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GRAND JUNCTION OFFICE

PRODUCTION EVALUATION DIVISION

GEOCHEMICAL AND GEOPHYSICAL RECONNAISSANCE IN NORTHERN PENINSULA MICHIGAN AND NORTHEASTERN WISCONSIN

By

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and

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(Grand Junction, Colorado)

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Ross L. Kinnaman
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ABSTRACT

600 H_2O spls

About six hundred water samples were collected from streams and subsurface sources during a reconnaissance study for uranium in an area of approximately 7,000 square miles comprising parts of northeastern Wisconsin and northern Peninsula of Michigan. Analyses were made for uranium and total conductivity was determined on all samples. Most samples were also analyzed for bicarbonate and sulfate ion and supporting analyses were run on selected solid samples from the geologic and hydrologic environment.

The purpose of the study was to evaluate geochemical methods of exploration for uranium in a geologic environment similar to that of the Algoma Mining District near Blind River, Ontario, and to ascertain areas of favorability for more detailed investigation in the future.

Preliminary experiments indicated the feasibility of hydrogeochemical methods for detection of uranium introduced into surface waters by small, low grade ore deposits. The results of the areal water sampling in Michigan and Wisconsin on the basis of two samples per township were treated statistically to obtain cut-off values for parameters used in differentiating anomalies from background values in water samples. Parameters of significance to these samples are the uranium content and total conductivity.

Several drainage areas in Michigan and Wisconsin were sampled which contained anomalous amounts of uranium, ranging from about 0.8 to 10.4 ppb (parts per billion) U_3O_8. The background value for U_3O_8 in waters ranges from less than 0.1 to slightly greater than 0.5 ppb. The lowest values are found in Michigan streams flowing over Archean greenstones and schists.

mpl

Anomaly parameters [U] & conduct.

[U] contents to be expected

backgrd [U] H_2O for area

geol areas w/ higher values

Higher values are found in streams draining Huronian metasediments or post-Huronian granitic rocks. Waters in northeastern Wisconsin have higher background values than those in Michigan, and anomalies are somewhat less pronounced. The maximum uranium content of sampled Wisconsin streams is 2.8 ppb, probably derived from granitic rocks of Archean age.

U max.

concl

The data indicate that hydrogeochemical studies are of value for delineating areas of favorability in the search for uranium in northeastern Wisconsin and northern peninsula of Michigan, and should be useful to evaluate other areas whose surface drainage contains dissolved solids representative of the rock materials within the drainage system.

GEOCHEMICAL AND GEOPHYSICAL RECONNAISSANCE IN NORTHERN PENINSULA MICHIGAN AND NORTHEASTERN WISCONSIN

INTRODUCTION

The 1957 field program of the Geophysics and Geochemistry Branch was outlined as a project to determine the applicability of a combined geophysical-geochemical investigation as a means of evaluating the uranium resources in the Precambrian metasedimentary and igneous complex of a part of the Lake Superior Region.

Location

The area of study is in the central and western portions of the Northern Peninsula of Michigan and a contiguous portion of northeastern Wisconsin. A few townships in the southwestern Ontario on the north shore of Lake Huron were also investigated and are indicated by hachure on Figure 1. The area within the U.S. lies between latitudes 45° 15' 00" and 46° 52' 30" N. and longitudes 87° 30' 00" and 90° 07' 30" W., and occupies an area of about 6500 square miles.

The shape of the area is broadly outlined by known Precambrian bedrock occurrences as shown in Figure 2. The area includes all of Iron, Dickinson, and parts of Marquette, Barage, Houghton, Ontonagon, and Gogebic Counties of Michigan, and all of Florence and Forest Counties and parts of Marinette, Langlade and Oconto Counties of Wisconsin.

Accessibility

Major towns include Marquette, Ishpeming, Ironwood, Iron Mountain, and Crystal Falls, Michigan and Florence and Niagara, Wisconsin. All are accessible by highways or railroads. Marquette, Ishpeming and Iron Mountain are scheduled stops for North Central Airlines flights from

Chicago. Airport facilities are available at most larger towns and a few landing strips are usable in other areas.

Originally the entire area was heavily forested with virgin pine and hardwood trees, but much of these timber stands were removed by 1910. In their place has developed a thick "bush" of second growth maple, and other deciduous trees, and small stands of pine.

Much of the area is accessible only by four-wheel drive vehicles over logging trails or abandoned railroad grades, and a considerable portion can be entered only on foot. The numerous streams, swamps, bridge and road disrepair, rough terrain and thick "bush" seriously hamper access to many areas by means other than walking.

