals with manganese and iron; high pH in lake waters can restrict transport of metals into the central portions of the lake; the amount of organic matter in the lake available for metal-organic complexing; and other factors distinguish one lake from another (Coker and Nichol, 1975; Timperley and Allan, 1974). These factors must be considered when evaluating and interpreting organic-rich (gyttja) lake sediment surveys. These considerations will be discussed later for the survey reported.

SAMPLING

Plate 1 shows the 75 lakes from which 270 gyttja samples were collected. Sampling was accomplished by use of a specially designed core sampler. The sampler was designed so that samples could be obtained at a desired depth within the gyttja, mixing of the sediment would be minimized, and the nature of the sediment could be easily determined by visual examination. The sampler consists of a two inch (5 cm) diameter, thin wall, transparent plastic tube 18 inches (47 cm) long. The plastic pipe is retained in an outer steel pipe by a threaded plastic cutting tip. A ball check valve is located at the top of the outer steel pipe to retard sample loss during retrieval of the sampler. A 20 lb. (9 kg) weight is located near the top of the sampler to increase penetration.

The sampler is lowered by a rope. When the sampler is returned to the surface, the plastic cutting tip is unscrewed and the plastic tube containing the sample is removed. The nature and color of the sample is readily apparent by examining the sample in the transparent plastic tube. The sampler yields, except for compaction, a rather undisturbed vertical section of the gyttja. Metal contamination is completely avoided as the sample only contacts the plastic portions of the sampler. The top 2 inches (5 cm) of the sample is discarded to avoid sample affected by redox reactions near the gyttja-water interface (Coker and Nichol, 1975), to collect a generally reduced sample (Timperley and Allan, 1974) which should not be greatly affected by seasonal variations in lake water chemistry, and to hopefully avoid recent pollution if it has occurred. Approximately 2.5 lbs. (1.1 kg) of sample is collected from each sample site. To obtain this amount of sample generally requires 3 to 8 sampling runs. As a result, a composite sample is collected and each sample site represents a sample area due to boat drift.

For each sample site, the water color, water depth, shoreline vegetation, topography, glacial deposit type(s), slope, boulder type(s), and rock type(s) in outcrop were recorded. For each sample, the degree of H_2S scent, gyttja quality, color, and texture were recorded. At some sample sites, the surface water and gyttja pH were measured.

Sampling was conducted from a boat, canoe, or rubber raft, depending upon access to the lake. Sample sites were selected to include major bays and basins within a lake, generally sampling the greatest depth within these areas. An electronic depth finder was used to locate the deeper areas and determine water depth. An approximate sample density of one sample per 1/4 square mile (.65 sq. km) of lake resulted. For lakes less than 1/4 square mile, two samples were collected in case of sample loss unless the lake was very small, in which case only one sample was collected.

SAMPLE PREPARATION AND ANALYTICAL METHODS

Samples were dried at less than 80°C. Drying resulted in the samples becoming extremely hard. As a result, the dried samples were disaggregated first with a rolling pin followed by grinding to −80 mesh (177 micron) with a Braun pulverizer using ceramic plates. The −80 mesh fraction was used for subsequent trace element analyses of all samples. Portions of some samples were ashed or charred for various analytical methods described later in this report. The ashing was accomplished by ignition at 500°C to eliminate organic material and combined water. The charring was done at 270°C which partially eliminated organic material and combined water.

Loss-on-ignition (LOI) was determined by igniting a 1000mg sample at 800°C. The analytical precision for LOI was determined by analyzing a −80 mesh standard gyttja sample with each batch of LOI determinations. The resulting precision, as calculated by use of the "t" distribution, was ±8% at the 95% confidence level.

All samples were leached for analysis of silver, cobalt, copper, molybdenum, nickel, lead, zinc, iron, and manganese by placing 2000mg of sample in a solution composed of 10mls 4M HNO_3 and 10mls 1M HCl for two hours at 90°C. This solution was then diluted to 100mls in a volumetric flask and analyzed on a Perkin-Elmer 303 Atomic Absorption Spectrophotometer. Lead and zinc were analyzed using Perkin-Elmer electrodeless discharge lamps (EDL) and power supply.

Arsenic was analyzed for all samples by digesting 1000mg of sample in concentrated HCl for one hour at 90° to 100°C. After 50 minutes, 1000mg of K I is added to the solution so that the arsenic (III) is oxidized to arsenic (V). The solution was then diluted and analyzed on the Perkin-Elmer 303 using an EDL power supply, deuterium background corrector, and arsine generator.

The analytical precision, at the 95% confidence level, for some elements, was determined by replicate analysis of 44 random samples (Garrett, 1969). The resulting precisions are: Co ±34%, Cu ±13%, Ni ±17%, and Zn ±17%. The analytical precision for the remaining elements was determined by the method previously described for LOI using a −80 mesh standard gyttja sample. At the 95% confidence level, these precisions are: As ±44%, Fe ±21%, and Mn ±13%. All molybdenum and most of the silver values were below the detection limit for the sample weight used; therefore, analytical precision could not be determined.

Several additional elements were determined and analytical methods tested on some samples besides those previously described. Sulfur was analyzed using a Leco sulfur titrator. Samples were charred at 270°C to eliminate the majority of organic material, but preserve sulfide, prior to sulfur analysis. Excessive amounts of organic material interferes with the analysis. A 1000mg sample of −80 mesh sample was used for analysis.

Some of the samples were analyzed by the following leach and digestion methods on the Perkin-Elmer 303.

1. Parr acid digestion bomb with concentrated HCl, HNO_3 and HF
2. Concentrated HCl, HNO_3, and HF
3. 4M HNO_3
4. Ammonium citrate (10% solution) and concentrated hydrogen peroxide
5. Ammonium citrate (10% solution) and hydroxylamine hydrochloride (10% solution)
6. EDTA (7% solution)

DESCRIPTION OF LAKES AND SEDIMENTS IN SURVEY AREA

Differences in the limnological environment of the lakes surveyed were observed throughout the region. These differences result from variations in the structure and lithology of the Precambrian bedrock, glacial gouging, glacial deposition, and post-glacial erosion and deposition. Certain areas within the region have lakes which are fault controlled. These lakes are elongated in the direction of the faulting and are relatively deep. Another area within the region produces lakes which are generally swamp bounded, regardless of the areal extent of the lakes. Another area produces lakes which are relatively shallow, regardless of the areal extent of the lakes or the surrounding topography. The amount of outcrop surrounding lakes varies locally throughout the region. The limnological setting of lakes has been reviewed by Nichol, et al. (1976).

Hoffman and Fletcher (1976) have recognized two contrasting limnological environments within an area they surveyed in British Columbia. They characterized the lakes by size and depth: (1) lakes greater than three kilometers long and deeper than six meters, and (2) smaller lakes with depths generally less than six meters. This geometric classification reflects the differences in lake chemistry (i.e., dissolved oxygen content, Eh, pH, etc.). For the survey reported, lakes were segregated based on lake area into three classifications to determine if chemical differences existed between lakes of different areal extent. These classifications are:

Small Lakes $\leq$1/4 square mile (.65 sq. km)
1/4 square mile (.65 sq. km) $<$Medium Lakes $\leq$1 square mile (2.6 sq. km)
Large Lakes $>$one square mile (2.6 sq. km)

Several characteristic differences were identified between Small, Medium, and Large lakes. Small lakes are generally bound by swamp or lowland and have a relatively dark water coloration of green, brown, or red-brown. The distinctive water coloration results from colloidal solution of humic material (Nichol, et al., 1976). The sediment of Small lakes generally contains some fibric-organic material along with fine-grained organic and non-organic material. The scent of H_2S was more prevalent in samples taken from Small lakes. The water depth of Small lakes was usually less than 15 feet.

The sediments of the Large lakes usually contain a greater fraction of non-organic sediment than the Small and Medium lakes. The Large lakes are generally surrounded by upland; however, localized swamp and lowland does occur. Nearshore sediment generally consists of sand and/or gravel and grades to clay, then organic-rich sediment as depth increases. In the transition from non-organic to organic sediments within Large lakes, stratified sediments are often encountered. This stratification usually consists of several inches of organic sediment underlain by sandy layers under which a light gray clayey sediment is encountered. Occasionally, these sediments are interlayered. In some areas, the organic-rich sediments contain sand-sized material. The depth at which organic-rich sediments occur in Large lakes varies locally, but are generally encountered below 25 feet of depth. Based on field observations, the organic content of the sediment increased with depth within a lake. If water coloration was detectable in Large lakes, it was generally a light shade of green to brown to red-brown. Water coloration was found to vary within Large lakes. The median water depth was 22 feet at the sites sampled in Large lakes.

The Medium lakes, in some respects, represent a transition between Small and Large lakes. The shores of Medium lakes are most often upland. The sediments of Medium lakes rarely contain fibric-organic material and contain less non-organic material than Large lakes. The sediments collected from Medium lakes are generally more gelatinous than the sediment from Small and Large lakes. The near shore sediments from Medium lakes may be sandy or gravelly, but the sediment grades rapidly to organic-rich sediment as water depth increases.

A slight contrast in the pH of the surface water and sediment, based on a limited number of measurements, appears to exist between Small, Medium and Large lakes (Table 1).

Examination of loss-on-ignition (LOI) determinations made on the samples gives a quantitative measure of the organic content. Coker and Nichol (1975) found that a well defined relationship exists between LOI and organic carbon. For Small lakes the LOI ranges from 28.36% - 85.16% with a median of 56%. Approximately 90% of the Small lake samples are above 38% LOI. The range of LOI for Medium lake samples is 15.84% - 74.06% with a median of 42%. The range of LOI for Large lake samples is 15.49% - 69.12% with a median of 28%. The data for Large lakes is somewhat biased due to the fact that a large portion of the samples are from Lake Vermilion which is generally low in LOI. Figure 3 shows histograms of LOI for Small, Medium, and Large lakes. Figure 4 shows histograms for LOI for all 75 lakes surveyed. Small, Large, and all 75 lakes' LOI data generally approximate a lognormal distribution from observation of probability graphs. The Medium lakes exhibit a bimodal distribution which approximates, overall, a lognormal distribution. From Figure 3, it is apparent that Medium size lakes, based on LOI, represent a transition between Small and Large lakes. The LOI, of all factors considered, appears to be the best single diagnostic characteristic of the limnological environments of lakes in the survey area. Also, because organics play an important role in metal accumulation in lake sediments (Mackereth, 1965), LOI is a significant consideration in the interpretation of gyttja lake sediment surveys.

The median water depth at sample sites for Small lakes is 13 feet, 24 feet for Medium lakes and 22 feet for

TABLE 1: pH Data From Organic Lake Sediments and Surface Water

	Organic Lake Sediment		Surface Water	
Lake Size	**Range**	**Mean**	**Range**	**Mean**
Small	6.2-8.2	7.5	7.2-8.3	7.7
Medium	6.1-6.6	6.2	7.7-7.9	7.8
Large	6.4-8.0	7.9	6.8-8.1	7.8

Large lakes. It should be noted that sampling depths did not exceed 55 feet, and, as a result, some of these lakes are actually deeper than the sample depth indicates. Seventy percent of the sample depths of Small lakes were less than 15 feet, whereas 70% of the Medium and Large lakes sample depths were less than 30 feet.

No clear relationship between the degree of H_2S scent and sample depth was observed. Also, no significant relationship was observed between sample color and sample depth or the lake size.

CHEMICAL NATURE OF ORGANIC LAKE SEDIMENTS FROM SURVEY AND EXAMINATION OF ANALYTICAL METHODS

Experiments on Select Samples

Preliminary testing of several digestion methods at the outset of the survey indicated that some methods yielded much higher contrasts of metal concentrations in the gyttja. These results were not completely conclusive as they were based on a limited number of samples from three lakes in which copper only was anomalous in one lake. The digestion methods are described in a previous section. These methods yielded highest contrast for copper in the following order: ammonium citrate/hydrogen peroxide (AC/HP); EDTA; 4M HNO_3/1M HCl (aqua regia); 4M HNO_3, ammonium citrate/hydroxylamine hydrochloride; and concentrated HCl, HNO_3, and HF. Even though AC/HP and EDTA gave better contrast than aqua regia, this testing, again, was not completely conclusive because of the samples used. Also, published accounts of gyttja lake sediment surveys had not reported use of either of these methods. As a result, it was decided not to use the AC/HP and EDTA methods. Coker and Nichol (1975) had used a near total metal perchloric digestion, but the concentrated HCl, HNO_3, and HF method, also a near total metal digestion, yielded lower contrast than all other digestions. Davenport, Hornbrook, and Butler (1975) had reported successful use of a weak aqua regia leach for organic lake sediments in Newfoundland. As a result, the aqua regia method described above was selected for application to all samples.

Upon completion of analysis of all survey samples by the aqua regia leach, 36 samples were selected to analyze several elements not previously considered and to again test analytical methods. These samples are generally representative of the entire 270 samples collected during the survey. The 36 samples were analyzed by two digestion methods (HCl, HNO_3, and HF in an acid digestion bomb; and AC/HP), and sulfur determinations were made by an induction furnace and Leco titrator. For both the sulfur analysis and the acid bomb, samples were charred at 270°C to eliminate the majority of organic material but preserve sulfide prior to analysis. Excessive amounts of organic material interferes with the sulfur analysis and inhibits use of the acid digestion bomb.

