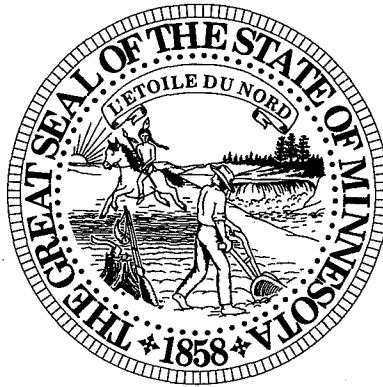


# RECONNAISSANCE SCALE WELL WATER GEOCHEMICAL SURVEY OF CENTRAL MINNESOTA



**Minnesota Department of Natural Resources  
Division of Minerals**

**Report 236-2**

**Hibbing, Minnesota  
1985**

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# **RECONNAISSANCE SCALE WELL WATER GEOCHEMICAL SURVEY OF CENTRAL MINNESOTA**

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**Minnesota Department of Natural Resources  
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# RECONNAISSANCE SCALE WELL WATER GEOCHEMICAL SURVEY OF MINNESOTA

by: D. W. BECKWITH and R. C. CLARK

## ABSTRACT

*A reconnaissance scale well water geochemical survey was conducted over portions of central and east-central Minnesota. The primary objective of the survey was to determine if the chemical analyses of groundwater obtained from domestic water wells would reflect differing rock types located beneath thick glacial overburden, and consequently, could be used to help evaluate the mineral potential of the area.*

*In the course of the survey, samples were collected from 226 water wells over an area of 2160 mi<sup>2</sup> (5600 km<sup>2</sup>). The survey area is underlain by Archean granites and gneisses, Early Proterozoic sedimentary and volcanic rocks and Late Proterozoic (Keweenawan) volcanic and sedimentary rocks, and includes drift from several phases of Wisconsin glaciation. The water was analyzed by atomic absorption spectrophotometry for Au, Ag, As, Cu, Ni, Pb, Zn, Fe, Ca, Mg, Na and K, and measurements of specific conductance, alkalinity, sulfate content and pH were made.*

*Statistical analyses were performed on the data in an attempt to identify relationships between elemental concentrations and other parameters that could be useful as indicators of bedrock geology. The effect of bedrock lithology, drift composition, bedrock penetration, plumbing composition and well depth on water chemistry was investigated. It was determined that there are differences in elemental concentrations of water analysis between rock types, and that many of these differences can be related to rock lithology. The effect of drift composition was found to be less prominent; the variation in water chemistry between drift types is only slight. The analysis also showed that pipe composition and whether the well penetrated bedrock or not had little effect on water chemistry. There was a correlation, however, between well depth and the concentration of some elements in the well water.*

*It was determined from correlation coefficients that Ca, Mg, alkalinity and specific conductance showed a moderate to strong positive relation to each other for each rock and drift subdivision. Other elemental pairs, however, showed little or no correlation.*

*Two areas of multi-element anomalies, consisting of mainly the major elements, were indicated by this survey, one occurring in the Glen Township Formation near Thor and the other in portions of the Thomson Formation.*

*This survey indicates that with a few modifications such as increased sampling density, additional analyzed elements and expanded analytical techniques, there may be some potential in using a reconnaissance scale well water sampling program for geologic interpretation purposes.*

## INTRODUCTION

A reconnaissance scale geochemical survey involving the collection and analysis of water from domestic wells was conducted over a portion of central and east-central Minnesota during the summer and fall of 1984 (Fig. 1). This area was selected because previous lake sediment geochemical surveys and drill core assays, as well as the regional geologic relationships, suggest that gold and sulfide mineralization may exist, and because the population density of the area is great enough so that a suitable number and distribution of wells could be sampled.

The project was initiated as a result of funding provided to the Minnesota Department of Natural Resources, Minerals Division, by the Legislative Commission on Minnesota Resources (LCMR). The primary objective of the survey was to determine if the chemical analysis of groundwater obtained from domestic water wells would reflect differing rock types located beneath thick glacial overburden where other exploration methods do not work well, and consequently, could be used to effectively evaluate the mineral potential of these different rock types. A well water sampling program conducted in eastern Canada (Dyck, Chatterjee, Gemell, Murrice, 1976) has suggested that well water surveys may be informative in delineating some types of mineralization. Portions of the study area in Carlton and Pine counties were included in a water well survey (emphasizing the evaluation of uranium potential of the area) conducted by the Minnesota Geological Survey under the direction of the National Uranium Resource Evaluation (NURE) Program of the United States Department of Energy in the summer of 1979 (Morey & Lively, 1980). The results of this survey, which involved a much greater sampling density, identified several radon and uranium anomalies in the groundwater.

Two hundred twenty-six water wells were sampled over an area of 2160 mi<sup>2</sup> (5600 km<sup>2</sup>) in parts of Aitkin, Carlton, Cass, Crow Wing, Mille Lacs, Morrison and Pine counties. The water was analyzed by atomic absorption spectrophotometry for Au, Ag, As, Cu, Ni, Pb, Fe, Ca, Zn, Mg, Na and K at the Division of Minerals chemistry lab in Hibbing, Minnesota by Janet Beitzel and Jean Drotts under the direction of Al Klaysmat. Measurements of alkalinity, pH, specific conductivity, SO<sub>4</sub>, and temperature were also made. Computer-assisted statistical analyses were later performed on the data to identify relationships between the different rock types/till types and trace element concentrations that would assist in mineral potential evaluation, and to determine what influence plumbing composition, bedrock penetration and depth had on water composition.

## GEOLOGY AND PHYSIOGRAPHY

### Precambrian Geology

The Precambrian rocks of the study area can be divided into three distinct terranes: 1) Lower Precambrian rocks, 2) Middle Precambrian stratified rocks, and 3) Upper Precambrian (Keweenawan) sedimentary and volcanic rocks (Fig.

2). Thick glacial overburden and the resultant scarcity of outcrop throughout much of east-central Minnesota has necessitated the use of geophysical and drill hole data in the interpretation of the geology. Only a brief discussion of the rocks will be presented here; however, detailed descriptions can be found in Morey (1978).

The Lower Precambrian rocks consist of a northern granite-greenstone terrane (2.7 b.y.) and a southern highly deformed gneissic terrane (3.5 b.y.) separated by a 30-60 km wide sheared, schistose zone termed the Great Lakes Tectonic Zone (GLTZ) (Sims, Card, Morey and Peterson, 1980). The McGrath gneiss (2.75 b.y.) located in the GLTZ northeast of Mille Lacs Lake is a coarse-grained, partly migmatitic quartzo-feldspathic gneiss locally cataclased during the Penokean Orogeny. At the end of the Archean, granite to tonalitic plutons such as the Giants Range granite (2.6-2.7 b.y.) located in the northwest corner of the study area were intruded along the southern edge of the greenstone terrane forming a relatively stable Archean craton.

During the Early Proterozoic the Animikie basin formed over the Lower Precambrian rocks and the Hillman migmatite (which appears to form the basement southwest of Mille Lacs Lake). The northeast-southwest trending basin was initiated by crustal foundering in an extensional environment. Basin infilling (2.0-2.1 b.y.) began with the deposition of the Denham Formation; a sequence of arenitic quartzite and siltstone with lesser dolomite and volcanic rocks (Fig. 3). Deposition continued with the formation of the Randall and Glen Township formations, two mafic to intermediate volcanic sequences with associated sedimentary rocks. Both formations contain some oxide to carbonate facies iron formation and pyrite-rich carbonaceous argillite. The Mille Lacs Group also includes the Little Falls and Trout Lake formations which are not known to exist in the survey area.

Following a period of uplift and erosion the Mahnomen Formation, a southward-thickening wedge of quartzite, siltstone and argillite, was deposited over the Mille Lacs Group sedimentary rocks. This was followed by the deposition of the cherty and slaty iron formation of the Trommald Formation, the principal iron formation of the Cuyuna Range. Continued foundering and subsidence of the basin led to the deposition of the Rabbit Lake Formation, a thick sequence of carbonaceous slate, argillite and greywacke with local mafic flows in the "lower member" and carbonate iron formation in the "Emily member." At the same time, the Thomson Formation, a thick (1 km) greywacke-argillite sequence (with associated carbonaceous-pyritic slate and volcanic rocks) was deposited by turbidity currents in the southeastern part of the basin. The rocks resulting from this second phase of deposition are referred to as the Animikie Group.

Deposition ended with the compression of the basin during the Penokean Orogeny (1.8-1.9 b.y.). The resulting deformation and metamorphism were asymmetric across the basin, being more intense in the southern portion than in the north. During and after the Penokean orogeny, synorogenic gabbroic to granodioritic dikes, sills and stocks and post-orogenic granitic plutons were intruded into the Middle Precambrian stratified rocks and adjacent gneisses.

The Precambrian history of east-central Minnesota



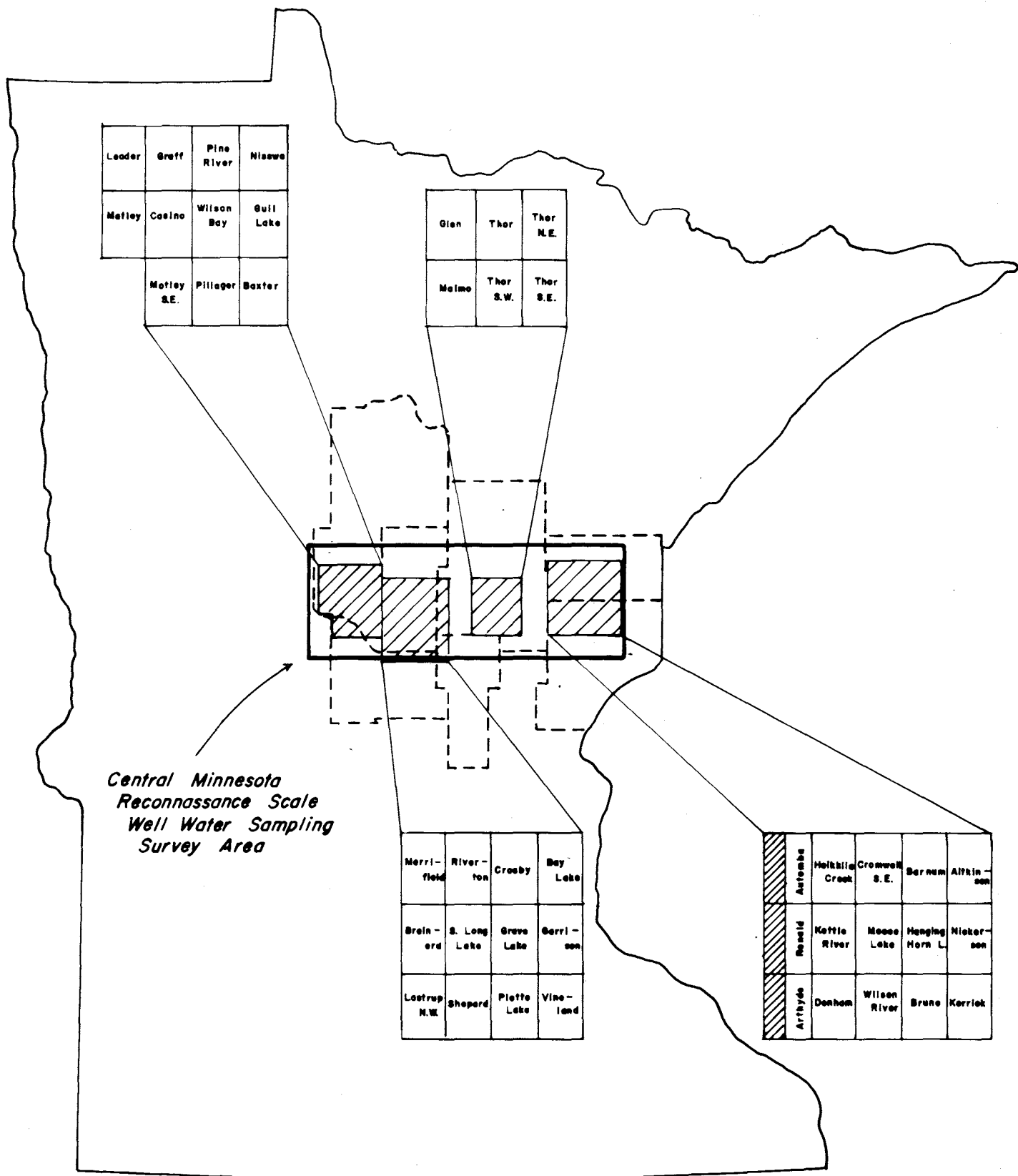
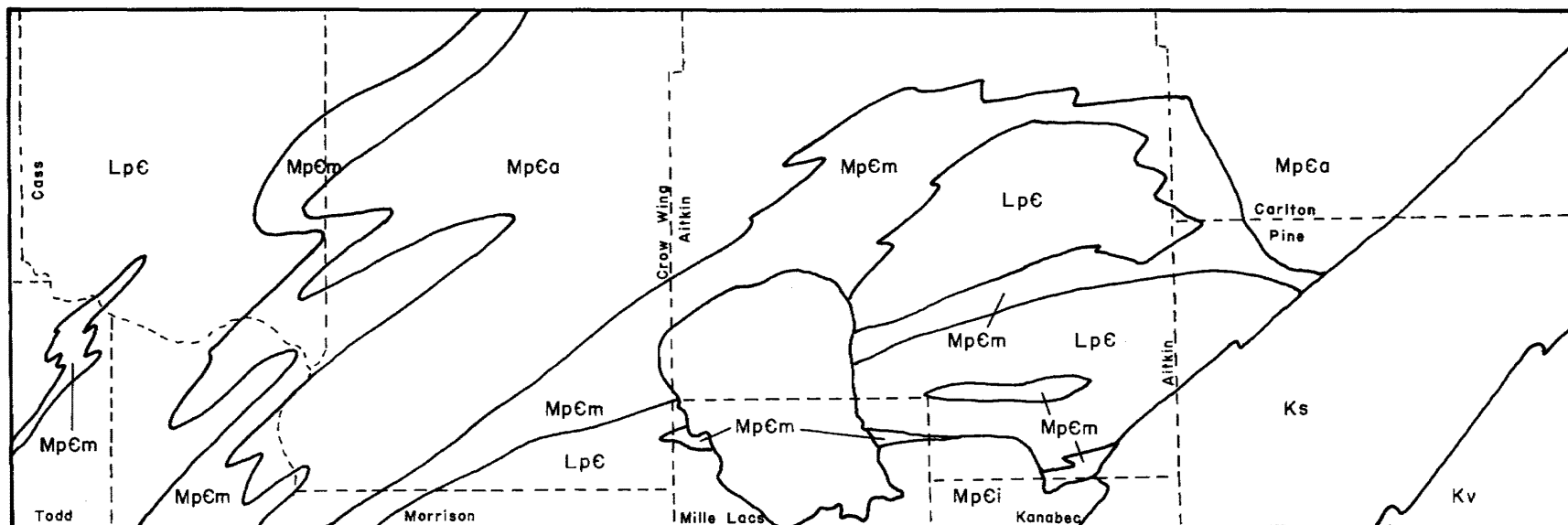
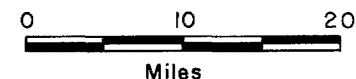