Climate

The area is characterized by a severe winter regimen with abundant snowfall and below-zero temperatures. Summer weather is moderate with daily high temperatures ranging in the 80 and 90's. The average annual precipitation for northern Michigan and northeastern Wisconsin is slightly annual ppt over 30 inches. Summer showers are common and give an average precipitation total of about 12 inches for the period May through September. Owing to the moderating influence of the Great Lakes, and the high latitude, the spring season is so retarded that field work cannot be started until late May. However, the fall frosts are delayed permitting field work through October.

Topography

The area comprising northeastern Wisconsin and Northern Peninsula of Michigan is a topographic highland and headwater drainage area. Its principal topographic features are the easterly trending Lake Superior basin and the marginal highlands to the south representing the northern flank of the Wisconsin high. Most of the ridges and valleys in these adjacent land areas lie parallel to the axis of the Lake Superior syncline and are due to erosion of parallel trending folds and faults produced by deformation along the major east-west structural axis.

The topography has been modified by numerous periods of glacial activity with a resultant leveling and rounding of ridges, deepening of some valleys and general masking of bedrock under varying thickness of glacial drift.

The highest point in the Michigan study area is Summit Mountain (about 1870 feet above sea level), 3 miles south of Negaunee. The lowest point is on the shore of Lake Superior whose mean elevation is 602 feet. In the Wisconsin portion the maximum altitude is about 1950 feet near Crandon, Forest County from which point the land surface slopes eastward to an elevation of about 750 feet near Crivitz.

Drainage

The area is part of the Lake Superior highland the runoff of which is tributary to the St. Lawrence drainage system. All the stream systems discharge their contents into Lake Superior or Lake Michigan. The largest is the Menominee River which with the Brule River forms part of the boundary between Michigan and Wisconsin, and drains approximately 3200 square miles of the area into Lake Michigan. The smaller remaining east-flowing streams drain a combined area of about 1400 square miles in Michigan and Wisconsin. About 2500 square miles of the Michigan highlands are drained by streams of varying size that discharge into Lake Superior.

The numerous lakes in the area owe their existance to former glacial conditions and are of two main types; those retained by morainal dams and those occupying kettles or other depressions.

Swamps cover a large part of the area and, in part, may indicate the position of former lakes that have been partially filled with vegetable debris so that their contents are bog-like accumulation of muck and peat with varying mixtures of inorganic materials. These areas in many instances are now cedar, tamarack or spruce swamps, interspersed in meadowlike expanses of sedge grass and other hydrophytic plants. Multitudinous channelways thread these areas and provide varying degrees of discharge for the water depending on the season and precipitation. Channel depth and width ranges from less than an inch to several feet.

As a whole, the areal drainage is very imperfect. The numerous lakes, swamps, waterfalls, and rapids are features of an immature drainage.

BACKGROUND INFORMATION

Land Status

Much of the land in the upper Peninsula and northeastern Wisconsin, with the exception of larger river valleys and along certain parts of Lake Superior, is devoted to timber and mining operations. Agricultural effort is limited to the valley flats along major streams and small areas near larger towns.

National forests and public domain are limited to a few townships having little value to the major industries. For the most part, large mining and lumber companies own or control vast holdings throughout

land ownership

the Michigan-Wisconsin area. A few private sportsman clubs have leased considerable acreage for exclusive use of members and to these areas access is difficult.

Mining

The western part of the upper Peninsula of Michigan and adjacent areas in northern Wisconsin have a long history of mining. Copper was reported to be present on the Keweenaw Peninsula by early explorers and missionaries as early as 1636, but it was over 200 years before these occurrences were successfully exploited. Iron ore was discovered in 1844 in the Marquette Range and by 1856 regular shipments were initiated thru the newly opened St. Marys River Ship Canal (Sault Ste. Marie Locks) connecting Lake Superior with the lower lakes. Production of iron in the Menominee Range began in 1872, followed by the Gogebic Range in the western part in 1884. Although many of the maringal mines have closed, production of both copper and iron ore has continued to the present time.

Although small amounts of sulfide minerals are common in the region sulfide ore bodies are rare. A few deposits are known in the Dead River Basin of Marquette County but ore grade sulfides have never been produced in quantity. A small amount of gold was produced in Marquette County, Michigan between 1882 and 1900 but operations ceased at the turn of the century.

Map Coverage

Topographic map coverage of the Upper Peninsula and northeastern Wisconsin has been extended and improved by the U.S. Geological Survey since about 1950 so that most of the area is now mapped on 7-1/2 and 15 minute quadrangles. Plainmetric, 15 minute quadrangle sheets prepared from air photos of northeastern Wisconsin constitute the recent coverage of that area. Base maps on a scale of 1 to 500,000 are available for both states and indicate the general drainage.