Comparison of the three digestion methods applied to the 36 samples again revealed that the HCl, HNO_3, and HF method gives a much lower anomaly contrast than the AC/HP and aqua regia methods. The aqua regia and AC/HP methods gave approximately equal contrast. Elements of interest in gyttja lake sediment surveys are generally those which have been chemically dispersed (Timperley and Allan, 1974). The AC/HP method may be more specific for chemically dispersed elements. Therefore, the AC/HP may have advantages over the aqua regia method, but additional testing would be necessary to prove or disprove this suggestion.

The median values of the elements analyzed by these methods in the 36 samples are given in Table 2 and the coefficients of determination (r^2) in Tables 3, 4, and 5. The r^2 values given in this report were either estimated by a simplified method described by Lepeltier (1969), or by actual regression. The method used is indicated on each table. All elements analyzed and LOI are approximately lognormally distributed. Water depth at sample sites is approximately normally distributed. Therefore, r^2 was determined by $\log y = a + b \log x$ except when water depth was correlated, in which case, $y = a + b \log x$ was used with water depth equal to y. Often the square root of r^2, called the coefficient of correlation (r) is used to compare relationships between parameters; however, the authors prefer r^2 as it indicates the percent of variability accounted for in the dependent variable y by considering the independent variable x.

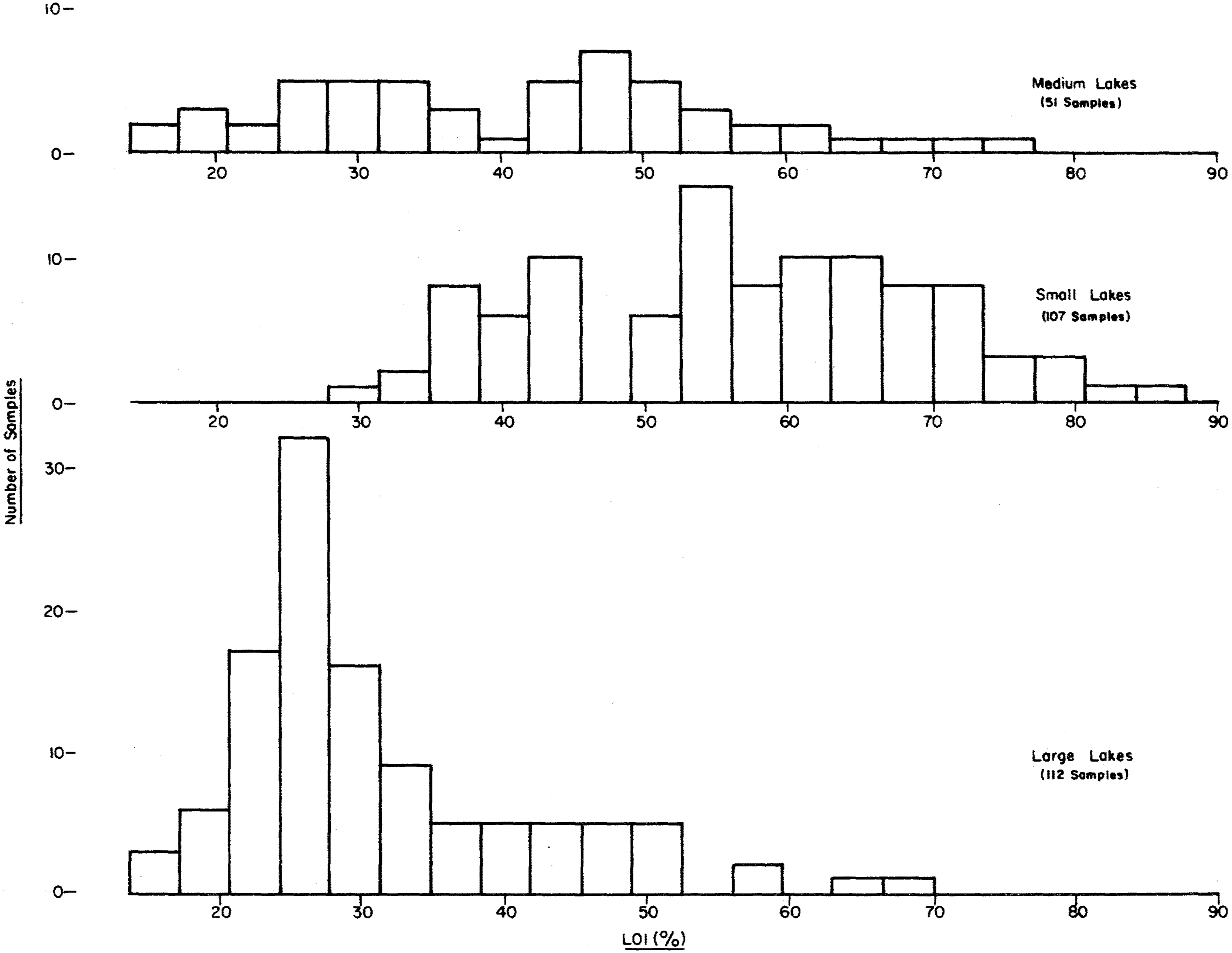

FIGURE 3: Histograms of LOI for Small, Medium and Large lakes.

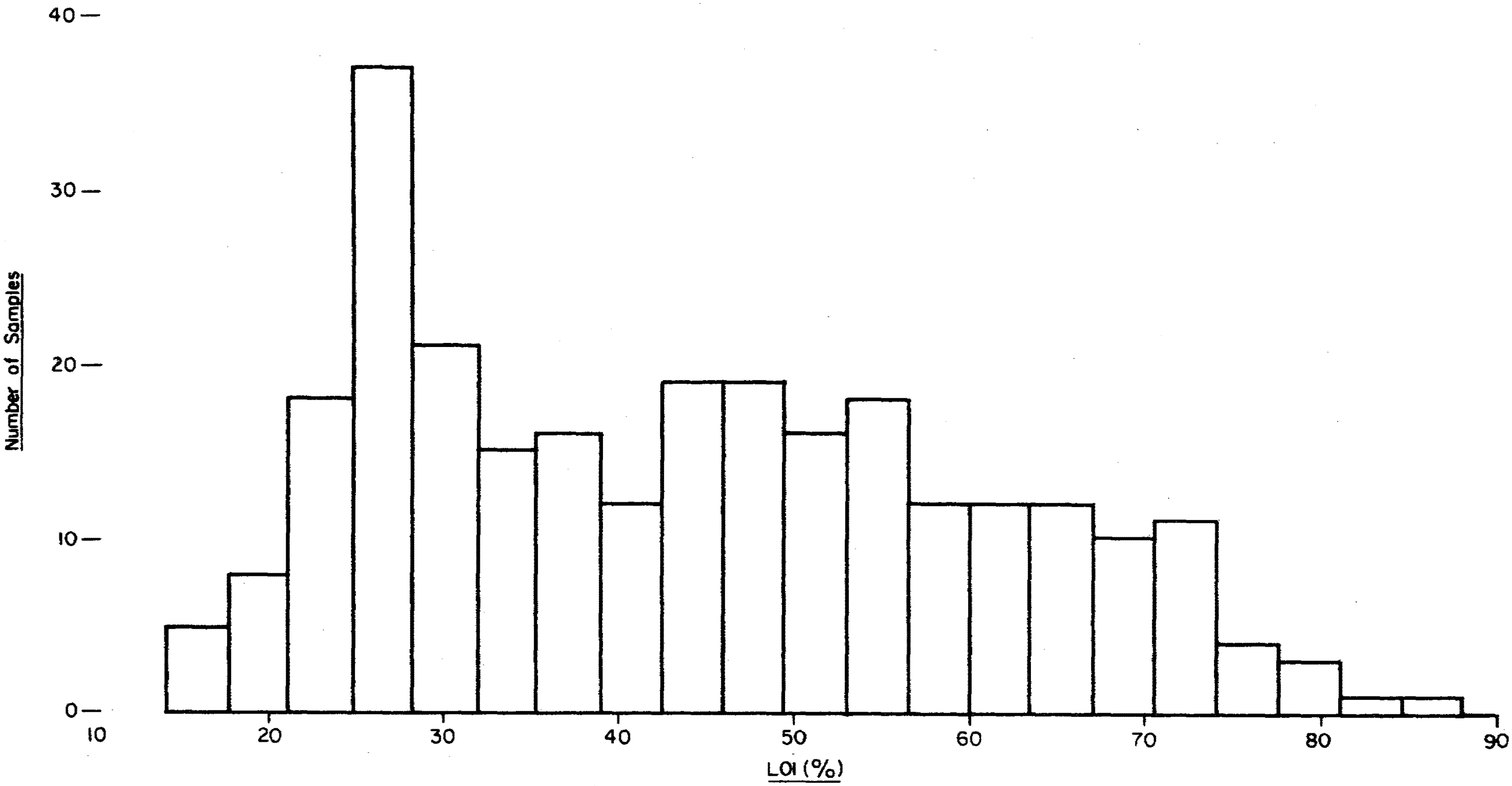

FIGURE 4: Histogram of LOI for all 75 lakes surveyed (270 samples).

The relative extractibility of the three digestion methods is readily apparent by examining Table 2. Although not shown in Table 2, the copper analysis by both the HCl, HNO_3, and HF and aqua regia digestions, when comparing analyses based on the original weight of an ashed sample and an unashed sample, indicates that the copper values are considerably reduced by ashing as reported by Peachey (1976). As a result, the copper value for the HCl, HNO_3, and HF digestion in Table 2 is lower than it would be if an uncharred sample were used. However, charred samples were necessary in order to analyze samples in the acid digestion bomb.

Chromium and nickel have a high r^2 (.80)(Table 5). Although not shown in the tables, chromium analyzed by HCl, HNO_3, and HF method gave an r^2 of .42 with nickel analyzed by aqua regia, and .41 with nickel analyzed by AC/HP. It would be expected that chromium is contained in primary silicate and oxide minerals. Based on the relationships of chromium and nickel, it appears that both the aqua regia and AC/HP methods are extracting a significant amount of nickel from primary silicate minerals.

Timperley and Allan (1974) have concluded that metal sulfide precipitation may be an important factor in the accumulation of metals in lake gyttja, with copper dominating other elements in these sulfides. Tables 3, 4, and 5 do indicate that sulfur has a weak positive relation to copper. All other elements display negative or no relation to sulfur. Sulfur does give a significant positive relation (Table 3) to percent weight loss and a significant negative relation to water depth. LOI (Table 3) also has a significant negative correlation to water depth. Therefore, it is suggested that sulfur is mainly concentrated in the organic portion of the gyttja.

Cobalt and nickel have significant negative correlation (Table 4) with sulfur by the AC/HP method and a significant positive relation with water depth. Therefore, it appears that a considerable portion of cobalt and nickel are concentrated in the non-organic portion of the gyttja. The same conclusion can be reached for cobalt, chromium, nickel, magnesium, and titanium (Table 5), and lead (Table 3).

Copper and organics appear to have a more definite relationship by use of the AC/HP (Table 4) compared to aqua regia (Table 3). Copper is the only element which displays a significant positive relation to organics by either of these methods.

The significant negative correlations of iron and manganese with LOI and percent weight loss (Tables 3, 4 and 5), and positive relation with water depth (Tables 3 and 5), suggest that iron and manganese are concentrated in the non-organic portion of the gyttja, as again LOI has a negative relation to water depth (Table 3). Furthermore, the weak correlation of iron and manganese with water depth by AC/HP (Table 4), a method which is more specific for Fe-Mn hydroxides than the other two methods (Rose, 1975; Meineke and Klaysmat, 1976), and the stronger correlation by the aqua regia and HCl, HNO_3, and HF methods (Tables 3 and 5), which extract significant amounts of clay and primary silicate held metal, suggests that Fe-Mn hydroxides are not a major component of the gyttja. In fact, Fe-Mn hydroxides are unstable in the reducing environment generally associated with lake gyttja (Timperley and Allan, 1974). However, shallow lakes often have a high dissolved oxygen content during the summer (non-ice) months (Hoffman and Fletcher, 1976) which should allow precipitation of Fe-Mn hydroxides. Therefore, Fe-Mn hydroxides should be more predominant in the shallow lakes surveyed.

HCl, HNO_3, and HF (Table 5) gives a low r^2 for cobalt to iron and manganese compared to that for aqua regia (Table 3). This suggests that the cobalt to iron and manganese display a weaker relation when extracting a larger portion of these elements from clay and primary silicate minerals. Intuition would also give the same conclusion that trace elements and Fe-Mn in clay and silicate minerals, considering several lakes across the region, would not have a consistent relationship. Therefore, an experiment was done to determine r^2 for copper and manganese analyzed by aqua regia, for shallow sample sites (< 15 feet) and deep sample sites (> 30 feet). The shallow sample sites gave an $r^2 = .14$ and deep sites gave an $r^2 = .00$. Therefore, it is suggested that Fe-Mn hydroxides are present in larger quantities in the shallower samples for reasons previously described.