Figure 1: Location Map of Minnesota Showing the Topographic Quadrangles Included in the Water Well Survey



**EXPLANATION**

- Ks** Keweenawan Sedimentary Rocks
- Kv** Keweenawan Volcanics
- Mp€i** Middle Precambrian Intrusive Rocks
- Mp€a** Middle Precambrian Sedimentary Rocks-Animikie Group
- Mp€m** Middle Precambrian Sedimentary Rocks - Mille Lacs Group
- Lp€** Lower Precambrian Granites and Gneisses



**Fig. 2: GENERALIZED PRECAMBRIAN GEOLOGY OF CENTRAL MINNESOTA**  
 (from Morey, Olsen and Southwick, 1981)

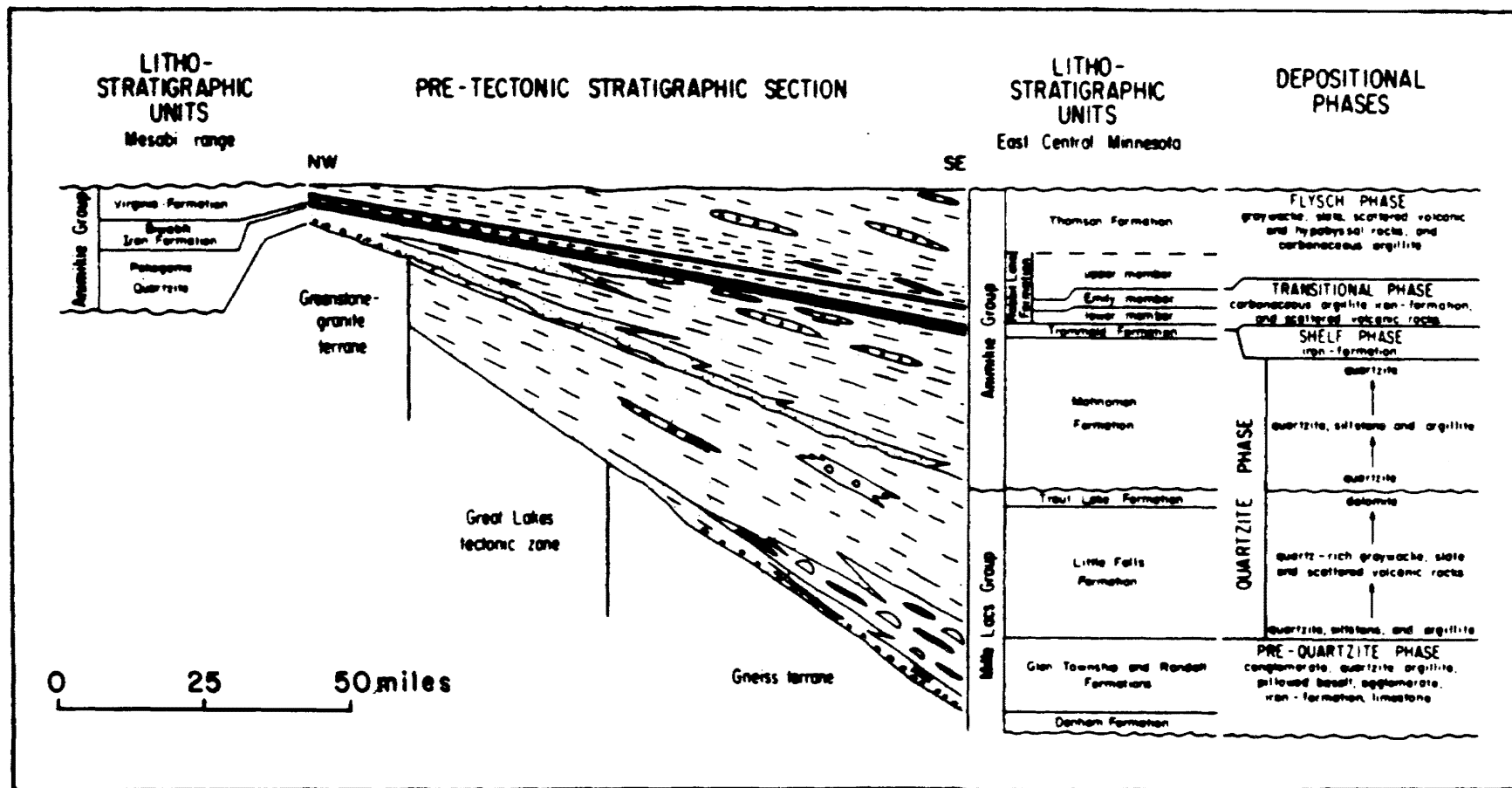


Figure 3: Pre-TECTONIC stratigraphic section through Animikie Basin. (Morey, 1979.)

ended with the deposition of the Upper Precambrian Keweenaw System (1.1 b.y.). This system includes the numerous basaltic flows and interbedded conglomeratic and tuff horizons of the Chengwatana Volcanic Group located in the southeast corner of the survey area. The slightly younger arkosic sandstones of the Fond du Lac Formation and the quartzose sandstones of the Hinckley Formation were later deposited over the volcanic rocks. Associated with the Keweenaw igneous rocks are several augite porphyritic basalt dikes and numerous diabase dikes and sills which intruded the Middle Precambrian stratified rocks.

Upper Cambrian and Upper Cretaceous sedimentary rocks were deposited over many of the Precambrian rocks, but most have since been removed by erosion.

## Glacial Geology

The Precambrian bedrock of Central Minnesota is buried beneath glacial overburden that ranges in depth from 0 to more than 400 feet (Fig. 4). The survey area was subject to multiple events of continental glaciation during Pleistocene time (Fig. 5), however, evidence of only the Wisconsin glaciers is indicated in the present-day glacial surficial deposits. Drift from all the major phases of Wisconsin glaciation (the Hewitt, St. Croix, Automba, Split Rock and Nickerson-Alborn phases) and from the four major ice lobes (the Wadena, Rainy, Superior and Des Moines lobes) is represented in the survey area (Fig. 6). Consequently, central Minnesota has a complex variety of glacial deposits with regard to composition, color, drift type, and spatial relationships (both lateral and vertical) between the drift types. An understanding of the glacial geology is important because the chemical composition of the drift may affect the chemistry of the groundwater as well as the migration of metals from bedrock to groundwater. Furthermore, the distribution of the drift has an important role in groundwater movement. The following simplified discussion of the phases of Wisconsin glaciation is based on Wright (1972b).

### *Hewitt Phase*

During the Hewitt phase (30,000-60,000 BP), the Wadena lobe advanced out of the Winnipeg lowland south-eastwardly into the Red Lakes lowland of northern Minnesota. It was then diverted towards the southwest by the Rainy lobe which was simultaneously advancing from the northeast, forming the Wadena drumlin field before terminating at the Alexandria Moraine Complex in western Minnesota. The eastern limit of the Wadena lobe is poorly defined because its drift is deeply buried by drift of the Rainy and Superior lobes, but it may have extended as far east as Mille Lacs Lake. Unlike the Alexandria Moraine complex at the western margin of the Wadena lobe, there is no surviving moraine complex along the eastern margin.

The drift of the Wadena drumlin field is composed of grey to light brown, sandy till with fragments of Paleozoic carbonate rock from the Winnipeg area, but lacks fragments of Cretaceous shale typical of eastern North Dakota. The Wadena lobe may have incorporated some Rainy lobe ice where the two lobes made contact near the eastern margin,

as the resulting till contains a mixture of indicator stones with a corresponding dilution of the carbonate content.

### *St. Croix Phase*

Upon retreat of the Wadena lobe, the Rainy lobe advanced from the north-northeast following a path roughly parallel to the Superior lobe which was moving out of the Lake Superior trough (20,000 BP). The combined Rainy-Superior lobe formed the St. Croix moraine, a nearly continuous, steep-fronted ridge of rugged topography that is traceable for 350 miles through Minnesota and Wisconsin, at its terminus. The Brainerd drumlin field south of Brainerd was formed by the Rainy lobe during the St. Croix phase, while a series of deep, southwest-trending tunnel valleys (some with associated eskers) near Willow River was eroded by meltwater beneath the Superior lobe. As the Rainy lobe retreated from the western St. Croix moraine, it formed a series of closely spaced recessional moraines and large outwash plains often strewn with large stranded ice blocks, especially in the Brainerd Lakes area.

The western St. Croix moraine is composed of brown, sandy till and associated ice contact gravels containing clasts of basalt, felsite, gabbro and iron formation indicative of the Rainy lobe. The brown, sandy till of the Brainerd drumlins is nearly identical to that of the St. Croix moraine. The eskers in the Willow River area, however, contain red sandy drift with clasts of red sandstone and shale diagnostic of the Superior lobe.

### *Automba Phase*

During the Automba phase (18,000 BP) the Superior lobe readvanced out of the Lake Superior basin and thence westward to the Mille Lacs Lake region where it formed the Mille Lacs moraine at its terminus. The northern segment of the moraine is very prominent on the west side of Mille Lacs Lake and can be easily traced to the east-northeast; however, the southern limit of the moraine fades out eastwardly. The Automba drumlin field along the Carlton-Aitkin county line was formed during this stage.

The drift of the Superior lobe in the Automba phase is similar to that of the St. Croix phase consisting of red sandy till with stones of red sandstone and shale.

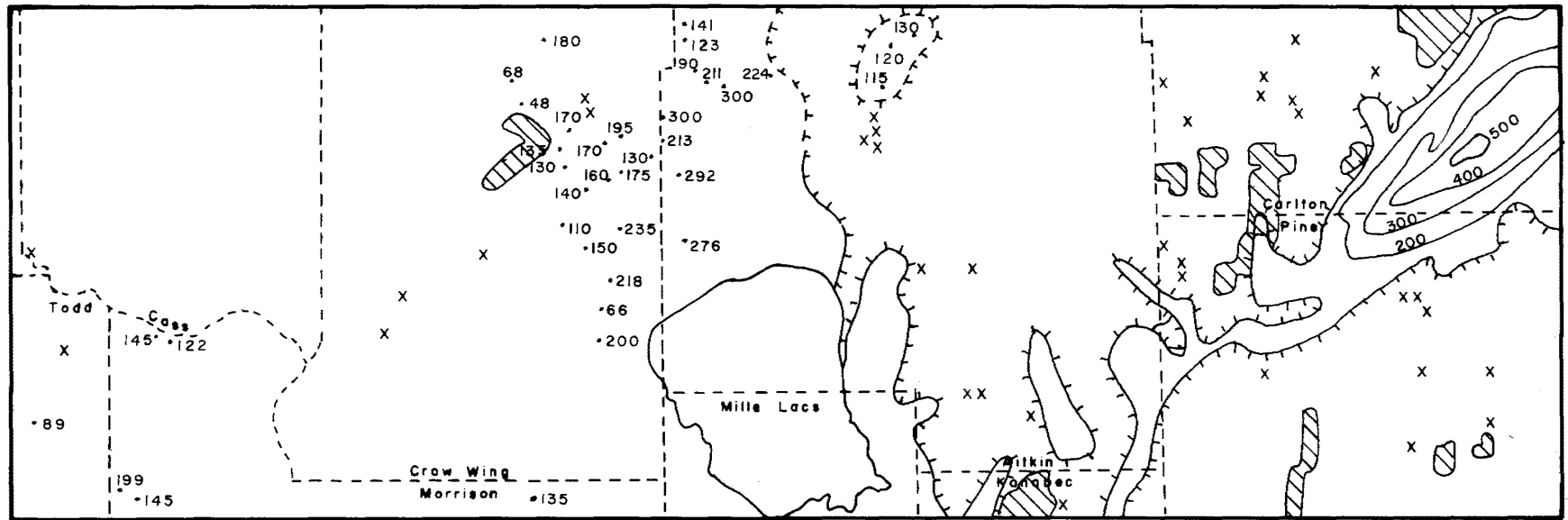
### *Split Rock Phase*

During the Split Rock phase (16,000 BP) the Superior lobe readvanced to near Sandstone depositing a thin, discontinuous blanket of red, clayey till over the till and outwash of previous phases of glaciation. No terminal moraine is apparent, but a small field of drumlins composed of red, clayey drift was formed just west of Moose Lake. Meltwater from the ice produced outwash fans among the hills of the Automba phase to the west, as well as several large eskers in the Barnum area.