The Centennial geologic map of the Northern Peninsula of Michigan at a scale of 1 to 500,000 published in 1936 by the Department of Conservation is the latest comprehensive geologic coverage in the Michigan portion of the area. Numerous detailed maps, generally of specific mining areas, appear in the literature and these together with maps prepared by U.S. Geological Survey provide reasonably complete coverage for the area.

Adequate geologic maps of northeastern Wisconsin are limited to that portion of the Menominee iron district which has been mapped by the U.S. Geological Survey. The general geologic map for the state of Wisconsin (1911) is available but differentiates the bedrock geology only in a general way.

Maps of Pleistocene deposits of the western margin of Lake Michigan are available in recent geologic publications.

NATURE OF INVESTIGATION

Purpose

A region in northern Michigan and northeastern Wisconsin, adjacent to the southwestern margin of the Canadian Precambrian shield, was selected as a test area for the evaluation of geochemical and geophysical methods of uranium exploration in a complex metasediment environment.

basis or reason for selection of area

The principal reason for the selection of the area was the similarity of stratigraphy and sedimentary features of Precambrian (Huronian) sediments with those of the Blind River district, located approximately 200 miles east in Ontario, Canada. Uranium was discovered there in a quartz pebble

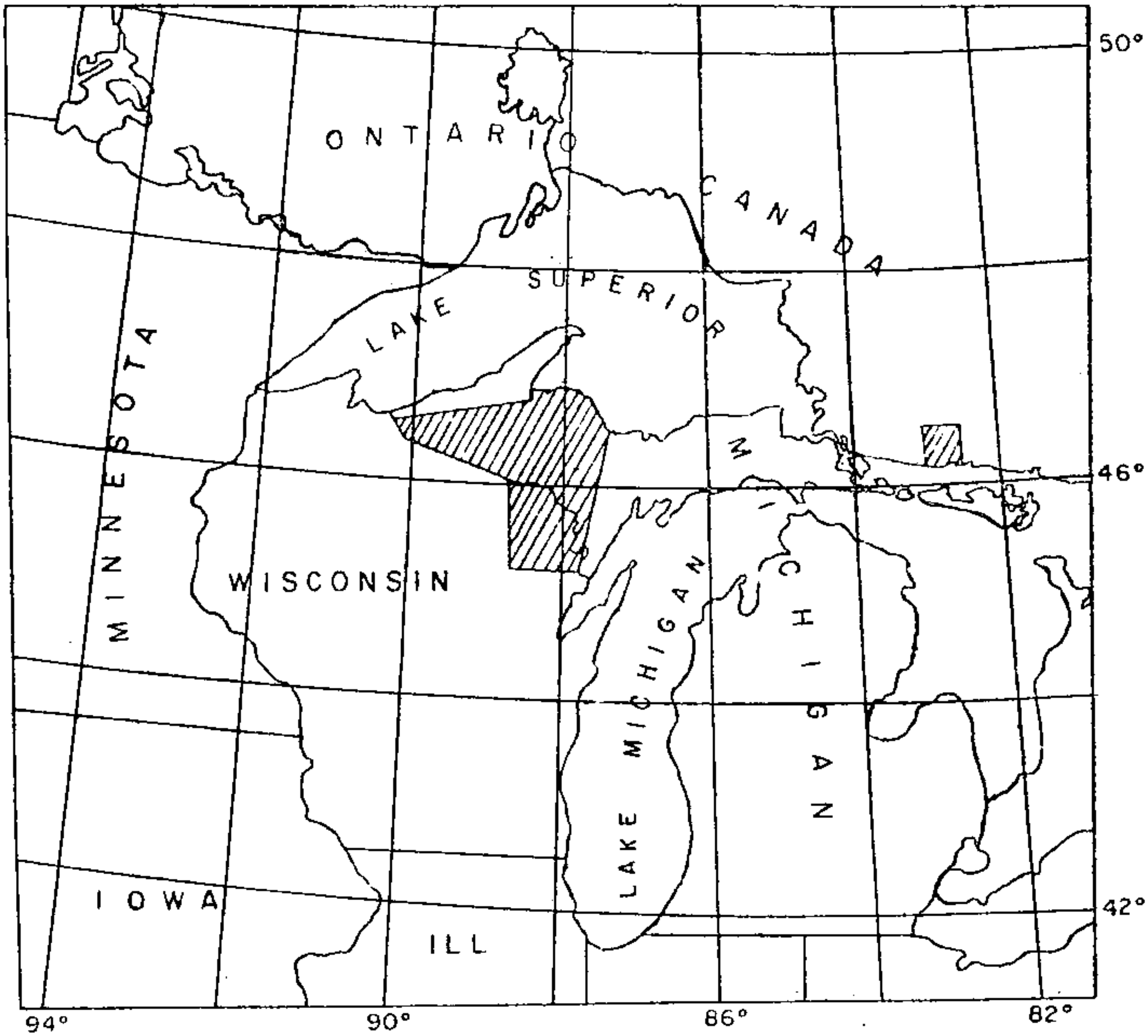

Figure 1. Index map of Lake Superior region

Matinenda fm

conglomerate phase of the Mississagi quartzite (Lower Huronian Bruce series) in 1953, and by 1957 the area had a reserve estimated variously between 100,000,000 and 300,000,000 tons of 0.10 to 0.17 percent ore.