Based on the above discussions, it is concluded that for the aqua regia method significant amounts of primary silicate and clay metals are extracted. A significant positive correlation of iron or manganese with a negative correlation to LOI for an element (Table 3) indicates that this element is concentrated in the non-organic portion of the gyttja sample. A positive relation to both iron or manganese and LOI indicates the element is dependent upon both the organic and non-organic components of the gyttja. A significant positive correlation of an element with only LOI would indicate that this element is dependent on the organic component. The coprecipitation and scavenging of trace elements by Fe-Mn hydroxides appears to only be of some importance in shallow water. Sulfur displays a positive relation with copper and percent weight loss.

Chemical Nature of All Samples

As previously mentioned, the accumulation of metals in lake gyttja is greatly dependent upon the limnological environment. The lakes within the survey are display an array of limnological environments. LOI appears to be a major quantitative indicator of the lake environment. Examination of LOI data from the survey revealed that small, shallow, swampy lakes yeild the highest LOI and very large lakes the lowest LOI. As a

TABLE 2: Median Element Concentrations by Three Digestion Methods for 36 Select Samples

	*As (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Mg (%)	Ni (ppm)	Pb (ppm)	Ti (ppm)	Zn (ppm)	*S (%)	Fe (%)	Mn (%)	**%Wt. Loss	*LOI (%)
***HCl, HNO$_3$ & HF		39	90	75	.38	88		1393	88		1.62	398		
4M HNO$_3$/1M HCl		12		36		36	10		77		1.07	370		
AC/HP		12		43		31			65		1.30	308		
Other Methods	.65									.42			32.8	41.4

* As, S and LOI determined by methods described in "Sample Preparation and Analytical Method" section.
** % Wt. Loss based on charring sample at 270°C.
*** Concentrations based on uncharred weight.

TABLE 3: Coefficients of Determination (r^2) for 36 Samples by Aqua Regia Method

	***S	Fe	Mn	***LOI	WD
***As	.00	.29	.45	*.09	.03
Co	*.01	.52	.55	*.36	.01
Cu	.08	*.04	.00	.19	*.05
Ni	*.15	.06	.01	*.20	.01
Pb	*.11	.05	.03	*.05	.17
Zn	.00	.06	*.01	*.01	.01
Fe	*.03		.86	*.62	.14
Mn	*.03			*.45	.28
**%Wt. Loss	.32	.03			
***LOI					*.37
***S					*.28

* Negative relation
** % Wt. Loss based on charring sample at 270°C.
*** As, S and LOI determined by methods described in "Sample Preparation and Analytical Methods" section.
WD = Water depth at sample site.
r^2 by simplified method (Lepeltier, 1969)

TABLE 4: Coefficients of Determination (r^2) for 36 Samples by AC/HP Method

	***S	Fe	Mn	**%Wt. Loss	WD
Co	*.40	.37	.02	*.37	.28
Cu	.02	.04	*.11	.48	.00
Ni	*.38	.06	.00	*.28	.14
Zn	.00	.28	*.01	.06	*.01
Fe	.02		.72	*.34	.03
Mn	*.02			*.34	.07

* Negative Relation
** % Wt. Loss based on charring sample at 270°C.
*** Sulfur by Leco titrator
WD = Water depth at sample site
r^2 by simplified method (Lepeltier, 1969)

TABLE 5: Coefficients of Determination (r^2) for 36 Samples by HCl, HNO_3 and HF - Acid Digestion Bomb

	***S	Fe	Mn	**%Wt. Loss	WD	Mg	Ni
Co	*.07	.04	.04	*.37	.20		
Cr	*.21	.00	.00	*.24	.19	.51	.80
Cu	.04	.00	*.01	.02	.01		.03
Ni	*.17	*.03	*.05	*.05	.08		
Zn	*.01	.00	.00	*.01	.02		
Fe	.02			*.02	.07		
Mn	.00	.76		*.19	.07		
Ti	*.18	.23	.28	*.66	.26		.06
Mg	*.23	*.21	.00	*.33	.19		.33

* Negative relation
** % Wt. Loss based on charring sample at 270°C.
*** Sulfur by Leco titrator
WD = Water depth at sample sites
All r^2 calculated on concentrations based on uncharred weight
r^2 by regression

result, the lakes were separated into three groups according to lake area, as described previously.

In addition to Lake Vermilion (Plate 1) being included in Large lakes, it was also considered by itself because of its very large area compared to other lakes. The LOI for all sizes of lakes and Lake Vermilion, considering all 270 samples collected in the survey, is approximately lognormally distributed. The median values for LOI and water depth at sample sites for the various lake sizes are given in Table 6. A decrease in LOI with lake size is evident.

All elements analyzed are approximately lognormally distributed. The median values for the elements for various lake sizes are given in Table 6. The mean element rating (Table 6) indicates that the highest mean element concentrations exist in Medium lakes and the lowest in Small lakes. However, a higher percentage of Medium lakes have anomalous metal values than Small and Large lakes.

Coefficients of determination (r^2) are given in Table 7. The organic content of the gyttja generally increases with increasing water depth within a lake, based on field observations. When comparing the LOI with water depth (WD, Table 7) for all sample sites and all lakes of a given size class, several observations can be made. LOI tends to increase with water depth at sample sites for Small lakes, but decreases with water depth for Lake Vermilion, Medium, and All lakes.

Many elements display a negative relation to LOI (Table 7); the most prominent being cobalt, iron, and manganese, and to a lesser degree, nickel, lead, and zinc. The negative relation suggests these elements are mainly contained in the non-organic portions of the gyttja. Copper and arsenic display a positive relation to LOI in most cases.

Manganese displays an excellent relationship with cobalt and iron (Table 7). Copper, nickel, and zinc occasionally have a good relationship with manganese. The correlation of iron with the various elements is nearly parallel to manganese, as would be expected from the strong relationship between iron and manganese.

Table 7 demonstrates that great differences do occur in the chemical processes between various sizes of lakes in the survey area. To further exemplify these differences, the r^2 was calculated for four Large lakes which have enough samples to make the regression meaningful. These r^2 are given in Table 8. It should be noted that the mean water depth at the sample sites is also very nearly the same for all four lakes.

To further illustrate the chemical differences between lakes, a survey was conducted on eight lakes, 110 miles southwest of the Lake Vermilion-Ely area in Aitkin County. This area contains mainly ice contact deposits resulting from a glacier different from the Lake Vermilion-Ely area called the Superior Lobe. Four of these lakes are approximately 1/4 square mile and four are one square mile in area. The r^2 for these lakes is given in Table 9. Comparing Table 9 with All lakes in Table 7 reveals many differences. For the Aitkin County lakes (Table 9) arsenic has a strong relation to iron; cobalt has practically no relation to iron and manganese; copper has a negative relation to LOI; water depth has strong negative relation to LOI; copper and nickel have a good positive relation to water depth. Other differences are also observed.

TABLE 6: Element Concentrations, LOI and Water Depth For All 270 Samples

	RANGE				
	S	M	L	LV	ALL
As(ppm)	0-8	0-6	0-6	0-6	0-8
Co(ppm)	2-31	4-24	5-41	6-20	2-41
Cu(ppm)	11-305	30-90	11-57	11-46	11-305
Ni(ppm)	2-280	0-180	9-108	9-40	0-280
Pb(ppm)	0-30	5-35	0-35	0-20	0-35
Zn(ppm)	19-265	30-170	10-212	10-178	10-265
Mn(ppm)	30-10,000	95-3,500	100-1,920	100-1,735	30-10,000
Fe(%)	.18-9.00	.64-7.76	.50-6.20	.50-6.20	.18-9.00
LOI(%)	28.36-85.16	15.84-74.06	15.49-69.12	15.69-49.98	15.49-85.16
WD(ft.)	1-50	8-45	5-55	5-50	1-55
n	107	51	112	58	270

	MEDIAN					*RATING			
	S	M	L	LV	ALL	S	M	L	LV
As	<1	1.2	1.2	1.5	<1	3	2	2	1
Co	9	14	12	13	12	4	1	3	2
Cv	43	58	27	22	36	2	1	3	4
Ni	20	41	26	24	25	4	1	2	3
Pd	11	13	13	13	12	2	1	1	1
Zn	72	80	77	96	76	4	2	3	1
Mn	230	610	570	740	450	4	2	3	1
Fe	1.0	1.8	1.6	1.7	1.4	4	1	3	2
LOI	56	42	28	27	42	1	2	3	4
Wd	13	24	22	19	18				
N	107	51	112	58	270				
Mean Element Rating:						3.1	1.4	2.7	2.0

S = Small Lakes
M = Medium Lakes
L = Large Lakes
LV = Lake Vermilion
ALL = All lakes sampled
n = Number of samples

WD = Water depth at sample sites (ft.)
*RATING: 1 highest, 4 lowest
Zero Values: As < 1 ppm, Ni < 2 ppm and Pb < 5 ppm
Ag: 272 samples < .01 ppm
Mo: All values less than 20 ppm

TABLE 7: Coefficients of Determination (r^2) for S, M, L, LV, and ALL Lakes For All 270 Samples

		Co	Cu	Ni	Zn	Fe	Mn	LOI	WD	n
	S					.45	.25	*.10	.10	107
	M					.12	.00	.56	*.01	51
As	L					.03	.04	*.01	*.11	112
	LV					.06	.06	.00	*.03	58
	ALL	−.09				.20	.03	.21	.00	270
	S					.36	.55	*.08	.04	
	M					.67	.55	*.36	.00	
Co	L					.48	.48	*.42	.00	
	LV					.74	.74	*.42		
	ALL					.74	.67	*.27	.14	
	S			.77	.15	.27	.29	.00	.14	
	M			.02	.36	.55	.11	.04	*.07	
Cu	L			.67	*.02	.00	*.01	.03	.04	
	LV			.58	*.22	*.04	*.07	.00		
	ALL	.01		.18	.03	.01	.01	.19	.00	
	S	.30				.26	.18	*.07	.05	
	M	.36				.15	.25	*.04	.37	
Ni	L	.14				.00	.00	*.02	.06	
	LV	.01				.00	.00	*.06		
	ALL	.27				.14	.13	*.18	.09	
	S		.05		.00	.09	.08	*.01	.00	
	M		.07		.25	.15	.15	*.04	.01	
Pb	L		.00		.05	.03	.08	*.09	.05	
	LV		*.03		.14	.07	.04	*.14		
	ALL	.06	.00		.02	.02	.04	*.03	.03	
	S					.01	.08	.09	.04	
	M					.25	.07	*.01	*.01	
Zn	L					.21	.38	*.42	.03	
	LV					.22	.53	*.18		
	ALL	.14				.14	.20	*.02	.02	
	S						.56	*.01	.06	
	M						.77	*.25	.01	
Fe	L						.72	*.48	.00	
	LV						.74	*.55		
	ALL						.79	*.22	.19	
	S							.00	.12	
	M							*.61	.07	
Mn	L							*.64	.02	
	LV							*.53		
	ALL							*.48	.19	
	S								.14	
	M								*.10	
LOI	L								*.01	
	LV								*.37	
	ALL								*.25	

* Negative relation (i.e., Co decreases with increase in LOI)

WD = Water depth at sample sites

n = Number of samples

r^2 by simplified method (Lepeltier, 1969)

TABLE 8: Coefficients of Determination (r^2) for Four Large Lakes

Lake	Cedar	Shagawa	Eagles Nest #3	Bear Head
Co & Fe	.56	.36	.30	.55
Co & LOI	*.13	*.35	.00	.01
Fe & Mn	.13	.55	.12	.69
Mean WD	30	24	30	28
n =	10	13	9	9

Mean WD = Mean water depth at sample sites
N = Number of samples
* Negative relation
r^2 by regression

TABLE 9: Coefficients of Determination (r^2) for Eight Lakes from Aitkin County

	As	Co	Cu	Ni	Pb	Zn	Fe	Mn	LOI
LOI	*.05	*.14	*.25	*.49	*.19	*.01	*.12	*.08	
Mn	.55	.49	*.01	.00	.10	.08	.71		
Fe	.45	.12	.00	.03	.14	.04			
WD	.13	.10	.36	.45	.09	.01	.20	.11	*.55

* Negative relation
WD = Water depth at sample site
Sixteen samples, two from each lake
r^2 by regression

INTERPRETATIONAL CONSIDERATIONS

At the outset of this survey it appeared, based on the success of the gyttja survey reported by Coker and Nichol (1975) and the apparent similar limnological environments of the Sturgeon Lake and Shebandowan areas of Ontario to the Vermilion-Ely area of Minnesota, that a gyttja lake sediment survey could be readily applied. Distinct differences, however, resulted which, in part, may be attributed to the analytical and sample preparation methods used. Coker and Nichol (1975) ashed the gyttja samples before analysis and used a near total metal digestion method. As described in this report, a study of digestion methods indicated that the 4M HNO_3/1M HCl leach on dry unignited gyttja gave a better contrast than a near total digestion on ignited samples. A similar aqua regia leach had also been reported by Davenport, Hornbrook, and Butler (1975) in Newfoundland. As a result, the 4M HNO_3/1M HCl was used on unashed samples for the entire survey.

Unfortunately, no known ore bodies exist within the survey area. An interesting showing of copper, previously described, does occur in the area. All other known showings are not as extensive and of as high a grade as this copper prospect located near Skeleton Lake. Skeleton Lake did yield highly anomalous copper values, but the known copper mineralization is about 1,000 feet down-drainage and 70 feet below the elevation of Skeleton Lake; however, preliminary geophysical surveys do indicate that a conductor exists in the vicinity of the lake. Other than this copper mineralization, all interpretational methods had to be developed by other means than simply reflecting known mineralization.