The till of the Split Rock phase is very clayey in nature, being derived from proglacial lake sediments that were deposited at the margin of the Superior lobe at the end of the Automba phase.

### *Nickerson-Alborn Phase*

The Superior lobe advanced for the final time during the Nickerson phase (12,000 BP) terminating at the Nickerson-Thomson moraine near Moose Lake. The moraine exhibits a very hummocky terrane with deep exposures of



### EXPLANATION



Isopach

- dashed where control is poor
- contour interval 100'
- hachured to indicate closed areas of less thickness

• 292 Isolated drill hole with depth to bedrock in feet

X Isolated outcrop



Areas of more or less continuous bedrock exposures

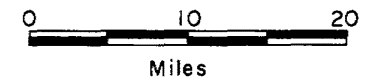


Figure 4. DEPTH TO BEDROCK IN CENTRAL MINNESOTA (from Olsen and Mossler, 1982)

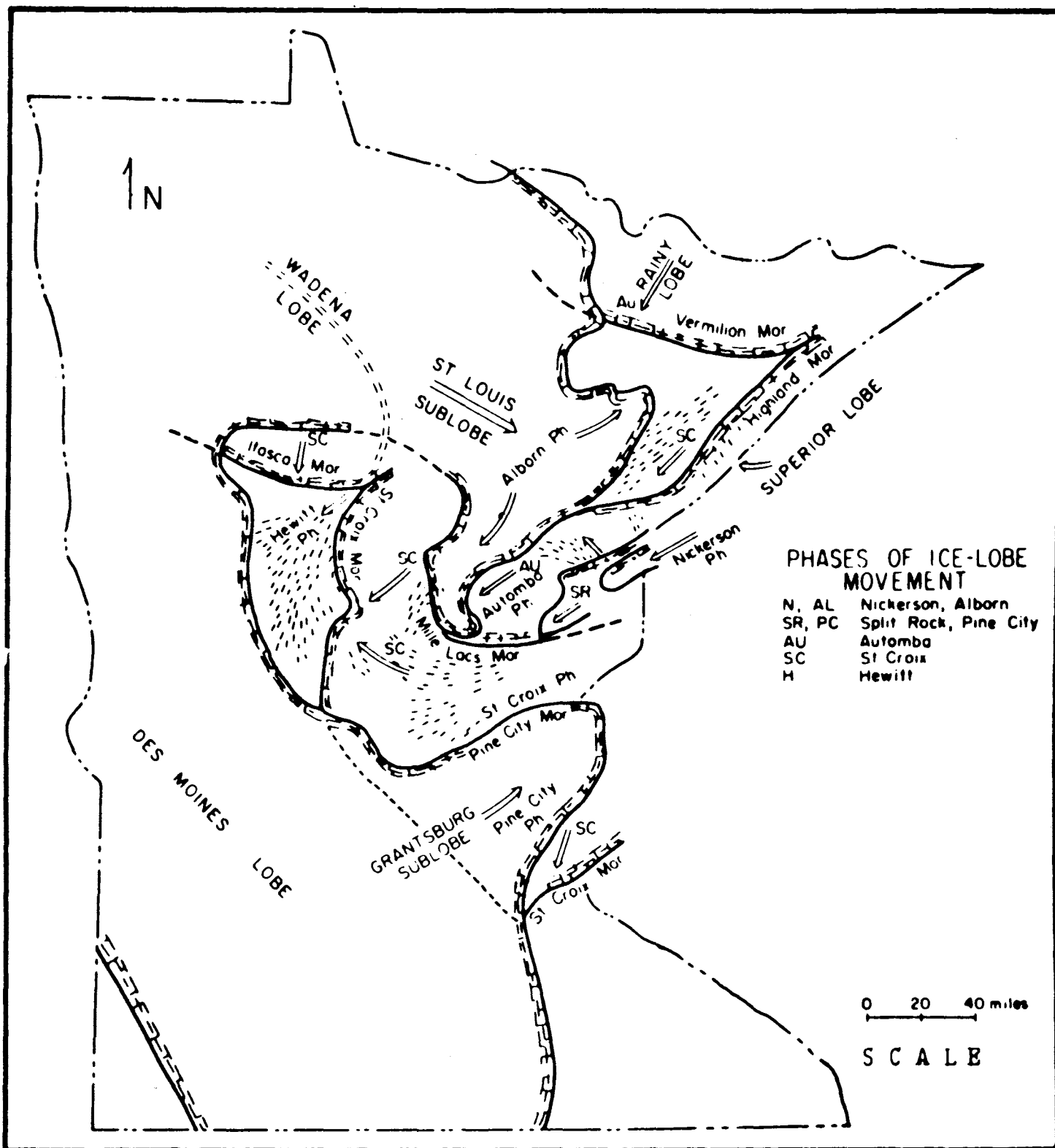
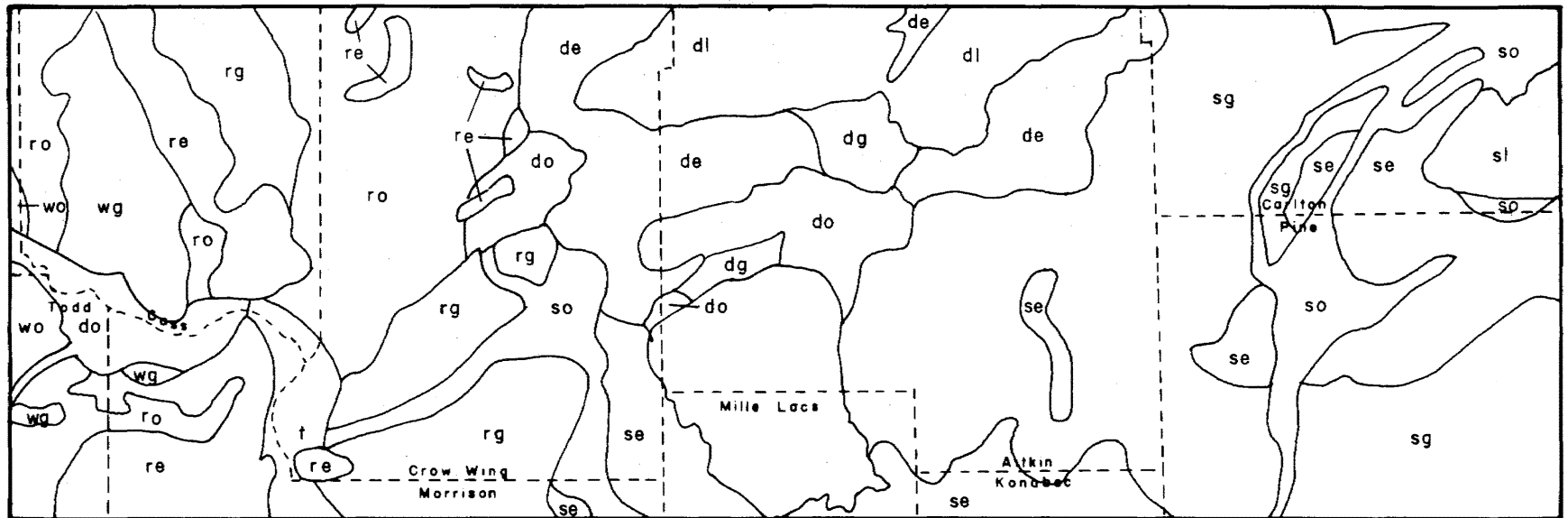


Figure 5 : Composite map showing main phases of Wisconsin glaciation in Minnesota (From Wright, 1972a)



**EXPLANATION**

Holocene

t terrace deposits

Pleistocene

Des Moines Lobe

dl glacial lake sediment & lake modified till

do outwash

dg ground moraine

de end moraine

Superior Lobe

sl glacial lake sediment

so outwash

Superior Lobe cont.

sg ground moraine

se end moraine

Rainy Lobe

ro outwash

rg ground moraine

re end moraine

Wadena Lobe

wo outwash

wg ground moraine

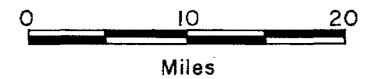


Figure 6. Quaternary Geology of Central Minnesota (from Hobbs and Goebel, 1982)

massive, red, clayey till in the south, whereas along the north margin the moraine consists largely of red, sandy till and outwash locally fronted by outwash fans and plains. As the Superior lobe retreated into the basin a large proglacial lake, Glacial Lake Nemadji, formed in front of it with deposition of sand near shore and clay in deeper water. As the ice continued to retreat a lower outlet was uncovered to the east lowering the lake level and forming Glacial Lake Duluth. Again, thick sequences of red sand and clay were deposited.

The Alborn phase of the St. Louis sublobe occurred contemporaneously with the Nickerson phase of the Superior lobe. This sublobe was formed by an eastward extension of the Des Moines lobe which had advanced into central Iowa. The sublobe spread eastward from the Red River lowland into the Red Lakes lowland where a sub-sublobe spread south to the north shore of Mille Lacs Lake. This sub-sublobe was responsible for the end moraines and outwash plains deposited north of Mille Lacs Lake. As the St. Louis sublobe withdrew, Glacial Lakes Upham II and Aitkin II formed at its front.

In this area the till is typically a pebbly clay or clayey till with variable amounts of limestone and Cretaceous shale fragments. The color of the till ranges from light brown to dark brown to reddish brown, depending on the origin of the clay that was incorporated into the ice as it passed over Glacial Lakes Upham I and Aitkin I. The reddish brown clay originates from the Superior lobe, the dark brown clay from the Rainy lobe, and the light brown clay from the St. Louis sublobe.

#### *Post-Glacial History*

The topography of the survey area has been locally modified by post-glacial processes. Terrace deposits composed of sand and gravel representing former floodplains and channels are found in the Mississippi River valley. Alluvium in the form of sand, gravel, silt and clay was deposited in channels and flood plains of many modern streams. Finally, deposits of peat formed in areas of poor drainage, particularly in parts of Aitkin County.

#### **Physiography**

The study area includes portions of seven physiographic areas of Minnesota established by Wright (1972a) including the Wadena drumlin area, the western St. Croix moraine area, the Brainerd-Automba drumlin area, the Sugar Hills-Mille Lacs moraine area, the Barnum clay-till area, the Glacial Lake Aitkin area and the Glacial Lake Duluth area (Fig. 7). The relief of the area is generally low to moderate with elevations ranging from approximately 900 feet in the Nemadji River Valley near Nickerson to more than 1525 feet north of Pillager. The area is partly forested with a mixed coniferous-deciduous forest, and a substantial portion has been cultivated.

The Wadena drumlin area is located in the extreme western portion of the survey area. The low-rising northeast-southwest oriented drumlins were formed by the Wadena

lobe and are partly obscured in places by outwash from the St. Croix moraine of the Rainy lobe.

The western segment of the St. Croix moraine transects the western part of the survey area in a north-south direction. The prominent moraine is about 6 miles in width and consists of rather hummocky terrane with many small kettle lakes. It has been transected west of Brainerd by a broad water gap formed by the Crow Wing River.

The Brainerd-Automba drumlin area constitutes a large portion of the central and eastern parts of the survey area. The area is marked by several drumlin fields formed by ice of the Rainy and Superior lobes. The drumlin fields are interrupted in several places by outwash plains and pitted outwash plains, particularly near Brainerd, resulting in flat topography characterized by numerous deep lakes.

The Sugar Hills-Mille Lacs moraine area is an arcuate shaped moraine complex in the central portion of the survey area formed from till and outwash of the Superior lobe with a cap of clayey till deposited from the St. Louis sublobe. Glacial Lake Aitkin, located immediately to the north, was dammed by the Sugar Hills-Mille Lacs moraine. The lake plain consists of a broad expanse of swamp covered silt and sand and has been transected by the meandering Mississippi River.

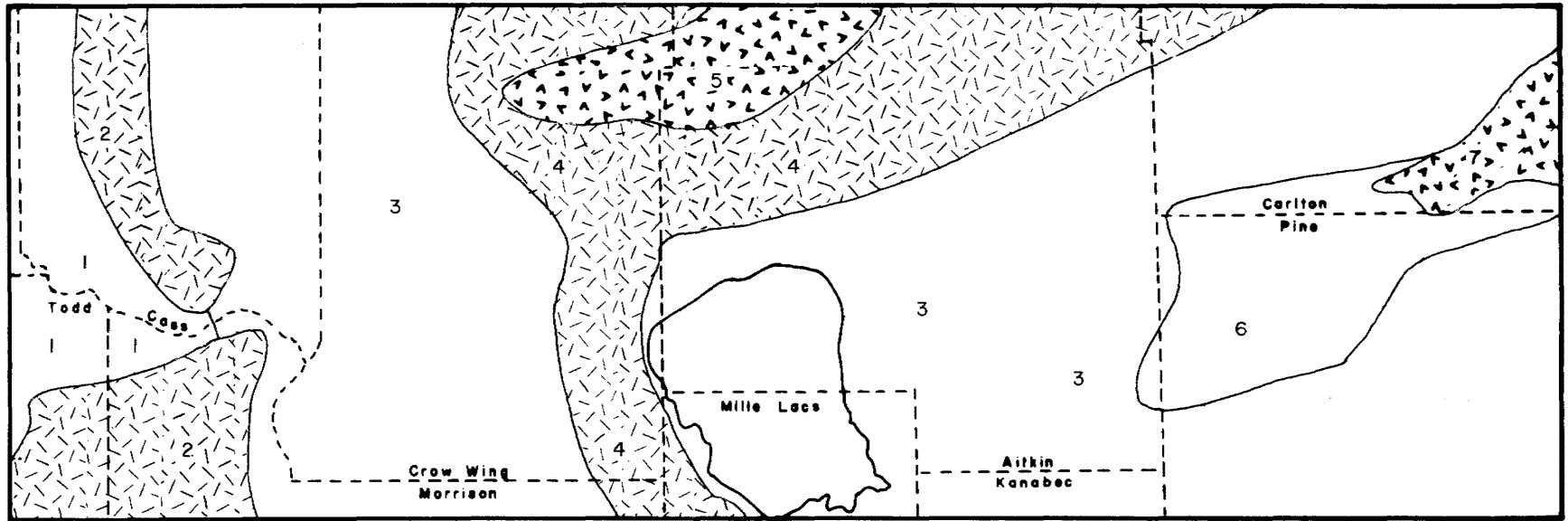
The Barnum clay-till area is located in the eastern portion of the survey area and is the result of at least two short advances of the Superior lobe. It is characterized by moraines, outwash and thin veneers of clayey till consisting of reworked proglacial lake clays.