cf Robertson (1962)

Preliminary Evaluation

A preliminary reconnaissance of Marquette, Baraga, Dickinson and Iron Counties, Michigan was made in May 1957, and some experimental tests were made on natural waters and various rock types of the area. As a result, it was determined that a hydrogeochemical evaluation would be the most economical and effective reconnaissance tool applicable to this area. Inasmuch as no large, uranium mineral occurrences were known, and only scattered radioactive anomalies were known from previous U.S. Geological Survey (1950) and Atomic Energy Commission (1956) airborne radiometric surveys, ground geophysical methods were not attempted.

It was believed that if sufficient interest in geophysical exploration was warranted, a series of tests over known uranium-bearing metasediments in the Blind River district of Canada would prove useful to establish the value of electromagnetic, self-potential and other techniques for the Michigan-Wisconsin area. Accordingly, arrangements were made with private operators in Canada to permit such tests as necessary to be performed at two properties in the Blind River district. The results of these experiments are discussed in a following section Geophysical Studies in Canada.

Field Methods

As a result of the preliminary reconnaissance it was decided that a base camp for field operations could be established on the Dead River 11 road miles northeast of Ishpeming, Marquette County, Michigan.

The field work on which this report is based was done between June 1, 1957 and October 15, 1957. From the first base camp near Ishpeming most of the northern Peninsula was sampled by two-man teams using Jeep transportation. About August 10, the base camp was moved to Iron Mountain, Michigan from which sampling of the remainder of Michigan and northeastern Wisconsin was completed by October 15.

Approximately 4716 square miles in the Upper Peninsula of Michigan and 2535 square miles in adjacent parts of northeastern Wisconsin were investigated by reconnaissance geochemical methods. Local areas for detailed geochemical and/or geophysical study were suggested by results of the field study and these were examined in somewhat greater detail as time permitted.

ACKNOWLEDGEMENTS

Appreciation is expressed to the staff of the Ishpeming Sub Office, U.S. Atomic Energy Commission, for field assistance during the hydrogeochemical reconnaissance program. Especial thanks are due L. P. Barrett for many and varied contributions relative to the geology of the entire area.

The writers are grateful to the staff of the Iron Mountain field office, U.S. Geological Survey, for maps and other information relative to the Menominee Range.

Thanks are extended the Rio Tinto Mining Company and especially to the staffs at the Algom Uranium Mine, Lts. and the Pronto Uranium Mines, Ltd., for many courtesies tendered Branch personnel during the geophysical tests in the Blind River District, Ontario.