It has been demonstrated that chemical differences do exist between lakes in the survey reported. These differences are attributed to variations in temperature, conductivity, dissolved oxygen, pH and Eh of the water and sediment, the organic and non-organic sediment composition, and other factors which are dependent upon the limnological environment of each lake (Coker and Nichol, 1975; Timperley and Allan, 1974). Considering the chemical differences between lakes, the objective of the survey reported is to place all lakes on a common datum so that trends in element values are discernible and meaningful across the entire survey area. Therefore, parameters had to be determined for each element of interest which would be least affected by the varying limnological environments.

Often common practice dictates that element ratios be used to normalize the effect of coprecipitation of one element with another (i.e. cobalt with manganese) where a strong correlation occurs between the two elements. Garrett and Hornbrook (1976) report that from a survey conducted in Saskatchewan using lake gyttja, zinc displayed a strong positive relation with LOI below 12% LOI. Above 12% LOI, zinc stabilizes and actually has a weak negative relation, but over 50% LOI displays a strong negative relation. They propose that zinc maintains a strong positive relation until the organic content is excessive at which point insufficient zinc is available to satisfy the adsorption capacity of the organic material. It is evident that below 12% LOI a Zn/LOI ratio will normalize the effect of LOI on zinc, but over 12% LOI this ratio will suppress zinc values which actually represent anomalous lake drainage basins. As a result, they conclude that samples with less than 12% LOI and greater than 50% LOI should be avoided. Coker and Nichol (1976) also report a similar relationship for zinc and LOI in the Sturgeon Lake area of Ontario. Based on preliminary studies, Garrett and Hornbrook (1976) also reported similar phenomenon for other elements. They found that uranium stabilized at 12% LOI, 2% iron, and 500 ppm manganese; zinc at 4% iron and 700 ppm manganese.

Observation of element vs. iron, manganese, and LOI graphs for this survey reveals similar relationships to those reported by Garrett and Hornbrook (1976), and Coker and Nichol (1976). Arsenic, which gives a positive relation to LOI for All lakes (Table 7), displays a fair positive relation below 60% LOI and a negative relation over 60% LOI. Arsenic, which gives a positive relation to iron for All lakes (Table 7), gives a positive relation below 5% iron and stabilizes to a weak positive relation over 5% iron. A similar relation is observed for arsenic and manganese, with arsenic stabilizing at 800 ppm manganese.

Cobalt, which gives a negative relation to LOI for All lakes (Table 7), displays a strong positive relation to 1-LOI over the entire range of values. The 1-LOI represents the portion of the sample remaining after ignition, the non-organic portion. The ratio Co/(1-LOI) represents the cobalt concentration on the non-organic portion of the sample. Cobalt, which gives a positive relation to iron for All lakes (Table 7), displays a strong positive relation below 3% iron and stabilizes over 3% iron. Cobalt and manganese display a similar relation, with cobalt stabilizing over 600 ppm manganese.

Copper, which gives a positive relation to LOI for All lakes (Table 7), displays a positive relation to LOI below 30%, stabilizes with a weak positive relation between 30-65% LOI, and has a negative relation over 65% LOI. Copper displays a positive relation to iron below 4% iron and stabilizes over 4%.

Nickel, which gives a negative relation to LOI for All lakes (Table 7), displays a consistent positive relation to 1-LOI over the entire range of values. Nickel gives positive relation to iron, manganese, and cobalt for All lakes (Table 7). Observation of these elements plotted against nickel indicates that a positive relation exists below 2.5% iron and 600 ppm manganese, with nickel stabilizing over these values. Based on preliminary results, nickel displays a fairly constant positive relation with cobalt.

Lead displays a weak positive relation to 1-LOI. Lead shows a positive relation to manganese below 600 ppm manganese and stabilizes over this value.

Zinc shows a weak positive relation to 1-LOI over the entire range of values. Zinc, which gives a positive relation to iron, manganese, and cobalt for All lakes (Table 7), displays a positive relation below 2.5% iron and a negative relation over 2.5%. Zinc shows a positive correlation below 800 ppm manganese and a weak negative relation over 800 ppm. Based on preliminary results, zinc displays a constant positive relation with cobalt.

As previously described, the coefficients of determination (r^2) (Table 7) for All lakes indicate that significant relationships do exist between the elements of interest and iron, manganese, cobalt, and LOI. However, examination of graphs of these elements of interest and iron, manganese, cobalt, and LOI reveal that the relationships often are not consistent across the entire range of values. For example, zinc displayed a positive relation below 800 ppm manganese and a weak negative relation over 800 ppm. If it was decided that a Zn/Mn ratio would normalize the zinc values and place the zinc values for all lakes surveyed on a common datum, anomalous zinc samples which contained more than 800 ppm manganese would be suppressed often to background values. As suggested by Garrett and Hornbrook (1976), this problem can be avoided by selecting samples which fall in the stabilized zone, in which case ratios are not necessary. However, for the survey reported, this would result in eliminating a majority of samples from the study. Therefore, other alternatives were explored.

Examination of Table 7 indicates that generally significant but often relatively weak relationships exist between the elements of interest and iron, manganese, and LOI. When several parameters display a relation to an element of interest, this indicates the element is dependent upon more than one variable which suggests that multiple regression should be applied in place of the single variable regression used for the study reported. With multiple regression, more variation of the element of interest can be accounted for and the resultant residuals used to represent the element as demonstrated by Davenport, Hornbrook, and Bulter

(1975) and Clarke (1976). However, the problems with ratios previously discussed would also be reflected in the use of multiple regression residuals using a $\log_{10}$ model. That is, the stabilization of elements at various parameter (i.e. iron, manganese, LOI, etc.) levels would result in residals suppressing otherwise anomalous elements values.

Considering the above discussion on coefficients of determination and the details of the relationships between elements and other sample parameter, an analysis was carried out which additionally examined characteristics of cumulative frequency distributions of the elements of element ratios, including percentile plots on maps of each element and element ratio.

Again the element concentrations between sizes of lakes was considerably different as shown in Table 6. Lognormal cumulative frequency distribution graphs were prepared for the element concentration and element ratios. For each parameter on the same graph, the distributions for Small, Medium, Large, and All lakes, and Lake Vermilion were plotted. The parameters for which the distributions of the various size classes of lakes would converge, would suggest that this parameter would place all sizes of lakes on a common datum. Furthermore, it was considered desirable to determine the separation of distribut ons near the high end of the values but not in the highly anomalous range. Therefore, determinations on distribution separation was made at the 70 and 90 percentile. The calculations were made by subtracting the value of the parameter at the lowest distribution from that of the highest and normalizing the values so that they were comparable to other parameters by dividing by the lowest value. The values obtained by this calculation are presented in Table 10. The average of the 70 and 90 percentile were considered to be of best use for establishing a common datum. For lack of a better name, these values have been called "distribution separation coefficients" (DSC). It should also be noted that some of these coefficients are quite large at the 90th percentile due to the large proportion of highly anomalous samples in Medium lakes; however, this should not have an adverse effect as parameters are compared on a relative basis for each element.

An analysis was done to determine the parameter for each element which gave the best common datum for all lakes surveyed. This selection, as described below, was done on the basis of examination and comparison of the coefficients of determination (r^2), cumulative frequency distributions, distribution separation coefficients (DSC), and percentile maps of each element and element ratio.

Arsenic

For all lakes from Table 7, arsenic is equally dependent upon iron and LOI which suggests it is equally dependent upon the organic and inorganic fractions of the gyttja. Multiple regression residuals do not appear feasible as both iron and LOI display inconsistent relationships with arsenic.

The DSC in Table 10 indicates that As/Mn yields the lowest dispersion among lake sizes and the arsenic concentration the second lowest.

Examination of the frequency distributions and percentile maps indicates that As/Fe values concentrate in Lake Vermilion, Medium, and Large lakes. As/Mn gives a fairly equal distribution over all sizes of lakes, but arsenic and manganese display an inconsistent relationship. As/LOI concentrates in Lake Vermilion because of the low LOI, and arsenic and LOI display an inconsistent relation. As/(1-LOI) tends to concentrate in Medium lakes, and displays an inconsistent relation. The arsenic concentration displays a fairly equal distribution among lakes sizes.

Based on the equal distribution of the arsenic concentration among lake sizes and its apparent equal dependence on both the organic and inorganic fractions of the gyttja, it was decided that the arsenic concentration yielded the best common datum for all lakes surveyed.

Cobalt

In Table 7 for All lakes, cobalt is dependent upon iron, manganese, and LOI. The iron and manganese have a positive relation and the LOI has a negative relation which suggests it is dependent mainly upon the inorganic fraction of the gyttja.

The DSC in Table 10 indicates that cobalt yields the lowest dispersion among lake sizes.

Examination of the frequency distributions and percentile maps indicates that Co/Fe values concentrate in Large lakes. Co/Mn concentrates in Small lakes. Co/(1-LOI) concentrates in Small lakes due to their high LOI. Cobalt values tend to concentrate in Large lakes.

Both iron and manganese display an inconsistent relation to cobalt and, therefore, were ruled out. Cobalt has a lower DSC than Co/(1-LOI) and, therefore, yields the best datum for all lakes surveyed.

Copper

For All lakes from Table 7, copper is mainly dependent upon LOI which suggests it is concentrated in the organic fraction of the sediment. However, copper displays an inconsistent relation to LOI.

The DSC in Table 10 indicates that Cu/LOI yields the lowest dispersion among lake sizes and the copper concentration the second lowest.

The frequency distributions and percentile maps indicate that the Cu/Fe values concentrate in Small and Medium lakes. Cu/Mn concentrates in Small lakes. Cu/(1-LOI) concentrates in Small lakes due to their high LOI. Cu/LOI concentrates in Small and Medium

TABLE 10: Distribution Separation Coefficients at the 70 and 90 Percentile

	70 Percentile						90 Percentile					
	Me	Me/Mn	Me/Fe	Me/ (1-LOI)	Me/ LOI	Me/Co	Me	Me/Me	Me/Fe	Me/ (1-LOI)	Me/ LOI	Me/Co
As	1.1	.4	1.1	1.0	2.8		.6	.8	.7	.8	.7	
Co	.1	1.6	.6	.6			.3	2.2	.6	1.1		
Cu	1.7	5.3	2.2	2.8	.9		2.6	6.5	4.2	5.2	.8	2.3
Ni	1.1	1.6	.4	1.3		.3	3.9	10.2	5.3	3.0		
Pb	.2	1.7	.5	.4			.2	2.6	.4	.5		
Zn	.2	2.4	1.0	.5	1.7	.5	.1	3.1	2.4	.8	1.2	.9
Mn	1.8						.5					
Fe	.7						1.4					

MEAN OF THE 70 AND 90 PERCENTILE

	Me	Me/Mn	Me/Fe	Me/ (1-LOI)	Me/ LOI	Me/Co
As	.8	.6	.9	.9	1.8	
Co	.2	1.9	.6	.8		
Cu	2.1	5.9	3.2	4.0	.9	
Ni	2.5	5.9	2.8	2.1		1.3
Pb	.2	2.1	5	5		
Zn	.2	2.7	1.7	.7	1.4	7
Mn	1.2					
Fe	1.1					

lakes. The copper concentration concentrates in Small and Medium lakes.

Because of the inconsistent relation between copper and LOI, the copper concentration, therefore, yields the best datum for all lakes surveyed.

Nickel

From Table 7 for All lakes, the positive relation of cobalt, iron, and manganese, and negative relation of LOI with nickel suggests that nickel is mainly concentrated in the inorganic fraction of the gyttja. Nickel does display a consistent relation to 1-LOI and cobalt, but an inconsistent relation to iron and manganese.

The DSC in Table 10 indicates that Ni/Co yields the lowest dispersion among lake sizes and the Ni/(1-LOI) the second lowest and the nickel concentration the third.

The frequency distributions and percentile maps indicate that the Ni/Fe and Ni/Mn values concentrate in Small and Medium lakes. Ni/Co concentrates in Medium lakes. Ni/(1-LOI) concentrates in Small and Medium lakes as a result of their high LOI compared to Large lakes. The nickel concentration has a fair distribution among lake sizes, but does concentrate in Medium lakes.

Clarke (1976) has suggested that cobalt, with its low variation, therefore, is a better index of background variation and coprecipitation than manganese. As a result, metal to cobalt ratios should not encounter the spurious values often obtained with manganese ratios.

The Ni/(1-LOI) tends to concentrate in high LOI lakes and, therefore, the nickel concentration yields the best datum for all lakes surveyed.

Lead

For All lakes from Table 7, lead does not display any significant relations. Therefore, it appears that lead is equally dependent upon both the organic and inorganic fractions of the gyttja.

The DSC in Table 10 indicates that the lead concentration yields the lowest dispersion among lake sizes.

Examination of the frequency distributions and percentile maps indicates that Pb/Mn, Pb/Fe, and Pb/(1-LOI) concentrates in Small lakes. The lead concentration concentrates in Medium and Large lakes.

Because the lead concentration has a more equal distribution among lake sizes, it yields the best datum for all lakes surveyed.