The Glacial Lake Duluth area in the extreme northeastern part of the survey area is a partly dissected clay plain that marks the former bed of Glacial Lake Duluth. The plain is composed of homogenous red clay and is deeply dissected by the St. Louis and Nemadji rivers.

The survey area is contained within portions of 7 watersheds as defined by the USGS Hydrologic Investigations Atlas (Fig. 8). The entire area is located within the Mississippi drainage system with the exception of the extreme northeast corner which is part of the Lake Superior drainage basin. Most shallow groundwater movement is from areas of local recharge toward local surface waters. Regional movement, particularly of deeper water, is generally toward the Mississippi River, the Kettle River or other major river systems.

The groundwater of the survey area is of the calcium-magnesium bicarbonate type with locally higher concentrations of iron. Total dissolved solid content generally ranges from less than 100 mg/l to 1600 mg/l with locally higher amounts in water from the Des Moines lobe drift (Morey and Lively, 1980). Water yields of Quaternary aquifers range from less than 1 gpm (4 lpm) for wells finished in till and lake sediments to over 500 gpm (1900 gpm) for wells finished in outwash (Brainerd Lakes area) and alluvium (Mississippi and Kettle River valleys). Most bedrock aquifers, particularly those in Archean and Proterozoic rocks, have relatively low water yields of 1-25 gpm (4-100 lpm) except in zones of secondary porosity resulting from faulting or leaching, where locally higher water yields are obtained. The Fond du Lac aquifer, on the other hand, has high water yields that typically range from 400 to 700 gpm (1600 to 2900 lpm) (Kanivetsky, 1978, 1979).





11

**EXPLANATION**

- 1. Wadena drumlin area
- 2. Western St. Croix moraine area
- 3. Brainerd - Automba drumlin area
- 4. Sugar Hills - Mille Lacs moraine area
- 5. Glacial Lake Upham area
- 6. Barnum clay-till area
- 7. Glacial Lake Duluth area




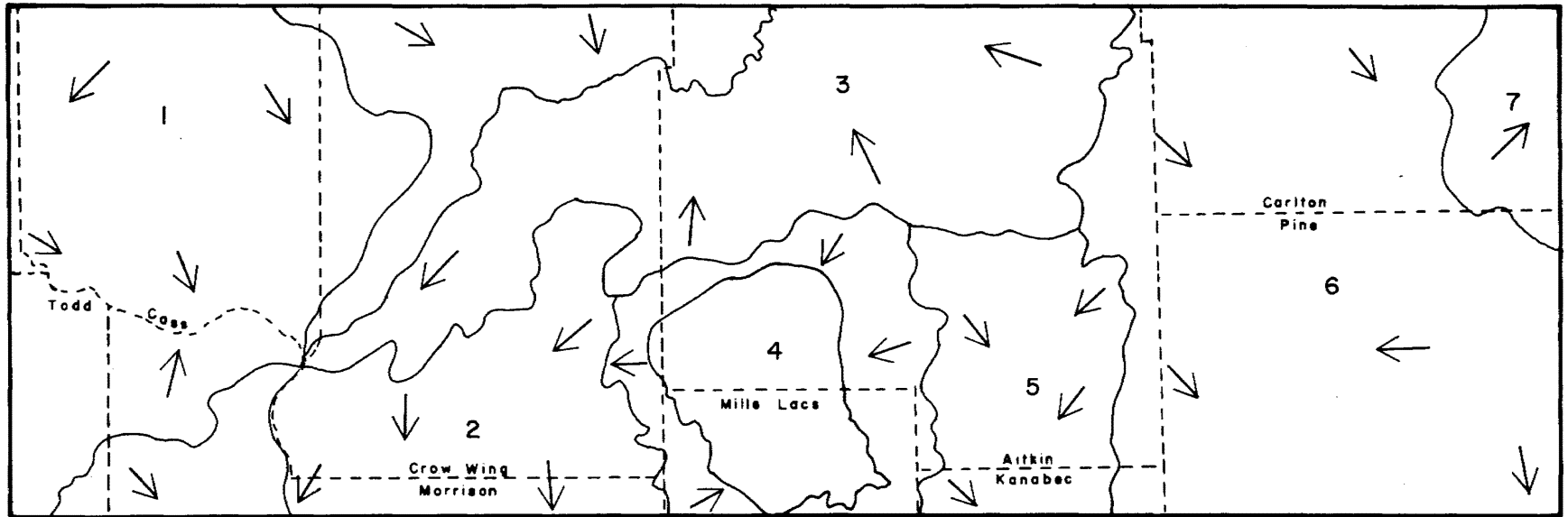
-  Moraines
-  Till plains and drumlins
-  Lake plains



Figure 7. Map of Physiographic Areas in Central Minnesota (from Wright, 1972a)



12

**EXPLANATION**

- Watershed Boundaries
- 1. Crow Wing River Watershed
- 2. Mississippi and Sauk Rivers Watershed
- 3. Mississippi Headwaters Watershed
- 4. Rum River Watershed
- 5. Snake River Watershed
- 6. Kettle River Watershed
- 7. Lake Superior Watershed
- County Lines
- ← Direction of Regional Groundwater Flow

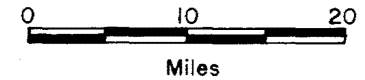
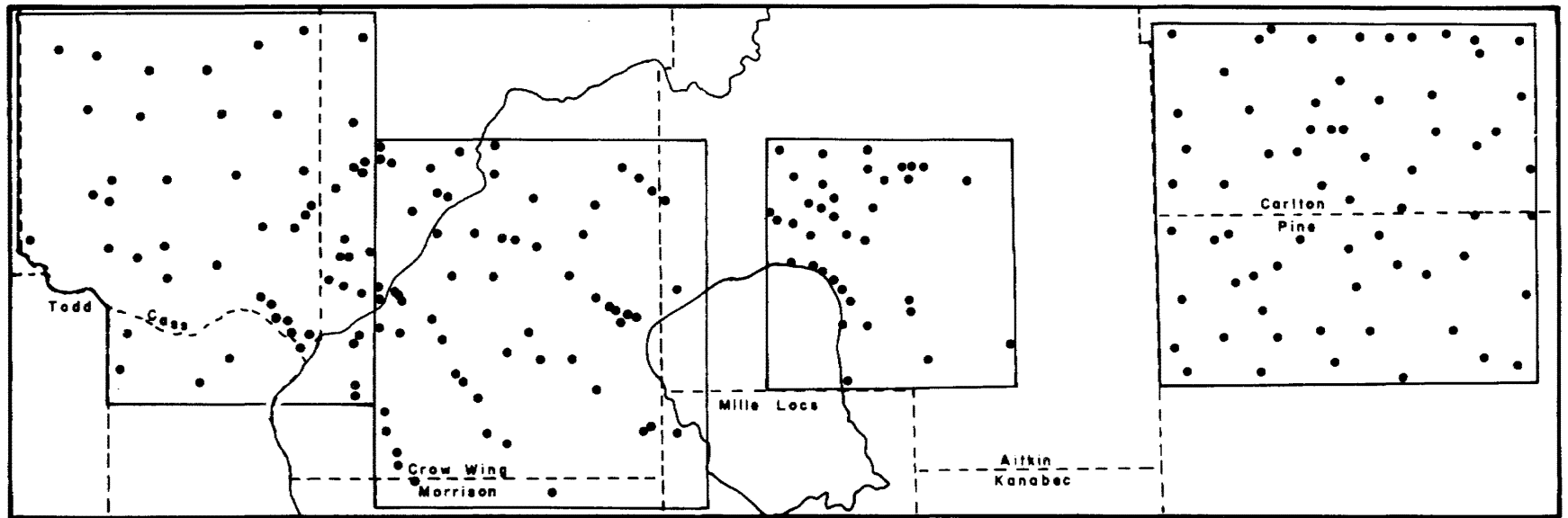
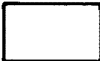



Figure 8. Map of Watershed Areas and Regional Groundwater Flow in Central Minnesota (from USGS Hydrologic Atlas)



-  Outline of sample areas
-  Individual water wells sampled

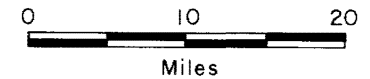


Figure 9. Location of Water Well Samples

## SAMPLING TECHNIQUE

Sample sites in this survey were selected to represent the various types of bedrock lithologies in the area. In areas of relatively complex geology (Middle Precambrian stratified rocks) at least one water well was sampled in each rock formation as the geology was traversed in several north-west-southeast trending "belts." In areas where the geology is rather simple, sampling was conducted on a grid basis with sample sites being located 2-6 miles apart. Actual sample densities were determined to a large extent by population density; however, sample density amounted to approximately one sample per 9.5 square miles (24.5 km<sup>2</sup>) (Fig. 9).

The prime sampling target was groundwater from frequently used, untreated, private domestic wells more than one year in age. To prevent contamination from stagnated water, wells were required to be used daily. New plumbing less than one year old was avoided to reduce the effects of pipe composition on water chemistry, and water systems using water softeners or other purification devices were not sampled. Wherever possible, wells that penetrated bedrock were sampled; however, in much of the study area very few wells were deep enough to reach bedrock.

Sampling procedures follow the guidelines of Ferguson and others (1977). Prior to the field work, sample bottles and filter systems were acid washed with dilute nitric acid and rinsed with doubly distilled water. At each sample site information on the type of well, age and depth of the well, and plumbing composition was obtained when available from the homeowner. Samples were taken as close to the well head as possible, usually at an outside faucet. After running the pump for 2-3 minutes to flush the system, two 500 ml plastic bottles and a Millipore filtering apparatus were rinsed twice and filled with water. The first 500 ml water sample was used to measure temperature, specific conductivity and pH and then discarded. The second 500 ml bottle was labelled and stored in a cooler for later sulfate and alkalinity analysis in the lab. The final sample, collected for metal analysis, was pressure filtered through 0.45 µm filter paper using a Millipore filtering apparatus into an 80 ml plastic bottle. The sample was immediately acidified with 0.1 ml concentrated nitric acid to keep the metals in solution, labelled, placed in a cooler and kept chilled until the analysis was completed.

A total of two hundred twenty-six wells were sampled throughout the sampling season. Forty-eight duplicate samples, two EPA standard samples and two distilled water "blank" samples were also submitted for analysis. Thirty-eight water wells, chosen because of apparently anomalous values for the trace metals, were resampled near the end of the field season.

### Chemical Analysis

Laboratory analyses were performed at the Minnesota Department of Natural Resources, Minerals Division in Hibbing, Minnesota. The alkalinity of the water was measured by titrating 100 ml of sample with 0.02N H<sub>2</sub>SO<sub>4</sub> to a pH of 4.5. Total alkalinity measured as mg/l CaCO<sub>3</sub> was de-

termined using the equation:

$$\text{Alk} = \frac{(B)(N)(50,000)}{\text{ml sample}}$$

where B is the ml of H<sub>2</sub>SO<sub>4</sub> of normality N needed to reach a pH of 4.5. Sulfate content was measured by injecting a stirred mixture of 100 ml sample, 5 ml conditioning agent and 0.2 ml BaCl<sub>2</sub> into an HF Instruments Model DRT-100 turbidity meter. Actual sulfate content in mg/l SO<sub>4</sub> was then determined from standard sulfate curves.

Each water sample for metal analysis was filtered and acidified with 0.1 ml concentrated HNO<sub>3</sub> at the time of sampling. Samples were analyzed for trace elements (Ag, Au, Cu, Ni and Pb) straight, with no dilution or reagents added, using a Perkin-Elmer Model 603 atomic absorption spectro-photometer (AA) graphite furnace. Arsenic was also analyzed using a graphite furnace; however, one part 1000 ppm NiNO<sub>3</sub> was added to each part sample prior to analysis. Major metals (Mg, Ca, K, Na) were diluted 10 times with doubly distilled water (distilled then deionized), and 10 ml of lanthanum chloride (LaCl) was added to each sample prior to analysis. LaCl reduces background ionization for samples being analyzed on the AA. The samples were then analyzed by the flame method on the AA. Iron was also analyzed by the flame method but no dilution or mixing with LaCl was required.

The analytical detection limits are given in Table 1. The determination of analytical variability was accomplished by the analysis of 12 duplicate samples from the original sampling and the analysis of 38 duplicate samples from resampled wells. The analytical precision was calculated from these analyses at the 95 percent confidence level using the "t" distribution according to a method adapted from Garrett (1973). The results of these calculations are shown in Table 1. All Au and Ag values and a majority of the Pb values were below the detection limit; therefore, analytical precision for these elements was not calculated.

Two EPA water pollution quality control check samples and two distilled water samples were submitted for analysis. Because only two of each of these samples were analyzed, the analytical precision could not be calculated. However, all analyzed values for the EPA standards fall within the published 95% confidence intervals, and all values for the blank samples were found to be below the analytical detection limit. The complete analytical data for the 226 wells are given in the Appendix.