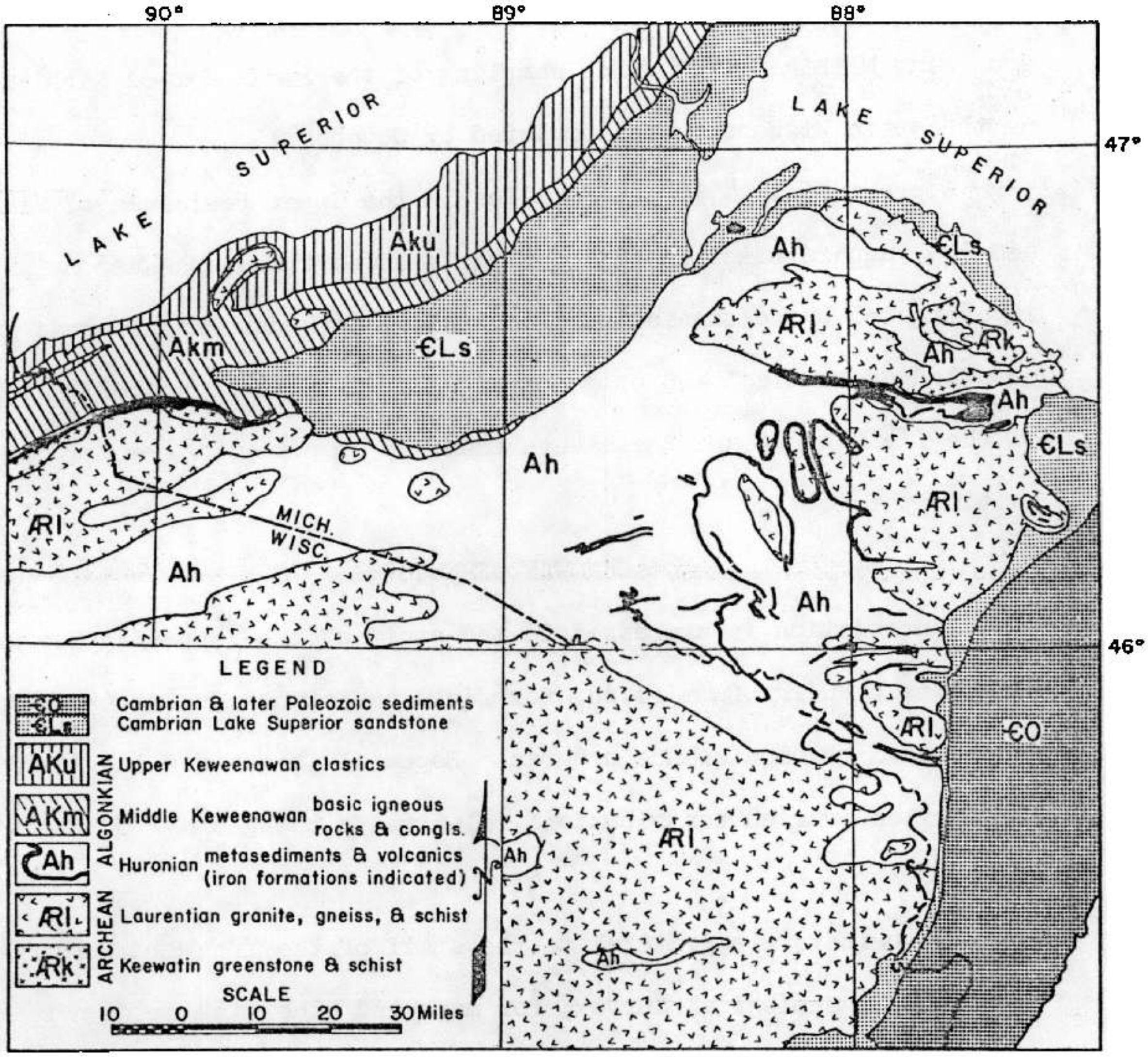

Figure 2.

Geologic map of Northern Peninsula of Michigan and northeastern Wisconsin

GEOLOGY

General

A knowledge of the geology of the area is necessary to provide a framework on which an evaluation of any uranium anomalies can be based.

The investigated area comprises a portion of a broad area known as the Lake Superior Region located on the southern margin of the Canadian shield. In this marginal setting is represented one of the thickest and most varied Precambrian successions known in North America. The Precambrian rocks here are represented by several thousand feet of sediments, at least four major unconformities, and three periods of extensive mountain building and plutonic intrusion. Not all parts of this sequence are everywhere present but their general development is clearly suggested throughout the Precambrian of the southern Canadian shield.

glacial cover

Glacial deposits of varying thickness are present over much of the region, and hence only the general features of bedrock geology are known outside the mining districts.

Bedrock Geology

Bedrock geology is best known in the east-west trending iron ranges of Michigan and northeastern Wisconsin, and in isolated east trending outcrops in Langlade and Oconto Counties, Wisconsin. In the area investigated are rocks of both igneous and sedimentary origin which in many places have been intensely affected by metamorphism.

The oldest rocks are greenstone schists and metasediments of the Keewatin series and intrusive granites, gneiss, and syenite of the Lauretian series (Plate I). These two series comprise the Basement complex of

Archean age. An extensive unconformity separates this complex from the overlying Huronian series in all parts of the Lake Superior region.

The Huronian series is divided into three subordinate series called the Lower, Middle and Upper Huronian. The Lower Huronian consists of quartzite, dolomite and slate; the Middle Huronian is composed of quartzite, slate and iron formation, with schist locally comprising the basal members in Wisconsin; and the Upper Huronian is composed of quartzite (locally missing), a great but unknown thickness of graywacke, slate (with thin iron members), and volcanic rocks. All these formations show various effects of metamorphism and many are locally intruded by basic dikes and sills.

Above the Huronian in northern Michigan are Keweenawan basic intrusive rocks, and a thick series of non-fossiliferous clastics. This clastic series is absent in Wisconsin and is present only along the northwestern part of the Northern Peninsula of Michigan. In the Marquette and Menominee districts the only representatives of the Keeweenawan are olivine diabase dikes.