Zinc

From Table 7 for All lakes, the positive relation of zinc with cobalt, iron, and manganese suggests that zinc is mainly concentrated in the inorganic fraction of the gyttja. However, zinc does not display a strong relation with 1-LOI.

The DSC in Table 10 indicates that the zinc concentration yields the lowest dispersion among lake sizes.

The frequency distributions and percentile maps indicate that Zn/Fe, Zn/Mn, Zn/Co, and Zn/(1-LOI) concentrate in Small lakes. Zn/LOI concentrates in Large lakes due to their low LOI.

Because of the equal distribution of the zinc concentration over all lake sizes, it yields the best datum for all lakes surveyed.

As mentioned previously in this section, only 36 samples were analyzed for chromium, magnesium, and titanium. Therefore, a rigorous analysis was not done to determine the best parameter to represent these elements on a common datum. Table 5 for percent weight loss and water depth suggests that chromium, magnesium, and titanium are mainly contained in the inorganic portion of the gyttja. As a result, these element concentrations will be based on the charred weight of the sample in the next section of this report.

From the above discussion for the various elements analyzed, metal/LOI ratios tend to concentrate in low LOI lakes, and metal/(1-LOI) ratios in high LOI lakes.

A perfect datum for all lakes surveyed is not possible due to drastic differences in limnological environments. Therefore, the parameters selected to represent each element are only those which more closely approach a perfect datum.

Hornbrook and Garrett (1976) have reported on an organic lake sediment survey they conducted in east-central Saskatchewan. They concluded that iron, manganese, and organics do not appear to be important scavengers, and extensive statistical treatment of the data, including multilinear regression, does not substantially improve the data. Therefore, their interpretation was also based on the element concentrations.

It is not necessarily suggested that the element concentrations should be used to evaluate a lake or several lakes within a specific area. The variation of r^2 values in Table 7 would suggest that r^2 values be calculated and analyzed for the particular lake or lakes considered with parameters selected for the lakes under consideration. Again, caution must be exercised in the use of ratios as previously described.

SURVEY RESULTS AND DISCUSSION

Plate 1 shows the lakes, with their names, sampled in this survey. Plates 2-8 show the element concentrations, based on the unignited sample, for various percentiles for arsenic, cobalt, copper, nickel, lead, silver, and zinc. Plates 9-11 give the chromium, magnesium, and titanium concentrations, based on the charred sample weight.

Observation of Plates 2-8 reveals that within a Small lake and, to a lesser degree, a Medium lake, the concentration of an element in the gyttja is often similar between samples. Large lakes, on the other hand, appear to have a diluting effect on the element concentrations. Therefore, anomalous values may be restricted to a bay or local depression within the lake, as also described by Tenhola (1976).

As described previously, no orebodies, other than iron, have been discovered in the survey area. However, an interesting copper prospect occurs south of Skeleton Lake (Plate 1). Although this showing is about 1,000 feet down-drainage and 70 feet below the elevation of Skeleton Lake, anomalous copper values (Plate 4) were obtained from Skeleton Lake. Preliminary geophysical surveys do indicate that a conductor exists in the vicinity of the lake.

In addition to Skeleton Lake, anomalous copper occurs in Island and Six Mile lakes (Plates 1 and 4). Six Mile Lake has the highest copper and silver of any of the lakes surveyed (Plates 4 and 7). High copper values were also obtained in Needle Boy (Plates 1 and 4) south of six Mile and anomalous zinc and silver in Five Mile (Plates 1 and 8) southwest of Six Mile. Anomalous zinc also occurs in Garden Lake and White Iron Lake, with scattered high zinc samples from several other lakes.

Arsenic was analyzed as an indicator for gold (Plate 2). Several scattered anomalous arsenic and silver values (Plates 2 and 7) occur throughout the region. Several of the more prominent anomalies include: Mitchell Lake; a small lake in Section 2-T62N-R13W which has anomalous arsenic, silver, and zinc (Plates 2, 7, and 8); an eastern bay of Lake Vermilion in Sections 1 and 12-T62N-R15W, which has anomalous arsenic and silver (Plates 2 and 7); and Purvis Lake with anomalous arsenic and lead (Plates 2 and 6).

Within the area surveyed, ultramafic rocks of the Newton Lake Formation (Figure 1) occur in T63N-R12W (Sims, 1973). As suggested in the previous section, especially chromium and titanium would be contained mainly in primary oxides and silicates derived from the bedrock directly or the glacial drift. The chromium and magnesium (Plates 9 and 10) does reflect these ultramafic rocks with apparent glacial dispersion down-ice in a southwesterly direction. Titanium (Plate 11) appears to reflect the more mafic rocks.

Anomalous nickel concentrations (Plate 5) also occur over the ultramafics previously described. Significant anomalies are observed for Hobo and Little Long Lakes (Plates 1 and 5). The high values in these lakes may be attributed to the high nickel content of the silicates in ultramafics; however, other lakes in the same area do not give similar nickel concentrations. Chromium (Plate 9) does have high values in these two lakes, indicating a lake sediment of higher ultramafic mineral content, but magnesium (Plate 10) has high values in several of the lakes in this area.

In addition to the reflection of bedrock geology by chromium, magnesium, and titanium; copper, nickel, lead, and zinc (Plates 4, 5, 6, and 8) appear to also reflect bedrock composition by comparing these Plates with Figure 1. Again, ultramafic rocks mainly occur within the Newton Lake Formation (Figure 1) in the northeastern portion of the survey area, and the more mafic to intermediate composition rocks occur in the southern and western portions of the survey area. In addition, as for chromium and magnesium, nickel (Plate 5) appears to be glacially dispersed in a southwesterly direction.

The previous discussion is limited primarily to the most striking results of the survey; however, examination of the maps do reveal other interesting features.

CONCLUSIONS

The element concentrations of unignited gyttja lake sediment, as opposed to ratios and residuals, best represent the trace element variations over the survey area using the sample preparation and analytical methods described.

Although no orebodies, other than iron, have been discovered in the survey area, anomalous copper was detected near a significant copper showing. Also, several of the elements analyzed do reflect bedrock composition, which indicates that gyttja lake sediment does reflect the chemical nature of the bedrock geology. Furthermore, geochemical surveys of gyttja lake sediments have been shown to reflect known mineralization. Several significant anomalies were located by this survey which deserve consideration.

For gyttja lake sediments, it has been suggested that trace elements can be chemically derived directly from a bedrock source and/or from glacial drift dispersed down-ice direction from a bedrock source (Coker and Nichol, 1975; Hoffman and Fletcher, 1976; Timperley and Allan, 1974). Furthermore, once the mobile trace elements are in solution, they may, depending upon chemical conditions of the stream and lake waters, be dispersed down-drainage from one lake to another lake (Cameron, 1975). These considerations must be made when attempting to locate the source of anomalies.

The element concentrations for this survey appear to best represent all 75 lakes; however, when considering an anomalous lake or lakes in an attempt to locate the anomalous source, the element concentrations alone may not best represent the element dispersion, and, therefore, other parameters (i.e. element ratios) may necessarily have to be considered. The parameters applicable for representing the various element most probably vary from lake to lake.

The anomalies obtained in this survey could be followed up by various geochemical methods (i.e. nearshore lake sediment, stream sediment, soil, etc.), including detailed evaluation of this survey, in combination with airborne and ground geophysics and geologic studies.

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*For this report, gyttja will be used to describe organic-rich lake sediments.