## STATISTICAL ANALYSIS

A statistical analysis of the elements and other parameters was conducted to identify various relationships and characteristics that may assist in the interpretation of the survey for mineral potential purposes. The parameter distributions were examined for normality compared to log-normality to determine whether log transformation was necessary to linearize the relationship of lognormal data prior to scatter diagram, correlation, and regression analysis. The various statistical parameters of the elements were compared for four major bedrock subdivisions and three major glacial deposit type subdivisions to determine if

Table 1: Detection Limits and Analytical Precision for Well Water Survey

Element	Detection Limit	Analytical Precision from Reanalyzed Samples
Ag	1 ppb	*
As	1 ppb	10.2%
Au	1 ppb	*
Cu	1 ppb	4.4%
Ni	1 ppb	11.8%
Pb	1 ppb	*
Zn	0.01 ppm	3.6%
Fe	0.1 ppm	4.3%
Ca	1 ppm	13.5%
Mg	1 ppm	2.2%
Na	1 ppm	1.3%
K	1 ppm	1.8%
SO <sub>4</sub>	1 ppm	*
Alk	0.1 ppm	*

\* not calculated

the bedrock or till type chemistry was reflected in the water samples.

### Analysis of Data Distribution

An analysis of the total data set was performed to determine if the elements and other parameters approximate a lognormal or a normal distribution. This analysis was performed by visually examining histograms and cumulative frequency distributions of the elements. It was concluded from this analysis that the parameters As, Cu, Ni, Pb, Fe, Zn, SO<sub>4</sub>, Mg, Na, K and specific conductance approximated a lognormal distribution, and these parameters were log<sub>10</sub> transformed prior to subsequent statistical analysis. Ca, pH, temperature and alkalinity appeared to more closely approximate a normal distribution and, therefore, no log transformation was necessary for subsequent analysis.

The range, arithmetic mean, standard deviation and median for these parameters are given in Table 2. The histograms and cumulative frequency distributions for the elements (for values above the detection limit) are shown on plates 2-11 (in pocket inside back cover).

Table 2: Distribution Statistics of the Element Concentrations

	Range	Arith. $\bar{X}$	Arith. $\bar{X}^*$	Std. Dev.	Std. Dev. *	Med.
As (ppb)	0-42	5.01	5.70	5.04	4.25	4
Cu (ppb)	0-111	4.86	7.21	12.15	9.82	1
Ni (ppb)	0-20	1.65	2.89	2.53	2.83	1
Pb (ppb)	0-8	0.44	1.90	0.95	1.45	0
Zn (ppm)	0-3.64	0.13	0.12	0.29	0.13	0.06
Fe (ppm)	0-34.0	1.38	1.43	3.56	2.56	0.2
Ca (ppm)	4-129	47.32	47.00	20.34	18.78	46
Mg (ppm)	2-70	18.84	18.21	11.99	10.79	17
Na (ppm)	2-69	11.61	11.14	13.78	11.84	7
K (ppm)	0-44	1.96	1.67	3.64	1.68	1
SO <sub>4</sub> (ppm)	0-144	11.83	13.02	17.81	14.05	5.0
Alk. (mg/l)	7.9-593.4	218.16	215.90	104.01	98.07	214.0
Spec. Cond. ( $\mu$ ohm/l)	95-1225	340.73	329.62	167.53	138.15	315
pH	6.4-8.6	7.69	7.69	0.43	0.43	7.7
Temp (°C)	6-20	12.47	12.47	2.39	2.39	12

Note: N = 226

\* mean and standard deviation calculated after the extraneously high and low (below detection limit) values were discarded.

A large percentage of the samples analyzed contained values that were below the analytical detection limit, particularly for the elements As, Cu, Ni and Pb. To reduce the bias that these low values might have on the remainder of the data, these values, as well as extraneously high values (as determined by visual examination of log transformed histograms) were subsequently discarded and new histograms and cumulative frequency distributions containing only values above the detection limit were plotted. New means and standard deviations were calculated from the revised data and are shown in Table 2. The mean values calculated for all the analyzed elements are in good agreement with published values of major and trace elements in groundwater (Hawkes and Webb, 1962; Rose, Hawkes and Webb, 1979) with the exception of Fe content, which is an order of magnitude greater than the average groundwater value.

### Relation of Bedrock and Groundwater Chemistry

Groundwater should reflect variation in the bedrock chemistry to be useful as an indicator of favorable geologic units and possible economic mineralization. Therefore, the relation of metal concentration in the water sample to four major bedrock geologic subdivisions in the survey area was investigated.

Statistical parameters were calculated for each of four major bedrock subdivisions. Because of the large number of rock formations present in central Minnesota, it was necessary to group similar rock units together to obtain sufficient data points within each subdivision. The four major bedrock subdivisions are: (1) the Archean gneisses and granites, (2) the Mahnomen/Denham Formation, (3) the Rabbit Lake/Thomson Formation, and (4) the Keweenawan sandstones. The Archean gneisses and granites include the McGrath gneiss, the Giants Range Granite and the Early Proterozoic Hillman migmatite. The Mahnomen/Denham Formation is a combined group consisting of quartzite, siltstone, argillite and minor volcanics of the Mille Lacs and Lower Animikie Groups. The Rabbit Lake/Thomson Formation is composed of greywackes, slates and minor volcanics of the Upper Animikie Group, and the Keweenawan sandstones include the Hinckley and Fond du Lac Formations. Several other rock units occur in the

area including the Glen Township Formation, the Randall Formation, various iron formations and several Mid-Proterozoic dikes and sills. However, an insufficient number of data points were located within these rock types; therefore, they were not included in the statistical analysis. The arithmetic mean, standard deviation and median are listed by rock type for each element in Table 3. As was the case for the total data set, the arithmetic mean and the standard deviation for each bedrock subdivision was calculated after values below the detection limit and extraneously high values were deleted. These values are also recorded in Table 3.

From Table 3 it is apparent that there are subtle to distinct differences in the concentrations of several elements between the rock type subdivisions. For example, water collected over the Rabbit Lake/Thomson Formation has relatively high Cu, SO<sub>4</sub>, alkalinity and specific conductance values. Water from the Archean gneisses and granites exhibits high Ca and Na values, and water from the Mahanomen/Denham Formation has a relatively high Fe content. Relatively low background values of As, Cu, Zn, Ca, Mg, alkalinity and specific conductance were found in water collected over the Keweenaw sandstones. The relative differences in the element concentrations of the groundwater are only in partial agreement with average relative abundances of the elements in the various rock lithologies (Hawkes and Webb, 1962; Levinson, 1980). This may be due, in part, to the fact that each of the four major rock subdivisions are not composed of a single rock type, but rather, they contain several different lithologies.

### **Relation of Glacial Deposit Type and Groundwater Chemistry**

The chemistry of groundwater may be affected to a large degree by the composition of the unconsolidated glacial material through which it passes. Therefore, the relation of water composition to three major glacial deposit subdivisions in the survey area was investigated.

Statistical parameters were calculated for each of three major glacial subdivisions representing surficial material deposited from the three lobes of ice that advanced over central Minnesota during the Pleistocene. The three subdivisions are (1) Rainy lobe deposits, (2) Superior lobe deposits, and (3) Des Moines lobe deposits. Deposits of the Rainy lobe are characterized by brown sandy till with clasts of basalt, felsite, gabbro and crystalline rocks typical of northeastern Minnesota. Deposits of the Superior lobe consist of red sandy to clayey till with stones of red sandstone and shale, and deposits of the Des Moines lobe are composed of light brown clayey till with limestone and shale fragments. Deposits of the Wadena lobe and Holocene alluvium also occur in the survey area; however, an insufficient number of data points were located within these deposit types, so they were not included in the statistical analysis. Because the difference in composition between the various types of glacial deposits (such as end moraine, ground moraine, or outwash) within an individual lobe is negligible, the effects of individual end moraine,

ground moraine and outwash units was not considered in the analysis. The subdivisions created for this analysis represent only surficial glacial deposits, however, the source of the material from which the well is actually drawing water from may not necessarily be the same as the surficial material. The arithmetic mean, standard deviation and median are listed by glacial till type for each element in Table 4. As was the case for the total data set and the data subdivided into bedrock type, the arithmetic mean and the standard deviation for each till type subdivision were calculated after values below the detection limit and extraneously high values were deleted. The resultant values are also recorded in Table 4.

### **Relation of Bedrock Penetration and Groundwater Chemistry**

Whether a well penetrates bedrock or not (that is, whether the well produces water directly from bedrock aquifers or from quaternary materials above the bedrock) may have an effect on the well water's composition. For that reason the relation of water chemistry to bedrock penetration was investigated.

The groundwater data base was subdivided into two categories—water from wells that terminated in glacial overburden and water from wells that penetrated bedrock. In many cases this distinction could be made from information by the well owner. In cases where the homeowner didn't know whether bedrock was penetrated or not, however, indirect evidence such as the presumed depth of the well and the approximate thickness of the surficial material (as determined from the depth to bedrock map in Fig. 4) was used to assign the well to one of the two subdivisions. The range, arithmetic mean, standard deviation and median was then calculated for each element. The resultant values are recorded in Table 5.

From Table 5 it is apparent that only subtle differences at best exist between the two subdivisions. Differences in the concentration of most of the trace elements between the two categories is negligible, although water from wells that terminated in the overburden have slightly higher values for Mg, Na, K, specific conductance and alkalinity. The limited differences in composition of the water between the two subdivisions can be attributed to the fact that water in bedrock aquifers and water in quaternary aquifers have a similar ancestry (Morey & Lively, 1980).

It can be seen from Table 4 that there are subtle differences in the concentrations of several elements between the different till type subdivisions. For instance, groundwater collected from Superior lobe deposits has relatively high values of Cu, SO<sub>4</sub>, specific conductance and alkalinity. Water from the Des Moines lobe glacial deposits has slightly lesser values of Ca, SO<sub>4</sub>, specific conductance and alkalinity and slightly greater amounts of As. Groundwater from the Rainy lobe deposits doesn't appear to be enriched or depleted in any of the analyzed elements. The failure to identify major differences between the drift subdivisions suggests that glacial deposit type probably does not play the dominant role in the variability of groundwater composition.

Table 3: Distribution Statistics of Well Water Element Data Segregated by Major Bedrock Subdivisions

Element	Rock Type	Range	Arith. $\bar{X}$	Arith. $\bar{X}^*$	Std. Dev.	Std. Dev.*	Med.
As (ppb)	Archean Gneiss & Gran.	0-24	5.42	5.82	4.64	4.57	4
	Mahnomen/Denham	0-42	4.90	5.70	6.56	4.65	3
	Rabbit Lake/Thomson	0-19	5.73	6.02	4.25	4.16	4
	Keweenawan SS	0-13	3.59	4.22	3.46	3.39	2.5
Cu (ppb)	Archean Gneiss & Gran.	0-22	4.15	6.32	5.85	6.25	1
	Mahnomen/Denham	0-111	5.36	5.80	12.41	7.14	1
	Rabbit Lake/Thomson	0-30	4.64	10.44	8.20	9.66	0
	Keweenawan SS	0-20	1.37	4.25	3.91	6.15	0
Ni (ppb)	Archean Gneiss & Gran.	0-14	1.22	3.33	2.79	3.94	0
	Mahnomen/Denham	0-6	1.16	2.23	1.46	1.47	0
	Rabbit Lake/Thomson	0-20	2.27	3.28	3.67	4.06	0
	Keweenawan SS	0-7	2.76	4.17	2.48	1.91	0
Pb (ppb)	Archean Gneiss & Gran.	0-5	0.40	1.75	0.87	1.39	0
	Mahnomen/Denham	0-8	0.65	2.33	1.30	1.81	0
	Rabbit Lake/Thomson	0-3	0.37	1.71	0.70	0.88	0
	Keweenawan SS	0-2	0.20	1.50	0.39	0.50	0
Zn (ppm)	Archean Gneiss & Gran.	0-0.35	0.08	0.10	0.08	0.08	0.05
	Mahnomen/Denham	0-1.47	0.16	0.15	0.25	0.15	0.07
	Rabbit Lake/Thomson	0-3.64	0.21	0.11	0.57	0.11	0.06
	Keweenawan SS	0-0.22	0.04	0.05	0.05	0.05	0.03
Fe (ppm)	Archean Gneiss & Gran.	0-6.4	0.89	1.09	1.42	1.50	0.2
	Mahnomen/Denham	0-17.0	1.82	2.33	2.93	3.41	0.4
	Rabbit Lake/Thomson	0-25.0	1.05	0.56	3.93	1.18	0.2
	Keweenawan SS	0-34.0	2.60	1.60	6.90	3.13	0.2
SO <sub>4</sub> (ppm)	Archean Gneiss & Gran.	0-71	10.21	13.69	16.16	17.43	4.2
	Mahnomen/Denham	0-37	8.90	10.78	8.38	8.07	6.0
	Rabbit Lake/Thomson	0-120	18.61	18.36	24.19	18.51	6.5
	Keweenawan SS	2-144	18.84	13.84	27.95	12.68	12
Ca (ppm)	Archean Gneiss & Gran.	12-129	56.51	54.78	19.68	16.39	55
	Mahnomen/Denham	4-95	49.51	50.28	17.75	17.27	47
	Rabbit Lake/Thomson	18-119	49.68	47.95	21.89	19.18	50
	Keweenawan SS	12-62	33.03	33.03	14.94	14.94	31
Mg (ppm)	Archean Gneiss & Gran.	4-64	22.93	21.95	12.04	10.36	20
	Mahnomen/Denham	2-56	17.93	17.90	10.07	11.16	15
	Rabbit Lake/Thomson	3-70	23.60	21.46	14.88	11.71	20
	Keweenawan SS	3-33	14.00	14.00	8.72	8.72	11.5
Na (ppm)	Archean Gneiss & Gran.	2-64	13.53	13.53	15.86	15.86	7
	Mahnomen/Denham	2-69	10.65	10.68	11.16	11.47	7
	Rabbit Lake/Thomson	2-47	10.31	10.31	8.98	8.98	7
	Keweenawan SS	2-48	12.38	12.38	12.99	12.99	6
K (ppm)	Archean Gneiss & Gran.	1-44	2.51	1.52	6.42	0.58	1
	Mahnomen/Denham	0-20	1.96	2.00	2.92	2.96	1
	Rabbit Lake/Thomson	1-26	2.29	1.70	3.90	1.12	1
	Keweenawan SS	1-3	1.65	1.65	0.67	0.67	1
Spec.Cond. μohm/l	Archean Gneiss & Gran.	200-1200	385.18	348.48	198.02	109.46	325
	Mahnomen/Denham	160-1225	350.29	335.47	170.32	132.02	307
	Rabbit Lake/Thomson	98-820	388.48	388.48	175.14	175.14	350
	Keweenawan SS	95-435	260.57	260.57	95.82	95.82	277
Alk. mg/l	Archean Gneiss & Gran.	27.4-593.4	253.53	245.44	96.73	82.25	250.7
	Mahnomen/Denham	7.9-438.5	202.23	207.40	91.48	93.13	224.0
	Rabbit Lake/Thomson	60.4-550.5	270.13	263.12	125.42	118.79	245.6
	Keweenawan SS	53.0-320.5	171.38	171.38	68.83	68.83	182.2
pH	Archean Gneiss & Gran.	6.4-8.2	7.66	7.66	0.37	0.37	7.7
	Mahnomen/Denham	6.4-8.6	7.60	7.60	0.38	0.38	7.6
	Rabbit Lake/Thomson	6.9-8.5	7.74	7.74	0.41	0.41	7.8
	Keweenawan SS	6.9-8.6	7.81	7.81	0.45	0.45	7.75
Temp °C	Archean Gneiss & Gran.	8-20	12.57	12.57	2.50	2.50	12.5
	Mahnomen/Denham	6-18	12.60	12.60	2.11	2.11	12.5
	Rabbit Lake/Thomson	8-17	12.12	12.12	2.77	2.77	12
	Keweenawan SS	8-16	11.53	11.53	2.11	2.11	11