Nearly flat-lying Cambrian and Ordovician sedimentary rocks are present on the eastern and northern margins of the investigated area, and generally mark the areal limits of the present work. Small outliers of Cambrian Lake Superior sandstone are present throughout the eastern extremities of the Marquette and Menominee ranges.

Unconsolidated Deposits

Overlaying the consolidated beds and covering a great part of the region are Pleistocene glacial deposits of variable thicknesses and numerous areas of Recent post-glacial sediment.

A. Glacial

The debris of glacial origin consists of till, outwash, and lacustrine deposits. The most common till in the Upper Peninsula contains much sand and fine gravel with occasional large boulders. Clay-rich tills are relatively rare. The Wisconsin till is composed largely of medium grained sand. The Wisconsin sediments and those adjacent in Michigan probably were derived from areas east of their present location. Their small grain size and carbonate content seem to indicate a source in Paleozoic clastic and limestones which are present on the west and northwest flanks of Michigan Basin.

Outwash deposits are characterized by fairly clean sand and gravel with relatively little fines. The terrane formed by the deposits is usually a flat, uninteresting plain, but it may contain kettles which are now occupied by small lakes or bogs. The light soil developed on outwash deposits supports only jackpine and small shrubs, giving the local name "jackpine plains" to these areas.

The last type of glacial deposits present are lacustrine and consist of flat-lying clays formed in glacial lakes. In the area of this report they occur only along the margin of Lake Superior.

B. Post-Glacial

Post-glacial deposits are those which formed after the ice had finally retreated, and include paludal, lake and alluvial deposits. Of these the paludal (swamp and bog) deposits are of greatest interest in the present study. Probably every tributary stream in the area originates in or flows through a paludal environment in its upper reaches. Swamps and bogs thus cover a considerable part of the surface area although individual deposits are of limited size. Such deposits consist mainly of gravel, sand silt, muck and peat localized along present drainage systems. Peaty organic deposits dominately are found along the small, ill-defined streams which drain marshy areas, and are frequently only a few inches to a few feet thick. They commonly overlie coarse, clean clastic beds of unknown thickness.

Further discussion of the sequence and distribution of surficial deposits is reserved for specific areas where hydrogeochemical studies were carried out.

C. Glacial History

The entire Lake Superior region was subjected to glacial activity by the advance of two or more ice lobes from centers in the Canadian shield during Pleistocene time. The earliest ice sheet is believed to have penetrated the area from the northeast, spreading from the Keewatin center located west of Hudson Bay. Little evidence of its history remains and the extent of its advance is not definitely known. The latest ice advance, called the Wisconsin stage, left varied deposits, and erosional features over the entire area of the Upper Peninsula and northeastern Wisconsin. In general, the direction of ice movement as deduced from striae recorded on bedrock, and alignment of deeper lake basins and drumlins, was from the north or northeast. The major source of the ice probably was the Labrador center east of Hudson Bay.

The principal effect of glacial activity on topography seems to have been a leveling of the land surface by filling of depressions. The resistant nature of much of the crystalline bedrock and its trend normal to ice movement resulted in bossing of the ledges and protection of the less resistant beds. Although knowledge of thickness of the glacial deposits is incomplete, the maximum known thickness if 400 feet near Conover, Wisconsin (L. P. Barrett, personal communication). Bedrock is exposed at the surface in much of Barage, Marquette and Dickinson Counties, Michigan, but in northern Wisconsin the prevalence of glacial material masks all but the more rugged bedrock areas.

CORRELATION

The stratigraphic succession in the iron mining districts of Michigan and northern Wisconsin is fairly well established, as it is in the Algoma District of Ontario. However, considerable uncertainty exists regarding the correlation between these areas. Likewise, the correlative equivalents of the Precambrian rocks outside the mining districts in northern Wisconsin and Michigan are incompletely known.

A generalized geologic correlation chart indicating the character of rock units of three distinctive areas in the Michigan-Wisconsin region is presented in Plate 1 as adapted from Leith et al (1935).

STRUCTURE

The major structural elements of the investigated portion of the Lake Superior region are the Lake Superior syncline to the north and the Wisconsin arch to the south. Imposed upon these features are the generally east-trending iron ranges and numerous re-entrant structures and minor uplifts such as the Republic Trough, Felch Trough and Amasa Oval. The iron ranges consist of faulted synclinoriums involving Huronian metasediments. In the Marquette and Menominee districts, Huronian beds are bounded by Archean rocks, whereas in the Gogebic range one side is in contact with Keweenawan lavas and the south margin lies unconformably on the Archean.

The alignment and orientation of structures in the iron districts indicate that intensive north-south forces compressed the areal mass of Huronian sediments, probably as much as one half in the Menominee range according to Bayley (1904, p. 498). There also appears to have been a strong compression in an approximately east-west direction which produced a pitch in the earlier folds and developed a complicated fracture system in the competent rocks.