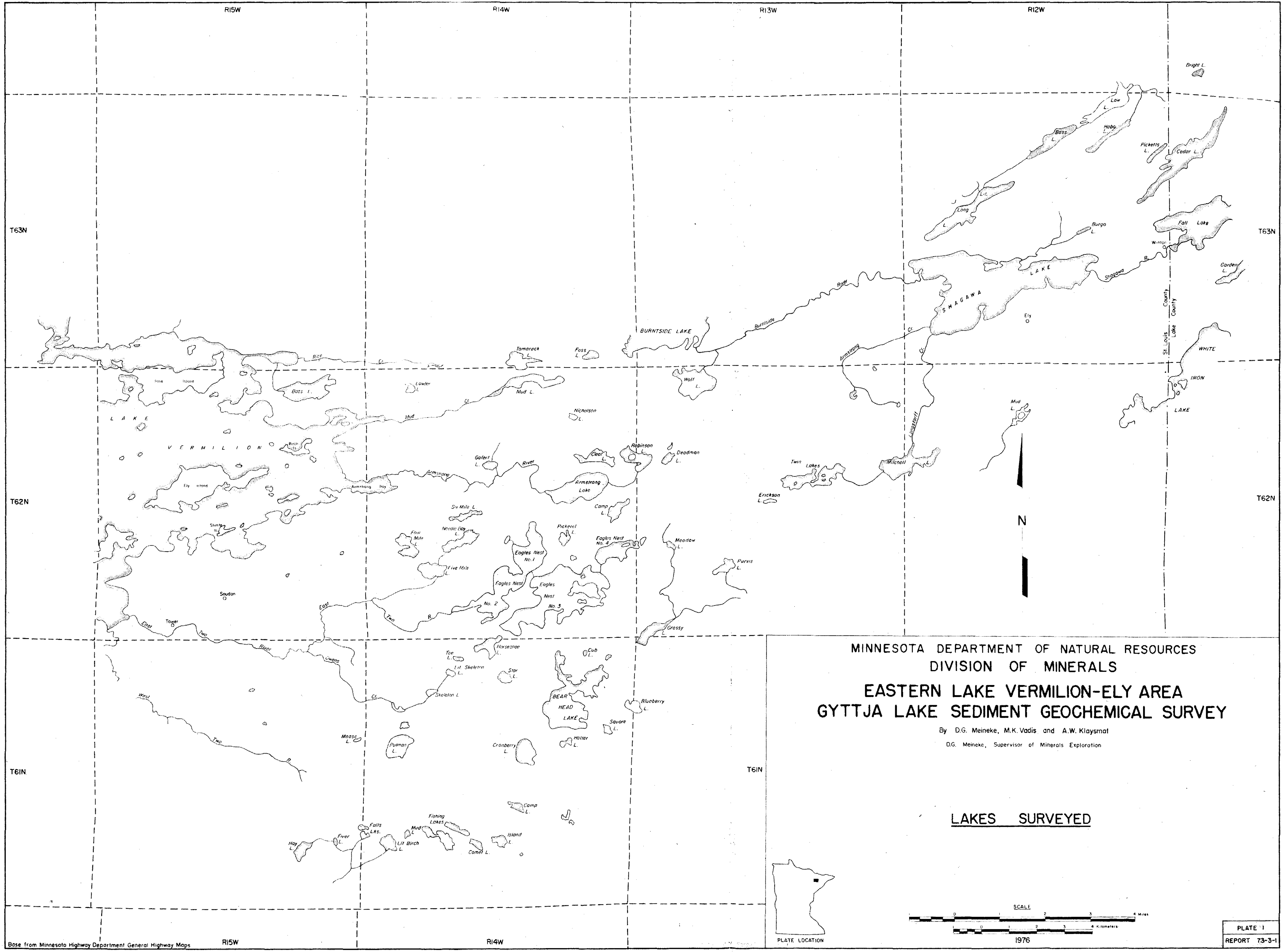
MINNESOTA DEPARTMENT OF NATURAL RESOURCES
DIVISION OF MINERALS

EASTERN LAKE VERMILION-ELY AREA GYTTJA LAKE SEDIMENT GEOCHEMICAL SURVEY

By D.G. Meineke, M.K. Vadis and A.W. Klaysmat

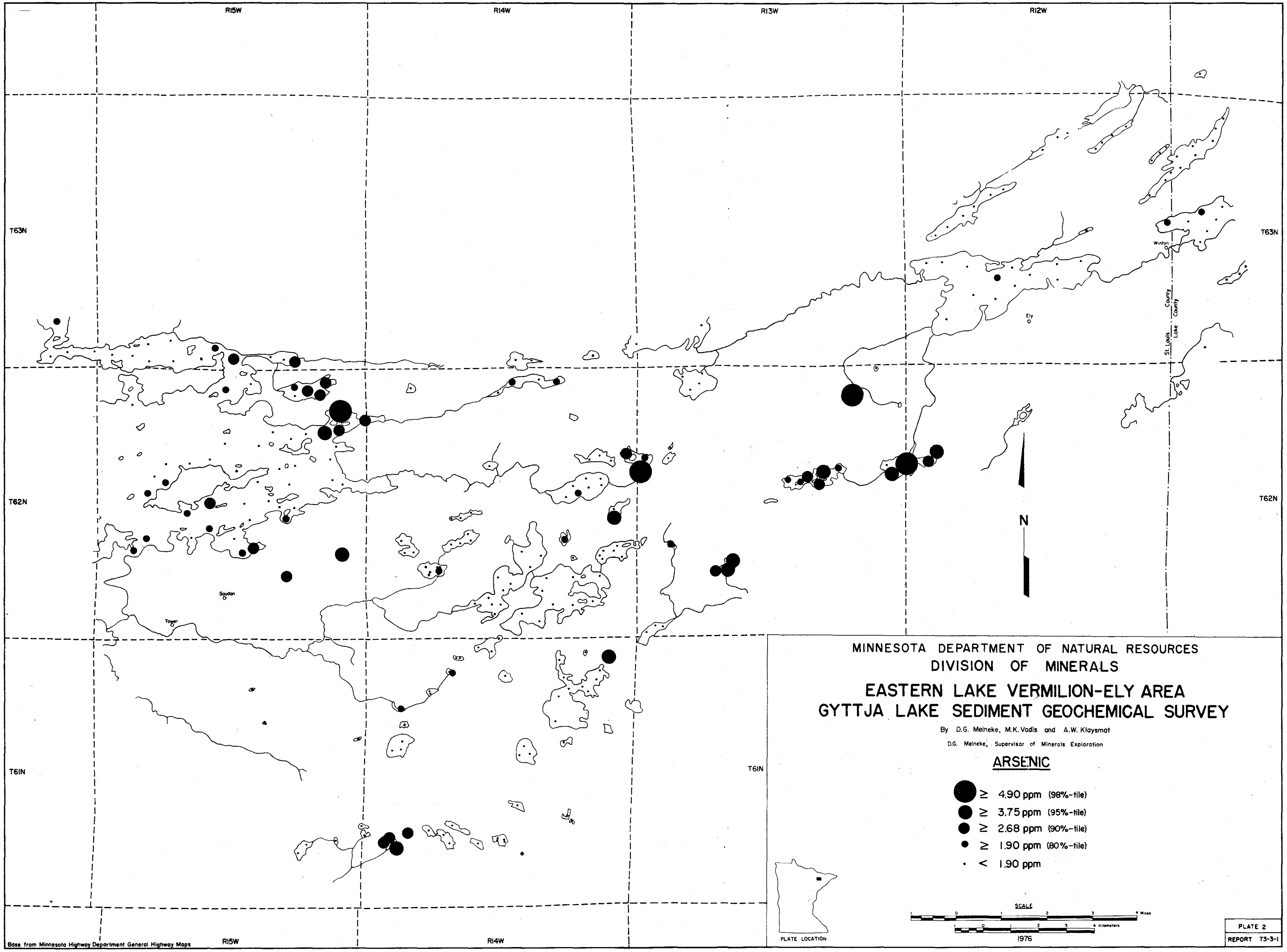
D.G. Meineke, Supervisor of Minerals Exploration

LAKES SURVEYED



1976

PLATE I
REPORT 73-3-1



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GYTTJA LAKE SEDIMENT GEOCHEMICAL SURVEY

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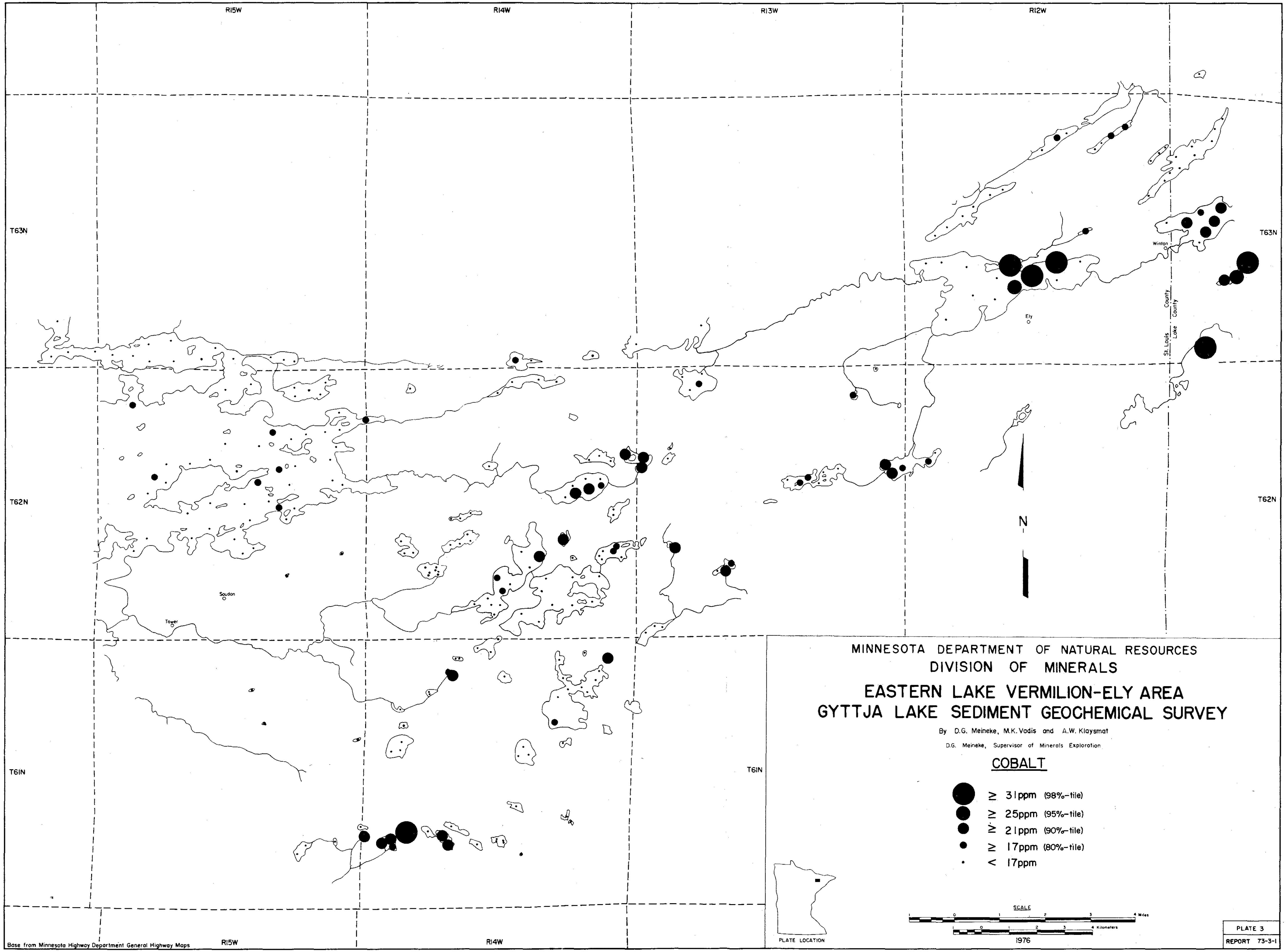
ARSENIC

- ● ≥ 4.90 ppm (98%-tile)
- ● ≥ 3.75 ppm (95%-tile)
- ● ≥ 2.68 ppm (90%-tile)
- • ≥ 1.90 ppm (80%-tile)
- · < 1.90 ppm

1976

PLATE 2
REPORT 73-3-1



Base from Minnesota Highway Department General Highway Maps

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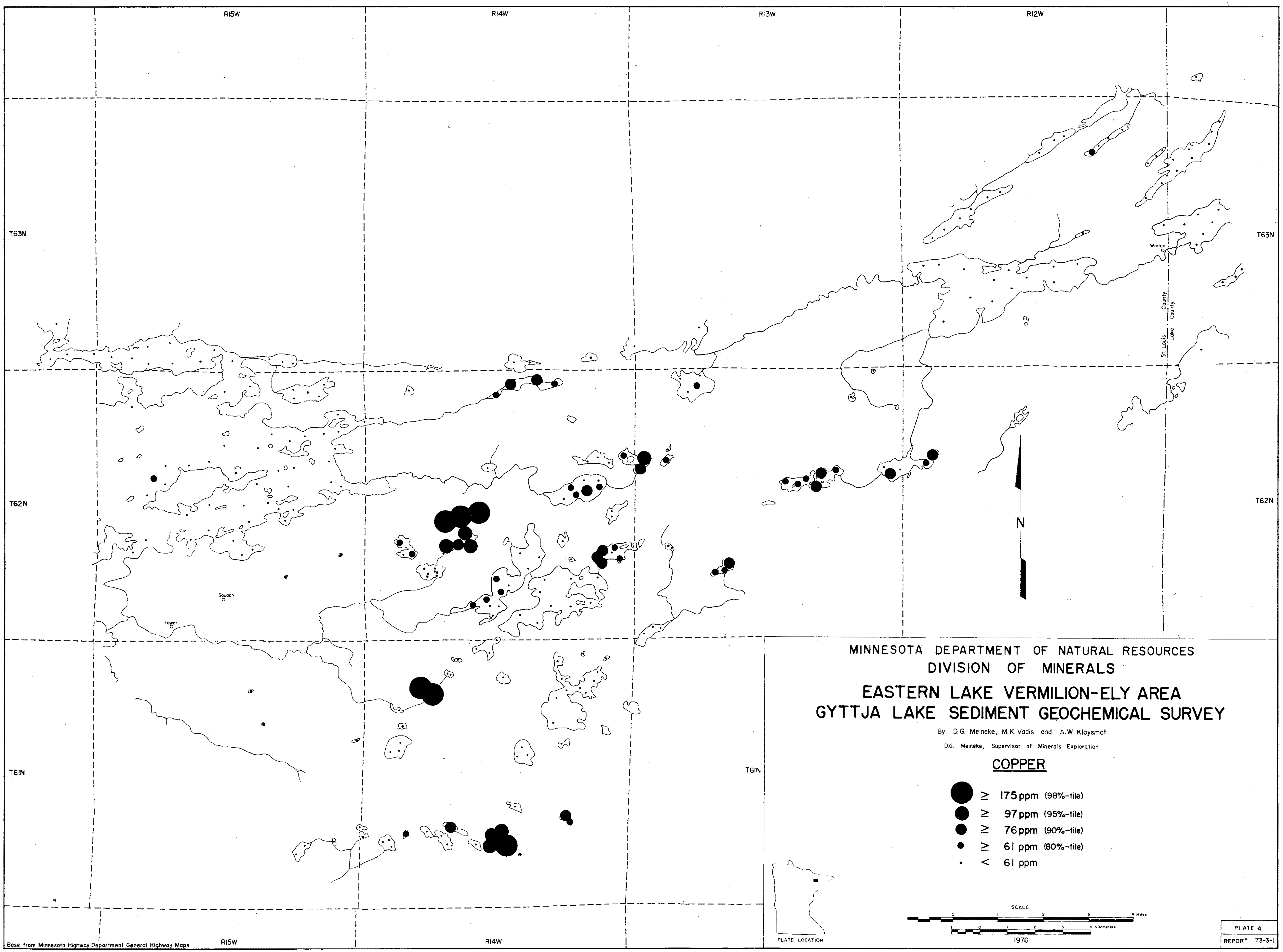
COBALT

● ≥ 31ppm (98%-tile)
● ≥ 25ppm (95%-tile)
● ≥ 21ppm (90%-tile)
● ≥ 17ppm (80%-tile)
• < 17ppm

1976

PLATE 3
REPORT 73-3-1



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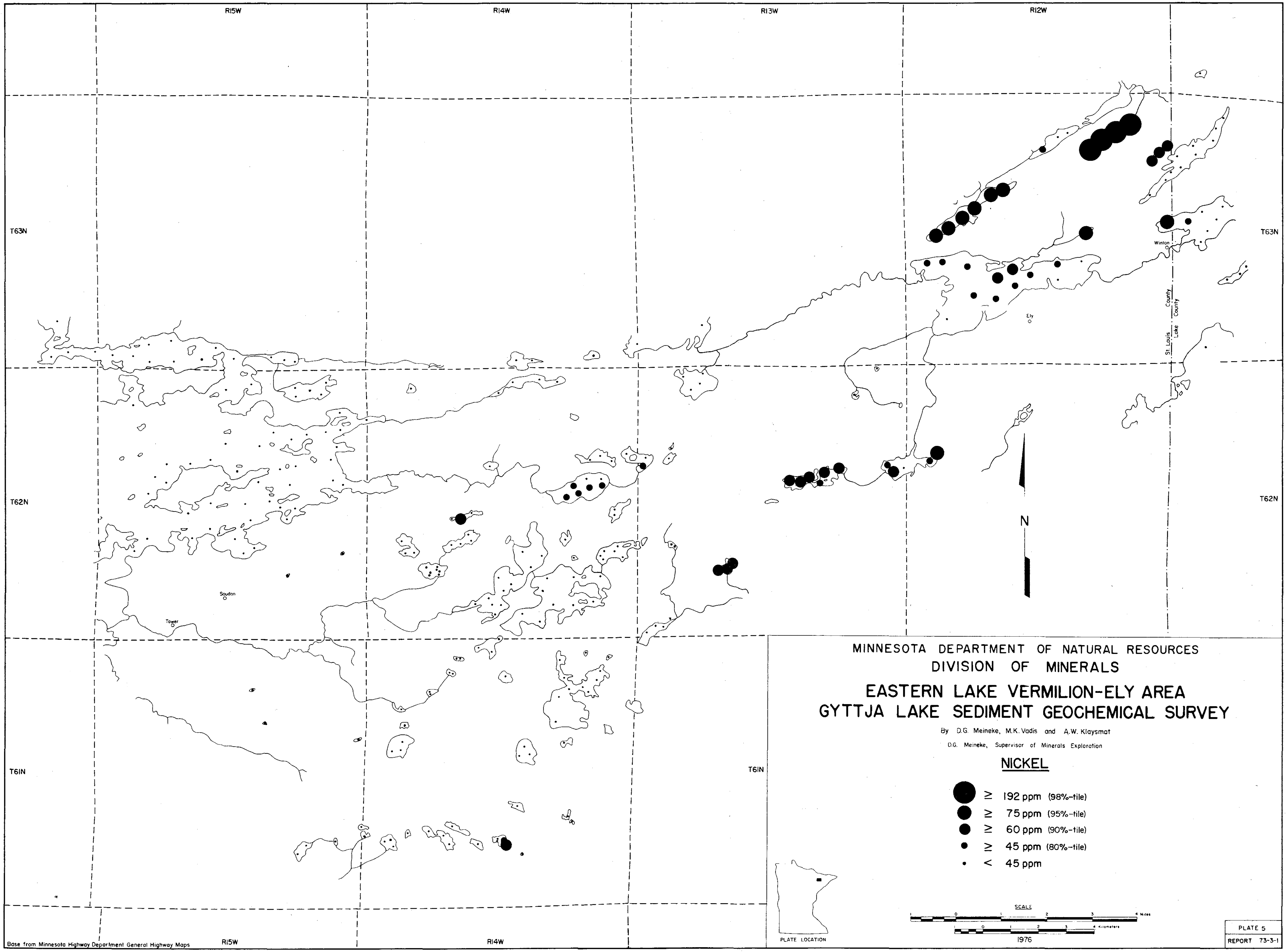
COPPER