Note: Archean Gneiss and Gran. N = 43  
Mahnomen/Denham N = 60  
Rabbit Lake/Thomson N = 41  
Keweenawan SS N = 26

\* mean and standard deviation calculated after the extraneously high and low (below detection limit) values were discarded.

Table 4: Distribution Statistics of Well Water Element Data Segregated by Major Tilltype Subdivisions

Element	Till Type	Range	Arith. $\bar{X}$	Arith. $\bar{X}^*$	Std. Dev.	Std. Dev.*	Med.
As (ppb)	Des Moines Lobe	0-19	6.15	6.97	4.49	4.16	6
	Rainy Lobe	0-42	4.13	4.76	5.98	4.05	3
	Superior Lobe	0-19	5.10	5.69	4.08	3.92	4
Cu (ppb)	Des Moines Lobe	0-48	5.16	6.54	9.68	8.50	2
	Rainy Lobe	0-111	6.26	6.04	16.88	11.66	1
	Superior Lobe	0-59	3.89	8.69	8.85	6.84	0
Ni (ppb)	Des Moines Lobe	0-8	1.71	2.36	1.72	1.64	1
	Rainy Lobe	0-14	1.10	2.36	2.20	2.84	0
	Superior Lobe	0-20	2.22	3.18	3.02	2.39	1
Pb (ppb)	Des Moines Lobe	0-8	0.76	2.63	1.60	2.26	0
	Rainy Lobe	0-3	0.50	1.60	0.80	0.86	0
	Superior Lobe	0-4	0.29	1.81	0.65	1.02	0
Zn (ppm)	Des Moines Lobe	0-1.47	0.15	0.14	0.23	0.12	0.07
	Rainy Lobe	0-0.78	0.10	0.14	0.13	0.14	0.06
	Superior Lobe	0-3.64	0.16	0.11	0.40	0.12	0.06
Fe (ppm)	Des Moines Lobe	0-17.0	1.23	1.47	2.96	3.19	0.2
	Rainy Lobe	0-25.0	1.63	1.84	3.45	2.31	0.4
	Superior Lobe	0-34.0	1.28	1.14	4.05	2.44	0.2
SO <sub>4</sub> (ppm)	Des Moines Lobe	0-35.0	6.75	8.56	7.46	7.45	5.0
	Rainy Lobe	0-42.0	8.32	10.16	9.22	9.25	5.0
	Superior Lobe	0-144.0	17.50	17.25	23.63	16.81	9.5
Ca (ppm)	Des Moines Lobe	9-98	40.33	41.09	21.26	20.94	35
	Rainy Lobe	4-89	51.01	51.65	17.66	16.90	49
	Superior Lobe	12-119	45.70	44.92	20.18	18.81	44
Mg (ppm)	Des Moines Lobe	3-64	17.80	16.68	14.51	12.74	14
	Rainy Lobe	2-34	15.45	15.45	7.77	7.77	15
	Superior Lobe	3-70	21.47	20.52	13.04	11.43	19
Na (ppm)	Des Moines Lobe	3-53	11.16	11.16	11.22	11.22	7.5
	Rainy Lobe	2-118	12.20	10.75	18.00	13.15	6.5
	Superior Lobe	2-48	11.30	11.30	10.07	10.07	7
K (ppm)	Des Moines Lobe	1-5	1.47	1.47	0.73	0.73	1
	Rainy Lobe	0-20	1.63	1.65	2.64	2.65	1
	Superior Lobe	1-26	2.06	2.06	2.65	2.65	2
Spec. Cond. ( $\mu$ ohm/l)	Des Moines Lobe	75-1075	307.04	288.31	192.49	152.39	260
	Rainy Lobe	155-1225	336.86	324.69	151.22	110.58	305
	Superior Lobe	95-820	353.07	353.07	153.17	153.17	340
Alkalinity (mg/l)	Des Moines Lobe	29.7-593.4	185.26	175.30	108.91	89.38	168.8
	Rainy Lobe	7.9-345.8	189.22	191.81	82.43	80.09	185.6
	Superior Lobe	53-550.5	244.74	241.49	108.59	104.47	230.0
pH	Des Moines Lobe	6.4-8.6	7.69	7.69	0.53	0.53	7.6
	Rainy Lobe	6.4-8.6	7.65	7.65	0.44	0.44	7.7
	Superior Lobe	6.9-8.6	7.73	7.73	0.39	0.39	7.8
Temp (°C)	Des Moines Lobe	9-17	12.55	12.55	2.02	2.02	12
	Rainy Lobe	6-20	13.02	13.02	2.51	2.51	13
	Superior Lobe	8-17	11.96	11.96	2.36	2.36	12

Note: Des Moines Lobe      N = 42  
 Rainy Lobe                N = 74  
 Superior Lobe            N = 95

\* mean and standard deviation calculated after the extraneously high and low (below detection limit) values were discarded.



## Relation of Plumbing Composition and Groundwater Chemistry

The chemistry of the water samples may be affected by the composition of the well and plumbing system through which it passes from its source in the aquifer to the sample site at the faucet. Therefore, the relation of water chemistry to plumbing composition was investigated.

Information on the composition of the plumbing system was obtained from the well owner and by direct observation, and it was determined that nearly all plumbing systems were composed of copper, galvanized steel, plastic, or some combination of the three. The groundwater data base was subsequently subdivided into two categories—water collected from plumbing systems containing copper pipes and water from systems with galvanized steel pipes. Plumbing systems consisting of both copper and plastic pipes were classified under the copper pipe category; similarly, systems with galvanized and plastic pipes were classified under the galvanized pipe category. When both copper and galvanized pipes were encountered in the same plumbing system, the data was classified under both categories, thus some duplication of data was recorded. The range, arithmetic mean, standard deviation and median was then calculated for each element, with the resultant values being recorded in Table 6.

From Table 6 it can be seen that there is very little difference in the element concentrations between water collected from systems with galvanized pipes and systems with copper pipes. Despite the fact that a few wells contained both copper and galvanized pipes and were assigned to both categories (thus tending to lessen the differences between categories), it appears that in this survey plumbing composition had little effect on groundwater chemistry.

## Relation of Well Depth and Groundwater Chemistry

The depth of the sampled well may be an important consideration in the interpretation of the water chemistry. Groundwater from shallow wells tends to have a more local source, and is more subject to contamination from the surface. Groundwater from relatively deep wells, on the other hand, usually has a more distant source and has a greater interaction with deeply buried bedrock.

The groundwater data base was initially subdivided into two categories—water from wells greater than 30 feet in depth and water from wells less than 30 feet in depth. Statistical parameters for each element were calculated and it was evident that a number of differences existed between deep and shallow wells for several elements. To ascertain the degree of influence that well depth had on these differences, the original data base was again subdivided into deep and shallow wells, this time with a 50 foot depth being used as the dividing line between categories. The range, arithmetic mean, standard deviation and median were again calculated for each element, and the results are shown in Table 7.

From Table 7 it is evident that there are a number of differences in element concentrations between deep and shallow wells. For example, water from wells less than 30 feet deep has more than twice the concentration of copper

than wells deeper than 30 feet; and water from wells greater than 30 feet has greater values for Fe, Ca, Mg, pH and alkalinity. When the data is re-examined using a 50 foot depth as the division between categories, it is apparent that most differences in element concentration between deep and shallow wells either decreases (as for Mg, pH and alkalinity) or disappears entirely (as for Fe and Ca). Only the copper concentration retains a large difference between deep and shallow wells when the 50 foot dividing line is used.

## Correlation Analysis

Correlation coefficients were calculated for the total data set using a univariate linear model. Elements that were previously determined to approximate a lognormal distribution were  $\log_{10}$  transformed prior to correlation calculations. The correlation coefficients were determined for both the original data set including values below the analytical detection limit and for the revised data set where element concentrations below the detection limit were discarded. The resulting coefficients determined from the two sets were very similar, thus only the coefficient calculated from the data set where values below the detection limit were discarded are shown in Table 8.

From Table 8 it can be seen that several parameters, namely Ca, Mg, alkalinity and specific conductance show a moderate to strong positive (0.44-0.66) relation for each other. Several other elements show much weaker relationships. Na, K, and specific conductance show a weak positive (0.12-0.13) relation for each other. pH shows a very weak negative relation with Zn (-0.11) and Cu (-0.17). Very weak negative relations are also apparent between Cu and Fe (-0.14) and between Cu and As (-0.12).

Linear correlation coefficients were calculated for each of the four major bedrock subdivisions described in the previous section. The results are listed in Tables 9-12. The relations of Tables 9-12 are somewhat variable between rock type but are generally similar to that of the total data (Table 8). Frequently, the correlation coefficients of Tables 9-12 are somewhat greater than Table 8 which may result from the smaller number of data points within each bedrock subdivision.

The relatively strong positive relation between Ca, Mg, alkalinity and specific conductance is very evident in all four bedrock subdivisions as it is in the total data set, and a moderate negative relation between Cu and pH is evident in all subdivisions except the Archean gneisses and granites. Several other element pairs correlate within individual bedrock groups including moderate negative relations of Fe with Cu and  $\text{SO}_4$  and positive relations of  $\text{SO}_4$  with K and Na in the Archean gneisses and granites, a moderate negative Fe to pH relation in the Keweenaw sandstones, and moderate positive Cu to Na and Mg relations in the Rabbit Lake/Thomson Formation. It should be mentioned that extreme care must be used when considering the significance of the correlation coefficients of the individual bedrock subdivisions because of the limited number of data points above the detection limit for some elements, particularly Pb, Cu and Ni.

Correlation coefficients were also calculated for each of

Table 5: Distribution Statistics of Well Water Element Data Segregated by Bedrock Penetration

Element	Bedrock vs Quaternary	Range	Arith. $\bar{X}$	Std. Dev.	Med.
As (ppb)	Bedrock	1-14	5.56	3.47	4.5
	Quaternary	1-24	5.77	4.61	4
Cu (ppb)	Bedrock	1-36	7.55	8.25	4
	Quaternary	1-59	7.08	10.35	3
Ni (ppb)	Bedrock	1-13	3.02	2.67	2
	Quaternary	1-14	2.60	2.20	2
Pb (ppb)	Bedrock	1-5	2.22	1.47	1
	Quaternary	1-8	1.82	1.44	1
Zn (ppm)	Bedrock	0.02-0.66	0.12	0.14	0.07
	Quaternary	0.02-0.78	0.13	0.12	0.08
Fe (ppm)	Bedrock	0.1-17.0	1.52	3.22	0.3
	Quaternary	0.1-11.8	1.38	2.11	0.4
SO <sub>4</sub> (ppm)	Bedrock	1-72	12.51	12.53	7.1
	Quaternary	1-71	13.27	14.72	6.2
Ca (ppm)	Bedrock	11-95	44.96	18.00	45
	Quaternary	12-106	48.04	19.09	46
Mg (ppm)	Bedrock	3-56	20.31	12.06	18
	Quaternary	2-53	17.20	9.96	16
Na (ppm)	Bedrock	3-53	12.02	10.83	8
	Quaternary	2-69	10.70	12.28	7
K (ppm)	Bedrock	1-7	1.90	1.04	2
	Quaternary	1-20	1.55	1.91	1
Spec. Cond. (μohm/l)	Bedrock	95-805	344.7	143.8	330
	Quaternary	75-820	322.0	134.6	230
Alkalinity (mg/l)	Bedrock	52.4-500.8	243.7	98.9	233.7
	Quaternary	27.4-492.0	201.8	94.5	197.1
pH	Bedrock	6.9-8.6	7.75	0.36	7.8
	Quaternary	6.4-8.6	7.66	0.46	7.7
Note: Bedrock	N = 75				
Quaternary	N = 151				