A number of domal uplifts in Iron County and re-entrants in the Republic area of Marquette County have axes trending north to northwest. The largest domal feature, the Amasa Oval, plunges to the southeast (Gair and Wier, 1956, p. 15), and may represent a vertical fulcrum about which complex compressive forces acted.

Faults, many of which are several miles in length and have displacement of 1,000 feet or more, are common in the iron mining district. Most are normal faults which parallel structural trends and are believed by local geologists to have been in part responsible for accumulation of many high grade ore bodies. High angle oblique normal faults and numerous cross-cutting faults are mapped in the Michigan area. Probably many other faults of considerable magnitude are present but unmapped.

Further discussion of local structural features and details of general geology is reserved for specific areas discussed under Detailed Areal Studies.

GEOCHEMICAL PROGRAM

The geochemical program was divided into two phases: (1) Reconnaissance studies, and (2) Detail studies. Reconnaissance studies were limited for the most part to the detection of uranium content of waters and rocks. In areas of particular interest a more detailed hydrogeochemical sampling program was used and in some cases soil samples were collected for analysis. A method for interpreting the geochemical data based on a statistical analysis of the data was studied and the results of the study are included in this discussion.

Definition of Terms

By common usage geochemical prospecting includes any method of mineral exploration based on systematic measurement of one or more chemical properties of a naturally occurring material such as rock, soil, stream sediment vegetation or water. If the natural material studied consists of water, either surface or ground water, the method is referred to more specifically as a hydrogeochemical method. The chemical property measured in hydrogeochemical method is commonly the trace element content of some element or group of ions in the water; in the case of the present investigation, uranium is the element sought, and associated parameters of the solvent such as pH, conductivity and alkalinity were commonly determined.

The measurements are made on water samples for the purpose of establishing the presence of a geochemical "anomaly" which represents an area or areas where the chemical pattern indicates an increased favorability for the occurrence of uranium in the vicinity of earth materials traversed by or leached with natural waters. Such anomalies can be recognized only by contrast with the "background" concentration

of the element or ions in the media. Following accepted practice, "background" as used in the present study, represents the normal abundance of uranium in waters where its abundance has been neither enhanced nor impoverished by mineralizing solutions or artifical contamination.

Background values can show considerable variation as a result of differing chemical and physical processes inherent in the natural materials and environment. The average value of background concentration of uranium in natural waters in the United States reported by Fix (1956) is about 0.1 part per billion (ppb). In uraniferous areas of the United States the average uranium background in water is 0.8 ppb but higher average values up to several ppb may exist in restricted areas. Such variations may be due to effects of the local environment but more probably reflect a source of material in the area containing greater than average amounts of uranium.

Sampling and Analytical Procedures

All water samples were collected in polyethylene bottles. Duplicate pint samples were taken to avoid errors of contamination and permit an independent check on chemical analyses. The temperature and pH of the waters were measured in the field. Other analyses were made in a trailer which had been converted into a chemical laboratory. (Appendix I). Determinations made in the laboratory were (1) Uranium, (2) Bicarbonate, (3) Sulfate and (4) Conductivity. Some water samples were analyzed for Ca^{++}, Mg^{++}, Na^{+}, K^{+}, and Fe^{+++} in the Denver Laboratory. Rock samples from outcrops encountered in the course of the water sampling program were collected; soil and sediment samples were taken from selected areas. All solid samples were shipped to the Geophysical and Geochemical Branch laboratories in Denver for analysis.

Reconnaissance water samples were collected on a density pattern of two samples per township. This sampling density made it possible to cover a large area without allowing the analytical requirements to become excessive. Those streams which appeared to contain abnormal amounts of uranium were selected for detailed studies, which involved additional sampling of the entire drainage system upstream from the suspected anomalies.

The pH of the water samples was measured in the field with a Beckman 18C pocket pH meter. The conductivity of water samples was measured with an Industrial Instrument, Inc. Conductivity Bridge, Model RC 16B 1. Two methods were used to determine sulfate: A titration procedure described by Fritz and Yamamura (1955) and a conductimetric procedure described by Polsky and Betz (1947). Uranium was analyzed fluorimetrically using Ostles' (1954) procedure for concentrating uranium. This procedure has been modified to decrease the operation time required to complete an analysis. Bicarbonate determinations were made by titrating with standard sulfuric acid using a Beckman automatic titrator. Details of these methods and the modification of Ostles' procedure are given in Appendix I.