● ≥ 175 ppm (98%-tile)
● ≥ 97 ppm (95%-tile)
● ≥ 76 ppm (90%-tile)
● ≥ 61 ppm (80%-tile)
• < 61 ppm

1976

PLATE 4

REPORT 73-3-1



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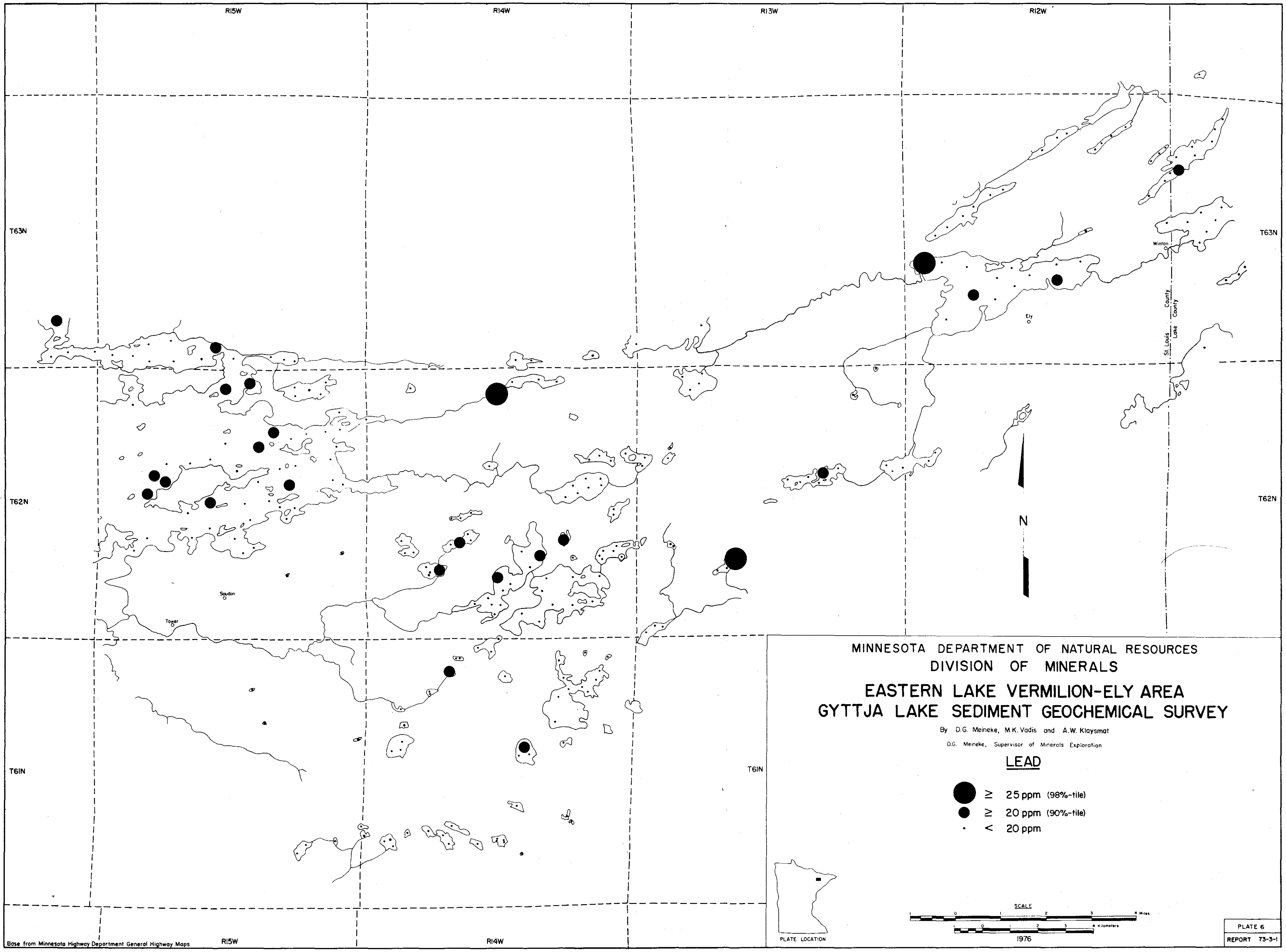
NICKEL

● ≥ 192 ppm (98%-tile)
● ≥ 75 ppm (95%-tile)
● ≥ 60 ppm (90%-tile)
• ≥ 45 ppm (80%-tile)
· < 45 ppm

1976

PLATE 5
REPORT 73-3-1



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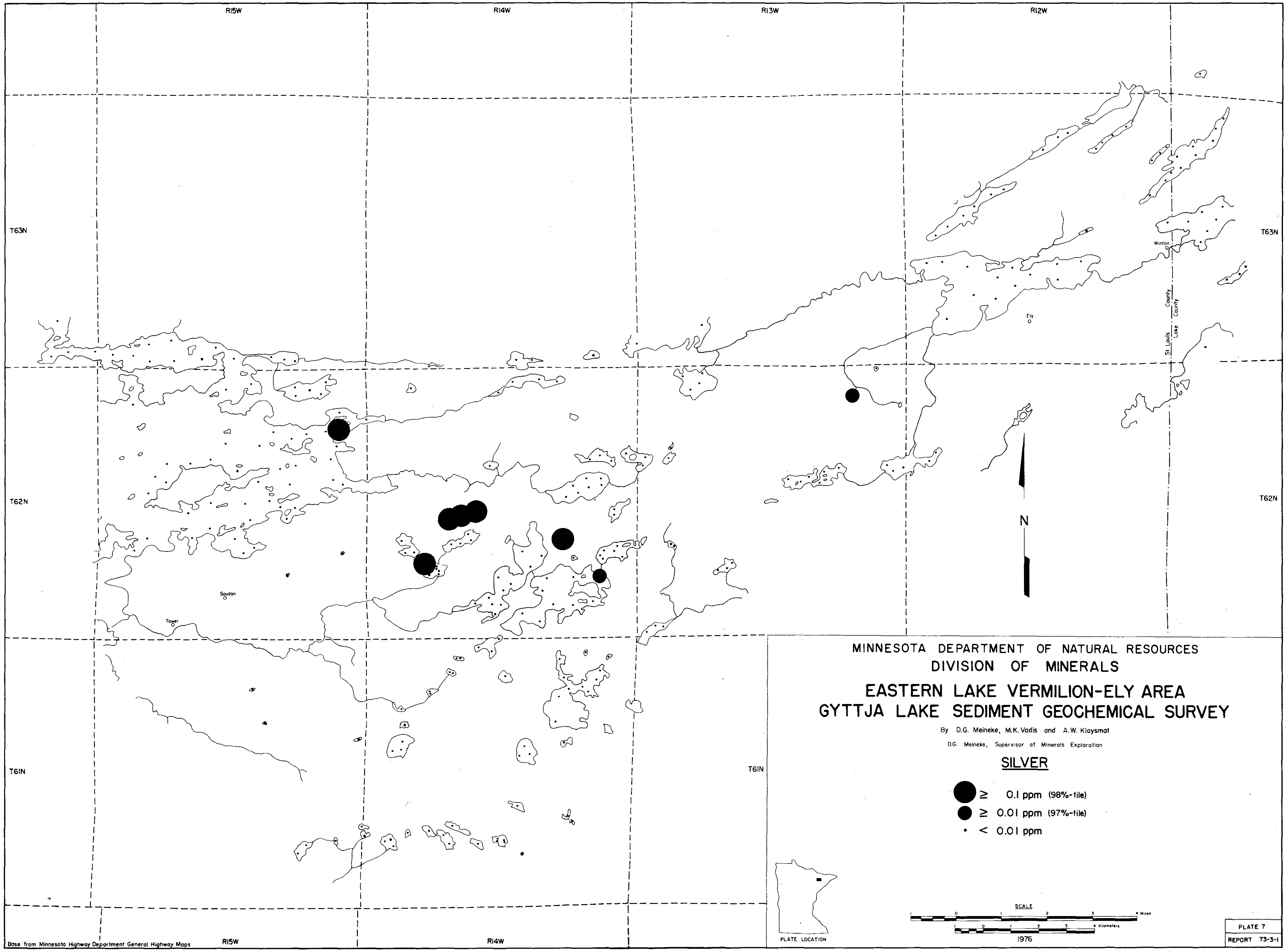
LEAD

● ≥ 25 ppm (98%-tile)
● ≥ 20 ppm (90%-tile)
• < 20 ppm

1976

PLATE 6
REPORT 73-3-1

Base from Minnesota Highway Department General Highway Maps



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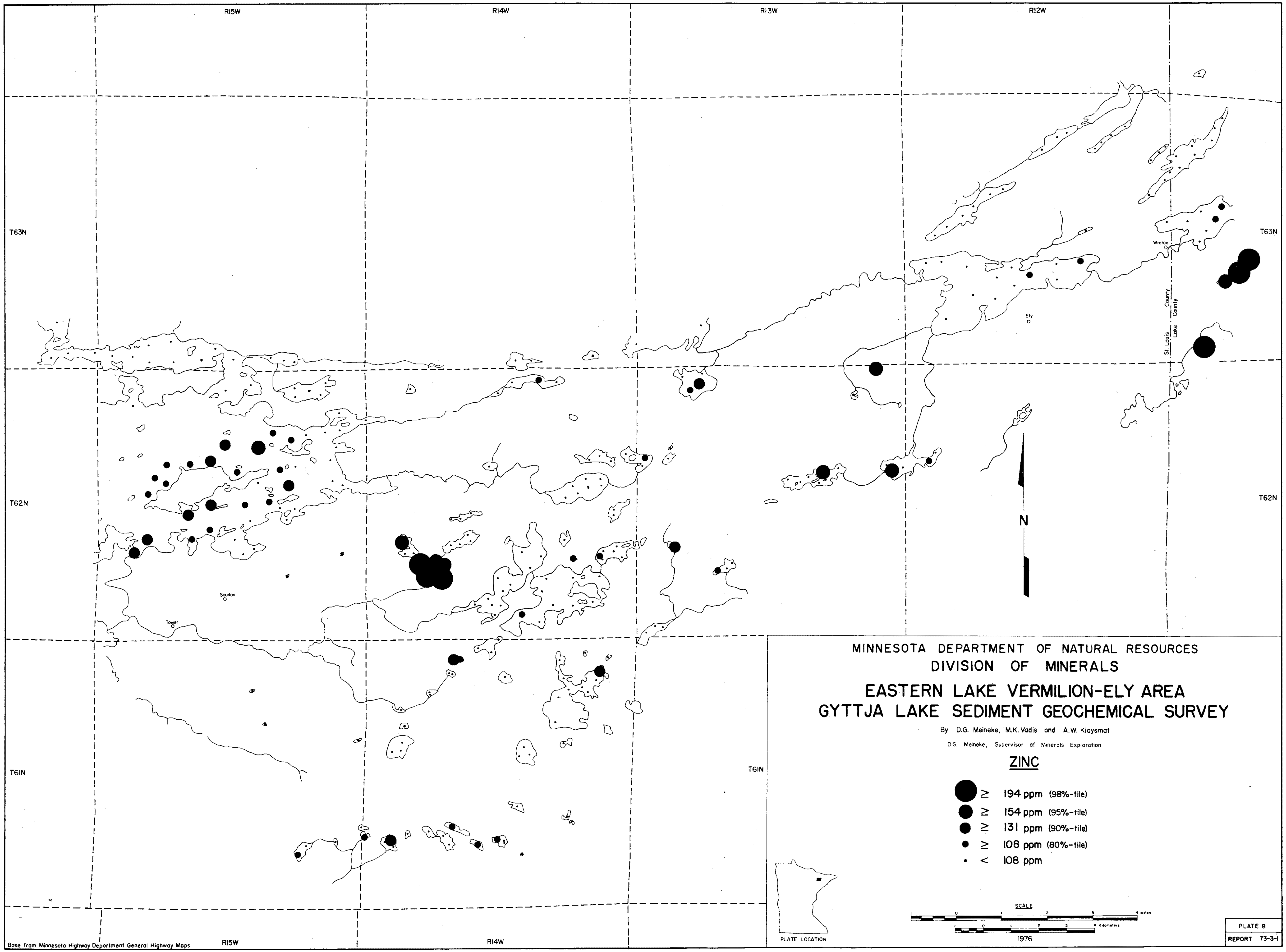
SILVER