Table 6: Distribution Statistics of Well Water Element Data Segregated by Plumbing Composition

Element	Pipe Composition	Range	Arith. $\bar{X}$	Std. Dev.	Med.
As (ppb)	Copper	29.7-500.8	5.54	3.67	5
	Galvanized	1-22	5.73	4.12	4
Cu (ppb)	Copper	1-59	7.18	10.02	3
	Galvanized	1-59	8.21	11.60	3
Ni (ppb)	Copper	1-14	2.96	2.99	2
	Galvanized	1-8	2.67	1.90	2
Pb (ppb)	Copper	1-5	1.83	1.11	1
	Galvanized	1-5	1.95	1.32	1
Zn (ppm)	Copper	0.02-0.66	0.12	0.13	0.08
	Galvanized	0.02-0.78	0.13	0.13	0.08
Fe (ppm)	Copper	0.1-11.8	1.14	1.85	0.4
	Galvanized	0.1-17.0	1.34	2.84	0.03
SO <sub>4</sub> (ppm)	Copper	1.5-72	11.08	14.06	5
	Galvanized	1-71	13.47	13.99	7
Ca (ppm)	Copper	12-98	45.56	17.66	44
	Galvanized	12-106	46.83	19.25	48
Mg (ppm)	Copper	2-49	17.65	10.28	16
	Galvanized	3-53	18.31	10.83	17
Na (ppm)	Copper	2-69	12.57	13.75	7
	Galvanized	2-53	10.77	10.89	7
K (ppm)	Copper	2-7	2.28	0.87	2
	Galvanized	1-20	1.63	1.82	1
Spec. Cond. ( $\mu$ ohm/l)	Copper	98-795	320.3	130.4	302
	Galvanized	75-820	334.4	144.3	320
Alkalinity (mg/l)	Copper	27.4-423.0	217.5	94.33	214
	Galvanized	29.7-500.8	219.3	98.31	215
pH	Copper	6.4-8.6	7.77	0.43	7.8
	Galvanized	6.4-8.6	7.72	0.44	7.75
Note: Copper	N = 89				
Galvanized	N = 121				

Table 7: Distribution Statistics of Well Water Element Data Segregated by Well Depth

Element	Depth (ft.)	Range	Arith. $\bar{X}$	Std. Dev.	Med.
As (ppb)	<30	1-14	4.16	3.16	3
	>30	1-24	6.26	4.42	5
	<50	1-24	5.28	4.33	4
	>50	1-22	5.96	4.05	5
Cu (ppb)	<30	1-59	11.28	13.26	6
	>30	1-48	5.48	7.95	2
	<50	1-59	10.55	12.60	6
	>50	1-35	5.07	6.79	2
Ni (ppb)	<30	1-7	2.76	1.76	2
	>30	1-14	2.72	2.59	2
	<50	1-13	2.62	2.25	2
	>50	1-14	2.75	2.44	2
Pb (ppb)	<30	ND	ND	ND	ND
	>30	1-5	1.83	1.21	1
	<50	1-5	1.45	1.15	1
	>50	1-5	1.87	1.12	1
Zn (ppm)	<30	0.02-0.78	0.16	0.15	0.12
	>30	0.02-0.66	0.11	0.12	0.07
	<50	0.02-0.78	0.13	0.13	0.08
	>50	0.02-0.66	0.12	0.13	0.07
Fe (ppm)	<30	0.1-1.6	0.37	0.45	0.1
	>30	0.1-17.0	1.62	2.83	0.5
	<50	0.1-17.0	1.43	2.89	0.2
	>50	0.1-13.5	1.46	2.51	0.5
SO <sub>4</sub> (ppm)	<30	1.5-64	13.60	15.26	6.6
	>30	1-72	12.88	13.41	7
	<50	1.5-64	14.04	14.81	6.75
	>50	1-72	12.44	13.48	6
Ca (ppm)	<30	12-106	45.38	24.31	39.5
	>30	12-96	48.24	17.32	49
	<50	12-106	47.54	21.90	46
	>50	12-96	47.32	17.34	47
Mg (ppm)	<30	2-56	16.25	12.94	12
	>30	3-53	19.50	10.22	18
	<50	2-56	17.29	12.78	14
	>50	3-49	19.00	9.58	18
Na (ppm)	<30	2-51	13.02	13.75	6
	>30	2-64	10.71	10.37	7
	<50	2-64	12.55	13.42	7
	>50	2-53	10.58	9.67	7
K (ppm)	<30	1-14	1.72	2.21	1
	>30	1-7	1.63	0.82	2
	<50	1-20	1.80	2.77	1
	>50	1-7	1.67	0.85	2
Spec. Cond. ( $\mu$ ohm/l)	<30	75-820	327.9	179.6	295
	>30	95-795	341.1	127.6	327.5
	<50	75-820	339.0	169.4	305
	>50	95-795	333.5	122.1	325
Alkalinity (mg/l)	<30	27.4-491.3	189.2	118.5	174.2
	>30	46.7-500.8	229.3	90.4	220.0
	<50	27.4-492.0	203.7	113.9	200.2
	>50	53-500.8	226.0	87.3	216.5
pH	<30	6.4-8.1	7.37	0.53	7.4
	>30	6.4-8.6	7.79	0.37	7.8
	<50	6.4-8.2	7.44	0.47	7.5
	>50	6.9-8.6	7.82	0.36	7.8

Note: Wells <30 N= 34  
Wells >30 N= 158  
Wells <50 N= 66  
Wells >50 N= 131  
ND = not determined

Table 8: Correlation Matrix for Samples from All Rock Types (N = 226)

	As	Cu	Ni	Pb	Fe	Zn	SO <sub>4</sub>	Ca	Mg	Na	K	Spec	Alk	Temp
pH	.08	-.17	-.01	0	-.07	-.11	-.01	-.02	0	0	0	0	0	-.01
Temp	.01	0	-.02	0	0	.06	-.03	-.01	-.03	-.04	0	-.02	-.05	
Alk	.01	0	0	-.05	.01	0	.01	.45	.66	.06	.08	.60		
Spec	0	0	0	0	.01	0	.08	.66	.63	.13	.12			
K	0	0	0	0	0	0	.03	.01	.04	.13				
Na	0	0	0	0	-.02	0	.09	0	.08					
Mg	0	0	.01	0	0	0	.04	.47						
Ca	0	0	0	0	.03	.01	.03							
SO <sub>4</sub>	-.01	.06	0	-.01	-.10	0								
Zn	-.01	.05	0	0	0									
Fe	0	-.14	0	0										
Pb	0	-.04	0											
Ni	0	.01												
Cu	-.12													

Note: Element data log<sub>10</sub> transformed prior to calculation of correlation coefficients with the exception of Ca, alkalinity, temperature and pH.

Table 9: Correlation Matrix for Samples Over the Rabbit Lake/Thomson Formation (N = 41)

	As	Cu	Ni	Pb	Fe	Zn	SO <sub>4</sub>	Ca	Mg	Na	K	Spec	Alk	Temp
pH	.06	-.60	-.06	-.14	0	-.11	-.22	-.28	-.12	-.20	0	-.29	-.12	-.03
Temp	.17	-.21	-.01	-.04	0	.01	-.10	-.08	0	-.04	-.03	-.02	-.04	
Alk	.10	.33	.03	-.33	.21	-.01	.13	.40	.67	.38	.15	.79		
Spec	.02	.26	.05	0	.12	0	.27	.57	.70	.34	.12			
K	.01	0	-.02	.32	.15	0	0	0	.09	.26				
Na	.01	.54	0	.11	.02	.03	.13	.06	.38					
Mg	.07	.47	.12	-.24	.15	0	.16	.22						
Ca	0	.30	.03	0	.08	0	.14							
SO <sub>4</sub>	-.07	.34	.01	.01	-.01	0								
Zn	-.05	.04	.02	-.11	-.03									
Fe	.09	-.21	.12	-.37										
Pb	-.11	.14	.25											
Ni	0	.21												
Cu	0													

Note: Element data log<sub>10</sub> transformed prior to calculation of correlation coefficients with the exception of Ca, alkalinity, temperature and pH.

Table 10: Correlation Matrix for Samples Over Archean Gneisses and Granites (N = 43)

	As	Cu	Ni	Pb	Fe	Zn	SO <sub>4</sub>	Ca	Mg	Na	K	Spec	Alk	Temp
pH	.10	0	0	.05	-.08	-.18	-.01	.04	.08	-.03	0	0	.07	-.01
Temp	0	0	-.03	.27	.01	.07	-.02	-.13	-.16	-.09	.01	-.13	-.15	
Alk	0	.02	.02	-.31	0	0	0	.44	.61	.03	-.01	.32		
Spec	0	0	-.07	.12	0	.03	.17	.61	.78	.06	.01			
K	-.10	.05	0	0	-.22	0	.48	0	0	-.01				
Na	.01	0	.03	.02	-.02	0	.37	.03	.07					
Mg	0	0	0	.07	-.03	0	0	.64						
Ca	0	.03	0	.05	-.01	0	.03							
SO <sub>4</sub>	-.04	.15	.01	.01	-.41	0								
Zn	-.05	-.05	0	.08	0									
Fe	.21	-.41	-.02	-.19										
Pb	0	-.13	-.11											
Ni	0	.05												
Cu	-.36													

Note: Element data log<sub>10</sub> transformed prior to calculation of correlation coefficients with the exception of Ca, alkalinity, temperature and pH.

Table 11: Correlation Matrix for Samples Over the Denham/Mahnomen and Related Formations (N = 60)

	As	Cu	Ni	Pb	Fe	Zn	SO <sub>4</sub>	Ca	Mg	Na	K	Spec	Alk	Temp
pH	.01	-.27	-.03	.08	-.03	-.16	0	0	.07	-.01	-.03	0	0	-.08
Temp	.02	.11	.03	-.05	-.07	.17	0	-.03	-.12	0	0	.01	-.12	
Alk	0	-.11	.06	0	0	0	0	.52	.73	.05	.06	.63		
Spec	0	-.01	0	-.08	0	0	.01	.75	.51	.14	.18			
K	-.08	.07	.05	-.08	-.13	0	.06	.03	.03	.15				
Na	-.03	.01	.06	0	0	-.03	0	0	.10					
Mg	0	-.08	.01	.03	0	0	0	.44						
Ca	-.01	-.04	0	.02	.03	0	0							
SO <sub>4</sub>	-.04	.03	0	-.09	-.04	.02								
Zn	-.07	.05	.08	-.01	0									
Fe	0	-.29	-.05	0										
Pb	.14	-.78	.22											
Ni	0	0												
Cu	-.11													

Note: Element data log<sub>10</sub> transformed prior to calculation of correlation coefficient with the exception of Ca, alkalinity, temperature and pH.

the three glacial type subdivisions (Tables 13-15). As can be seen from the tables, the coefficients tend to suggest the same general relationships as for the bedrock categories. Once again, Ca, Mg, alkalinity and specific conductance show a strong positive relation, especially in the Des Moines lobe drift. Moderate negative relations of Cu with Fe and pH are also evident in some of the subdivisions.

Table 12: Correlation Matrix for Samples Over Keweenaw Sandstones (N = 26)

	As	Cu	Ni	Fe	Zn	SO <sub>4</sub>	Ca	Mg	Na	K	S	Alk	T
pH	.19	-.33	-.08	-.50	-.01	.05	-.03	0	.29	.05	.02	0	0
T	.06	-.23	-.08	.01	0	-.12	.02	0	-.23	0	0	0	
Alk	-.08	-.09	.10	.08	-.01	-.21	.59	.64	.01	.12	.64		
Spec	-.03	-.02	.08	.03	-.01	-.02	.57	.59	.15	.35			
K	.03	-.16	0	0	-.02	.01	.02	.04	.26				
Na	0	-.02	0	-.12	-.03	.10	-.04	0					
Mg	-.22	0	.21	.03	.01	-.07	.66						
Ca	-.05	-.02	.21	.20	0	-.18							
SO <sub>4</sub>	.02	.28	-.06	-.21	0								
Zn	0	.41	.11	0									
Fe	-.06	-.06	.09										
Ni	-.05	-.20											
Cu	.35												

Note: Element data log<sub>10</sub> transformed prior to calculation of correlation coefficients with the exception of Ca, alkalinity, temperature and pH.

Table 13: Correlation Matrix for Samples from Superior Lobe Drift (N = 95)

	As	Cu	Ni	Pb	Fe	Zn	SO <sub>4</sub>	Ca	Mg	Na	K	Spec	Alk	Temp
pH	.12	-.27	-.02	0	-.12	-.13	-.02	.10	-.07	0	0	-.06	-.04	0
Temp	.15	-.06	-.05	0	0	0	-.07	.01	0	-.06	0	0	0	
Alk	.03	0	-.01	-.11	.04	.02	.01	.46	.68	.09	.04	.70		
Spec	.01	0	0	0	-.02	.05	.11	.63	.75	.16	.11			
K	0	-.01	-.02	.09	0	0	.02	.01	.03	.11				
Na	0	.07	0	.08	-.02	0	.05	0	.08					
Mg	0	.02	0	-.15	0	.06	.02	.48						
Ca	0	0	0	.08	.06	.06	.05							
SO <sub>4</sub>	0	.05	0	-.04	-.09	.01								
Zn	0	.22	0	-.17	0									
Fe	0	-.39	0	0										
Pb	.02	0	0											
Ni	-.04	.01												
Cu	-.04													

Note: Element data log<sub>10</sub> transformed prior to calculation of correlation coefficients with the exception of Ca, alkalinity, temperature and pH.

Table 14: Correlation Matrix for Samples from Rainy Lobe Drift (N = 74)

	As	Cu	Ni	Pb	Fe	Zn	SO <sub>4</sub>	Ca	Mg	Na	K	Spec	Alk	Temp
pH	0	-.01	-.01	-.03	-.01	-.08	-.02	0	.05	-.06	-.04	-.01	0	-.05
Temp	0	0	0	-.01	0	.09	0	-.03	-.04	-.01	0	-.01	-.12	
Alk	.03	0	.05	-.02	.02	-.03	0	.52	.50	0	0	.31		
Spec	0	0	0	-.04	0	-.02	.09	.73	.30	-.09	.04			
K	-.02	0	.04	-.01	0	0	.05	0	0	.07				
Na	0	0	.03	.01	0	-.02	.15	0	.05					
Mg	0	-.01	.02	0	0	-.03	.07	.48						
Ca	0	-.01	0	-.01	.01	-.02	.03							
SO <sub>4</sub>	-.02	.01	0	-.14	-.18	0								
Zn	0	-.03	0	.02	.01									
Fe	0	-.25	-.01	.12										
Pb	-.24	-.08	-.01											
Ni	0	0												
Cu	0													

Note: Element data log<sub>10</sub> transformed prior to calculation of correlation coefficients with the exception of Ca, alkalinity, temperature and pH.

Table 15: Correlation Matrix for Samples from Des Moines Lobe Drift (N = 42)

	As	Cu	Ni	Pb	Fe	Zn	SO <sub>4</sub>	Ca	Mg	Na	K	Spec	Alk	Temp
pH	.26	-.33	0	0	-.13	-.12	0	0	.13	.09	.04	.13	.06	-.07
Temp	0	.06	0	.15	-.01	.28	-.04	-.01	-.11	-.02	0	-.08	-.06	
Alk	.01	-.08	0	-.01	.01	0	0	.74	.77	.16	.25	.85		
Spec	.04	-.16	0	.06	.01	0	.02	.80	.85	.18	.28			
K	.01	0	0	0	-.04	.03	0	.12	.27	.23				
Na	0	-.01	0	-.05	-.03	-.01	0	.06	.11					
Mg	.04	-.18	0	0	0	-.02	.02	.70						
Ca	-.03	0	0	0	0	.05	.05							
SO <sub>4</sub>	0	.09	0	0	0	-.03								
Zn	-.15	.15	.03	0	0									
Fe	0	-.01	-.02	-.23										
Pb	.21	-.05	.05											
Ni	0	0												
Cu	-.48													

Note: Element data log<sub>10</sub> transformed prior to calculation of correlation coefficients with the exception of Ca, alkalinity, temperature and pH.



## Interpretational Considerations

It is evident from the chemical and statistical analyses that there is some degree of variability in well water composition across the survey area. However, the significance of the variability is difficult to assess because so many factors, both those taken into account and those that could not be evaluated, have an important effect on water chemistry. The interpretation of the data for geologic information and mineral potential purposes, therefore, depends to a large degree on the determination of what factors actually control the composition of the water.

Each water sample was assigned to a specific group of rock lithologies and to a specific drift type. Statistical analyses were then performed, and it was determined that there was some difference in water composition between the different rock groups and drift types. But it was not conclusively determined how much relative influence the bedrock composition and the drift composition had in controlling water chemistry. For example, it was determined that water from the Rabbit Lake/Thomson Formation and from the Superior lobe (which are spatially coincident) had relatively high Cu and SO<sub>4</sub> contents. However, it is very difficult to assess how much effect rock type and drift type actually had on the high Cu and SO<sub>4</sub> content; in all likelihood both variables had some influence on water chemistry.

The assignment of each water well to a bedrock or drift subdivision entails some uncertainty in itself. The bedrock subdivisions are not homogenous; each contains several related, but chemically different lithologies, so individual wells within each subdivision may not penetrate the exact same rock type. The glacial drift subdivisions were based only on surficial geology. In places where drift from the different ice lobes overlap, the drift at the surface may be very different from that at the depth from where the water is actually produced.

The mobilization, transport and deposition of the trace elements involves variable and complex chemical processes (Levinson, 1980). The element concentrations observed in the water samples are a result of Eh, pH, complexing and other chemical factors that were not able to be controlled during the sampling. Variations in these factors can affect the availability of metals at their source and the mobility of metals during transport, and thus the elemental concentrations in the water collected. The degree of interaction of groundwater with bedrock is also quite variable and uncertain across the survey area. Some aquifers have little contact with bedrock and thus, water from these aquifers may not be good indicators of bedrock geology. The presence of clay layers may also influence water chemistry. Not only do these layers act as impermeable barriers to water flow reducing interaction between aquifers, but they may also significantly alter water chemistry by adsorbing elements into their structure.

In general, it was determined that plumbing composition had little effect on water chemistry. However, for individual wells this may not be the case. Water composition may be influenced by the amount of material precipitated within the pipe, the frequency of well use, the volume of water flow, the type of soldering present, the age of the plumbing, and a number of other related factors. For example, one well containing a galvanized sand point less than a month old was resampled three months later, and it was noticed that

the Zn content of the water decreased from 1.55 ppm to 1.03 ppm over that three months.

The chemistry of each major bedrock subdivision produces its own background levels in the groundwater and should be considered during interpretation. It is possible that lower concentration anomalies over a lower background may be as, or more, significant than high concentration anomalies over a high background. Anomaly to background contrast should be considered.

The scope of this project entailed that sampling be performed over a rather large surficial area encompassing a large number of different rock units. Consequently, a relatively small number of samples per rock type were used in the statistical analyses. Values below the detection limit and extraordinarily high values may carry an inordinate degree of influence on the calculated results. The actual numerical results of the analyses may not be statistically exact, and therefore should be used as only a general indication of the relationships present.

Despite the fact that there are a large number of variables involved in the well water survey, an analysis of the data indicates some consistency to the process. If the operative processes were random or inconsistent, the element concentrations of the water would not reflect those of bedrock (Table 2) and bedrock elemental association would not be reflected in the water (Table 3) to any significant degree.

## Discussion

Symbol maps using symbols designed and used by the Geological Survey of Canada were constructed to depict the concentrations of As, Cu, Ni, Fe, SO<sub>4</sub>, Zn, Mg, Ca, Na and alkalinity, and are shown on Plates 2-11 (in pocket inside back cover). The symbols represent ranges of concentrations that were determined by ranges of percentiles of the cumulative frequency distribution and by increments of ppm or ppb for each element. The ranges of percentiles selected for some elements are approximate because actual concentrations of the elements in ppm or ppb doesn't necessarily coincide with ten percent or 20 percent ranges. (The 2-3 ppb interval for As, for example, correlates with the 27 to 47 percent frequency range.) In addition, for elements that have many points below the detection limit, a skewed percentile range is used, with all below detection limit values (up to 45 cumulative percent for Cu and Ni) included within the lowest concentration range. At high concentrations, the ranges are reduced to illustrate the distribution of the most anomalous samples (i.e. percentages of 90-95%, 95-97.5% and 97.5-100%). As is evident from the plates, there are several areas with anomalous values for many of the major elements. However, most of the trace elements (As, Cu, Ni and Zn) showed relatively consistent background values across the survey area. High values were found in areas underlain by the Glen Township Formation for Ca, Mg and alkalinity near Thor in Aitkin County and for Na along the northeast shore of Mille Lacs Lake. High Ca content from areas overlying volcanic rocks near Borden Lake in Crow Wing County and high Fe content in the water from the iron formation area north of Brainerd in Crow Wing County were also observed. Plate 12 illustrates samples where two or more elements exceed 90 percent cumulative frequency. Two general areas with

several multi-element anomalies are present in the survey area. The first is located near Thor in Aitkin County and the second is located in central and southern portions of the Thomson Formation in Carlton County. In both cases, the majority of anomalous elements are the major elements such as Ca, Mg, SO<sub>4</sub> and alkalinity. The element concentrations for any sample can be determined by first locating the sample site and sample number on Plate 1 and referring to the appendix where concentrations are listed.

### Summary and Conclusions

A reconnaissance scale geochemical survey that involved the collection and analysis of groundwater samples from 226 domestic wells was conducted over an area of 2160 sq. mi. in central Minnesota. The water samples were analyzed for Ag, As, Au, Cu, Ni, Pb, Fe, Zn, Ca, Mg, Na and K by atomic absorption techniques. Measurements of alkalinity, pH, SO<sub>4</sub> content and specific conductance were also made, either in the field or in the lab.

Statistical analyses were performed on the water well data in an attempt to identify relationships between elemental concentrations and other parameters that could be useful as indicators of favorable geologic units and possible economic mineralization. The effect of bedrock lithology, drift composition, bedrock penetration, plumbing composition and well depth on water chemistry was investigated. The analysis indicated that there are differences in the concentration of several elements between rock types. The relatively high Cu and SO<sub>4</sub> content in the Rabbit Lake/Thomson Formation is in good agreement with known sulfide mineralization in that area. Higher Ca and Na values in the feldspar-rich Archean gneisses and granites and higher Fe content in the Mahnomen/Denham Formation (which is located near the Trommald iron formation and contains some associated mafic volcanics) are also geologically consistent. The effect of drift type is less conclusive; any differences in water chemistry between the different drift types is only slight, and aren't always consistent with the composition of the drift. Water from the carbonate-rich Des Moines lobe, for example, had a slightly lesser Ca content than the other drift types. The analysis also showed that in this survey pipe composition and whether the well penetrated bedrock or not had little effect on water composition. There was some correlation, on the other hand, between well depth and elemental concentrations. Cu content was found to be significantly higher in shallow wells than in deep wells.

Correlation coefficients were calculated for the total data set, each bedrock subdivision and each drift type subdivision. In all cases Ca, Mg, alkalinity and specific conductance showed moderate to strong positive correlation, and is particularly high in the carbonate-rich Des Moines lobe drift. Other parameter pairs, most notably Cu and pH, show weak relations in some of the rock and drift subdivisions.

Two areas of multi-element anomalies, consisting of mainly the major elements, were indicated by this survey, one occurring in the Glen Township Formation near Thor in Aitkin County and the other in central and southern portions of the Thomson Formation in Carlton County.

This survey indicates that there may be some potential in using a reconnaissance scale well water sampling program for mineral potential evaluation. However, in geologi-

cally complex areas such as central Minnesota, a greater sampling density should be used to ensure adequate coverage of all the different rock types. Seasonal or other time-related variations in water chemistry determined by periodic sampling of individual control wells should also be considered. Several elements not included in this investigation, particularly Sb, F and Mn (Boyle, 1974) could be useful as indicator elements and should be included in subsequent surveys. And finally, since gold and silver occur in natural waters in minute amounts not detectable by ordinary analytical techniques, solvent extraction techniques similar to that recently developed by McHugh (1984) could be used in the direct analysis of well water for gold and silver content.

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## **APPENDIX**











Samp. Num.	Twp.	Rge.	1/4 Sec.	Rock Type	Till Type	Depth ft.	As ppb	Cu ppb	Ni ppb	Pb ppb	Fe ppm	SO4 ppm	Ca ppm	Mg ppm	Na ppm	K ppm	Zn ppm	pH	Spec. Cond. ohm/l	Aik. mg/l	Temp. °C
303	45.00	21.00	15	AADDK	K	S 320	.1	.1	2.00	.1	.1	9.50	49.00	40.00	22.00	2.00	.33	7.30	395.00	419.80	10.0
304	44.00	19.00	35	CAAAC	S	S 110	.1	20.00	3.00	.1	.01	18.00	16.00	8.00	6.00	1.00	.01	6.90	130.00	53.00	9.0
308	44.00	17.00	30	CDDCA	K	S 28	.1	6.00	7.00	.1	.1	62.00	62.00	39.00	23.00	1.00	.29	7.10	600.00	230.00	8.0
309	46.00	20.00	10	DCBAB	RL	S 16	2.00	4.00	3.00	.1	.2	28.00	40.00	16.00	13.00	26.00	.01	7.30	350.00	197.40	10.0
310	46.00	20.00	33	BDDDD	RL	S 18	4.00	30.00	2.00	.1	.01	64.00	106.00	40.00	28.00	1.00	.08	6.90	695.00	491.30	9.0
311	46.00	20.00	24	DBBBC	RL	S 310	4.00	29.00	6.00	.1	.01	31.00	55.00	33.00	6.00	1.00	1.18	7.40	430.00	343.10	8.0
315	47.00	20.00	30	CDDDB	RL	S 26	3.00	14.00	20.00	.1	.01	120.00	119.00	44.00	47.00	3.00	.24	7.20	820.00	470.10	8.0

Note: Below detection limit values are recorded as .1 for As, Cu, Ni, Pb, SO<sub>4</sub> and K and as .01 for Fe and Zn.

#### APPENDIX KEY

##### 1/4 Sec.

A = NE $\frac{1}{4}$   
 B = NW $\frac{1}{4}$   
 C = SW $\frac{1}{4}$   
 D = SE $\frac{1}{4}$

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##### Rock Type

<u>File Symbol</u>	<u>Formation</u>	<u>Map Symbols</u> (Plates 1-12)
AG	Archean Gneisses & Granites	gs, gr, gu, hm, mcgn
ML	Mille Lacs Group/Denham Formation	mlu, dfg
G	Glen Township Formation	gtc, gtm
RL	Rabbit Lake/Thomson Formations	ru, tgs
I	Iron Formations	EIF, rif, tf
MA	Mahnomen Formation	ma
MV	Mid-Proterozoic Mafic Volcanic Rocks	mif, mlb, rfm
S	Keweenawan Sandstones	fs, hs
K	Keweenawan Volcanics	mu, ap, cm, r

##### Till Type

<u>File Symbol</u>	<u>Lobe</u>	<u>Map Symbols</u> (Plates 1-12)
S	Superior Lobe	smg, sme, scg, scs, sla, slc, sne, so
D	Des Moines Lobe	dce, dcg, do
R	Rainy Lobe	rse, rsg, ro
W	Wadena Lobe	wag
T	Terrace Deposits	td