- ● ≥ 0.1 ppm (98%-tile)
- ● ≥ 0.01 ppm (97%-tile)
- • < 0.01 ppm

1976

PLATE 7
REPORT 73-3-1

Base from Minnesota Highway Department General Highway Maps



Base from Minnesota Highway Department General Highway Maps

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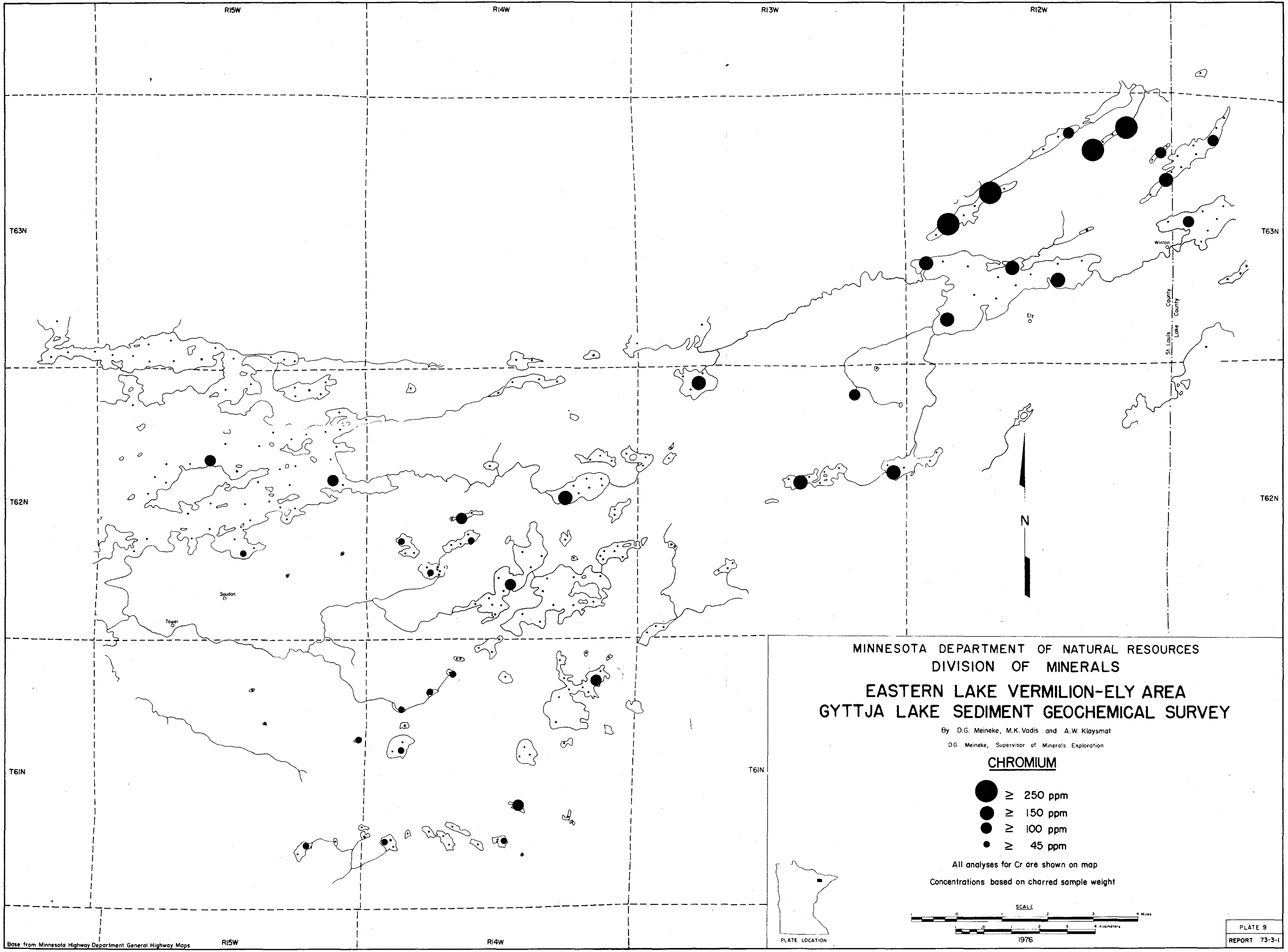
ZINC

●	≥	194 ppm (98%-tile)
●	≥	154 ppm (95%-tile)
●	≥	131 ppm (90%-tile)
●	≥	108 ppm (80%-tile)
•	<	108 ppm

1976

PLATE 8

REPORT 73-3-1



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CHROMIUM

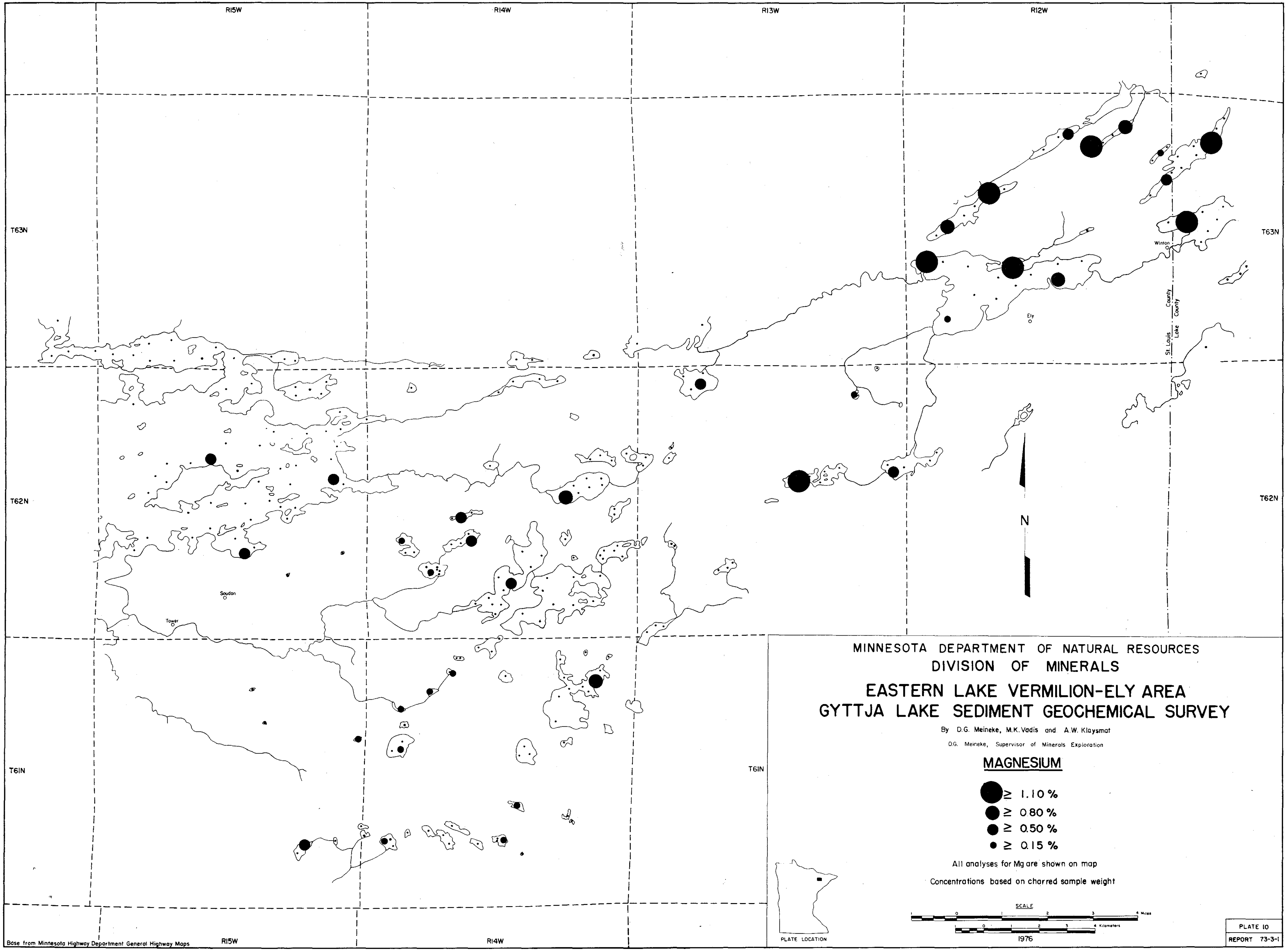
- ● ≥ 250 ppm
- ● ≥ 150 ppm
- ● ≥ 100 ppm
- • ≥ 45 ppm

All analyses for Cr are shown on map

Concentrations based on charred sample weight

1976

PLATE 9
REPORT 73-3-1



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MAGNESIUM

● ≥ 1.10 %
● ≥ 0.80 %
● ≥ 0.50 %
• ≥ 0.15 %

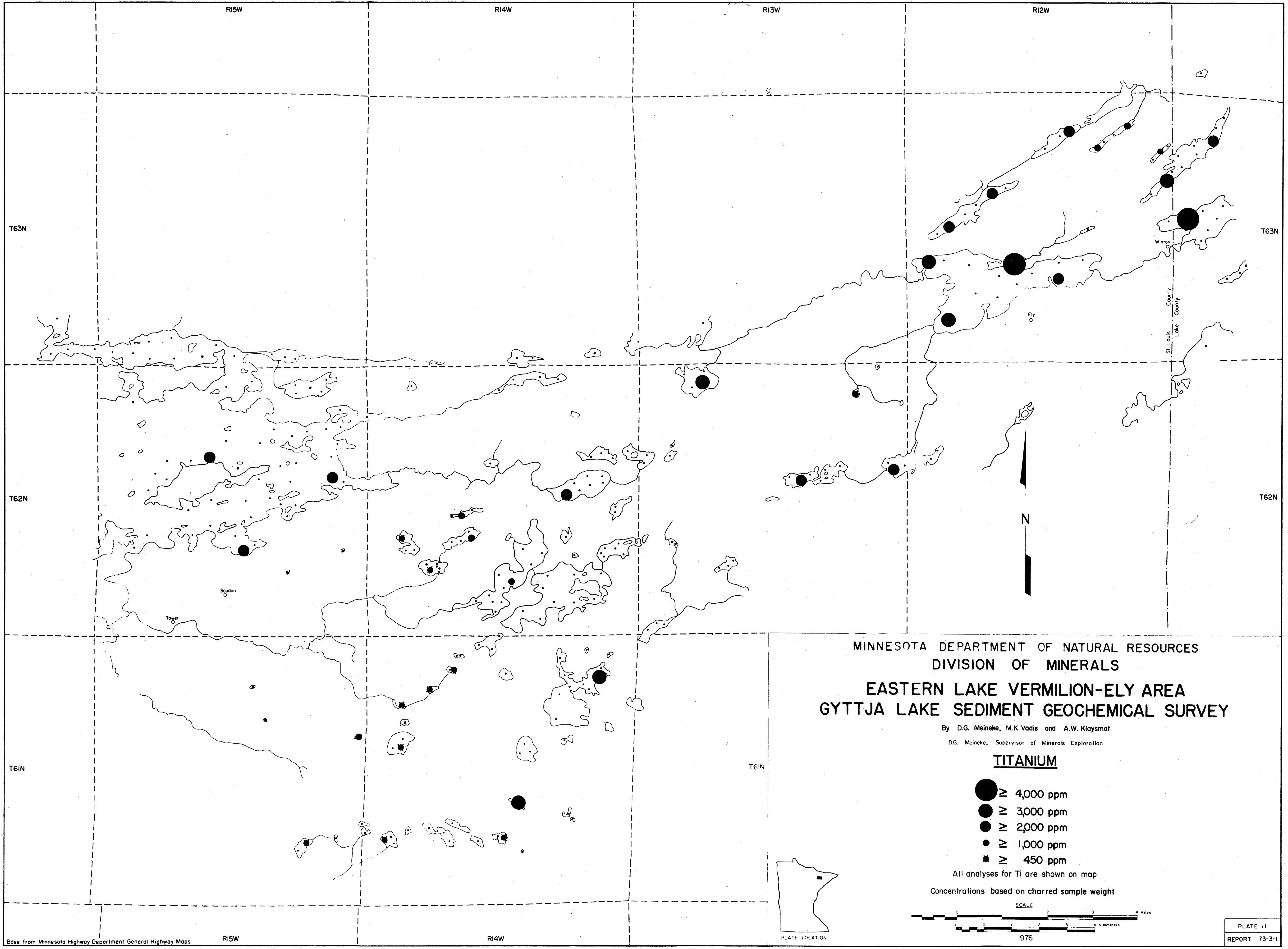
All analyses for Mg are shown on map

Concentrations based on charred sample weight

1976

PLATE 10
REPORT 73-3-1

Base from Minnesota Highway Department General Highway Maps



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TITANIUM

● ≥ 4,000 ppm
● ≥ 3,000 ppm
● ≥ 2,000 ppm
● ≥ 1,000 ppm
● ≥ 450 ppm

All analyses for Ti are shown on map

Concentrations based on charred sample weight

1976

PLATE 11

REPORT 73-3-1