Orientation Studies

Preliminary orientation experiments are essential to all geochemical exploration projects in order to determine which method offers the best possibilities for locating the target. Samples should be collected from areas of known uranium occurrences and from areas of normal uranium distribution. In the case of anticipated hydrogeochemical reconnaissance, the major objective is to determine whether or not uranium can be detected in the waters and what contrast exists in the uranium content of water from the two areas. In addition to suggesting the best method of attack orientation studies are useful for determining the most effective and efficient sampling pattern.

Three localities in Michigan in which small uranium deposits are known were selected for orientation studies: Huron River; Plumbago Creek; and Green Creek.

Huron River (Skanee Quadrangle)

Small quantities of uranium and copper minerals were discovered in 1949 along the east branch of the Huron River, in Sec. 1, T. 51 N., R. 30 W., Baraga County, Michigan. Pitchblende and secondary minerals occur as very small discontinuous stringers and pods in calcite and quartz cementing the breccia within a low-angle shear zone exposed in the small gorge cut by black, locally carbonaceous slates of the upper Huronian Michigamme slate. A geologic sketch map and schematic cross-section are given by Vickers (1955a).

Surficial cover in the area is thin owing to the rugged character of the bedrock, but where present it consists mainly of morainic lake washed clays.

The locality was examined early in the summer of 1957 and several small, radioactive zones were found with a portable scintillation detector. One of these lay at the lip of a small cascade in the stream bed, and gave a radiometric reading (uncalibrated) of approximately .20 mr/hr.

Nine water samples were collected in the Huron River area, six of which were from the main stream and three from tributaries. Only two of these samples contained detectable amounts of uranium. One sample, collected 50 feet downstream from the known radioactive zone, contained 0.40 parts per billion* (ppb) U_3O_8. Water further downstream was found

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* One part per billion equals 10^{-9} grams per gram.

to contain less than 0.05 ppb U_3O_8. The other sample containing uranium (0.20 ppb U_3O_8) was collected downstream below a second small radioactive zone.

All samples were found to have a low conductivity (ca. 60 micromhos). The uranium to conductivity ratio (see page 30) for the sample containing uranium is 660.

Green Creek (Ishpeming Quadrangle)

An occurrence of metatorbernite and bassetite and associated copper minerals was reported by Vickers (1955b) in altered carbonaceous and quartzose slate of probable upper Huronian age. The occurrence is located in N-1/2, Sec. 19, T. 46 N., R. 26 W. Marquette County, Michigan, in a small inlier of Huronian metasediments between the Gwinn iron district to the southeast, and the Marquette iron district to the northwest.

Green Creek, a small, southeast flowing tributary to the Middle Branch of the Escanaba River traverses the southern margin of the Huronian inlier-Archean granite contact. The predominate surficial cover consists of glaciofluvial outwash sands and gravels.

A sample from Green Creek downstream from the prospect contained 0.40 ppb U_3O_8 with the U/K ratio equal to 667. Five hundred yards further downstream the uranium concentration was down to 0.25 ppb but downstream 4-1/2 miles no additional decrease was detected.

It was concluded from these preliminary experiments that uranium can be detected in surface waters from areas of low grade uranium deposits. There is a rapid decrease or "fadeout" in the uranium content of the water downstream which makes the detection of anomalies impossible as distance is increased beyond a few hundred yards. These decreases are caused by either dilution or loss of uranium from the waters by such processes as adsorption and coprecipitation.

The background values for uranium in waters in this areas are extremely low (ca. 0.20 ppb). This fact indicated the need for additional quality data on the waters, such as bicarbonate and conductivity, which could be used to normalize the waters and facilitate the differentiation of normal and anomalous waters.

Plumbago Creek (Herman Quadrangle)

Minute crystals of metatorbernite occur in closely spaced slickenside surfaces of a kaolinized diabase dike that cuts graphitic upper Huronian Michigamme slate in central Baraga County, Michigan. The altered dike, which is exposed only in an abandoned graphite quarry along the boundary between Sections 9 and 16, T. 49 N., R. 33 W., has a thickness of about 4 feet, and an exposed length of about 240 feet. Pyrite is present in both the dike and adjacent host rock as small veinlets, fracture fillings and disseminated crystals. Vickers (1955c) described the area, and reported that the slate contained .003-.004 percent uranium and approximately 30 percent carbon. Channel samples of the dike contained from 0.005 to 0.037 percent uranium, with the higher values found at the floor of the quarry.

Plumbago Creek is a small stream that heads about 0.3 miles above the quarry and is partially impounded by waste rock from the quarrying operation.

Six water samples were collected from streams within a two mile radius from the graphite quarry. Plumbago Creek, samples 650 feet from the quarry, was found to contain 0.65 ppb U_3O_8. The U/K ratio for this

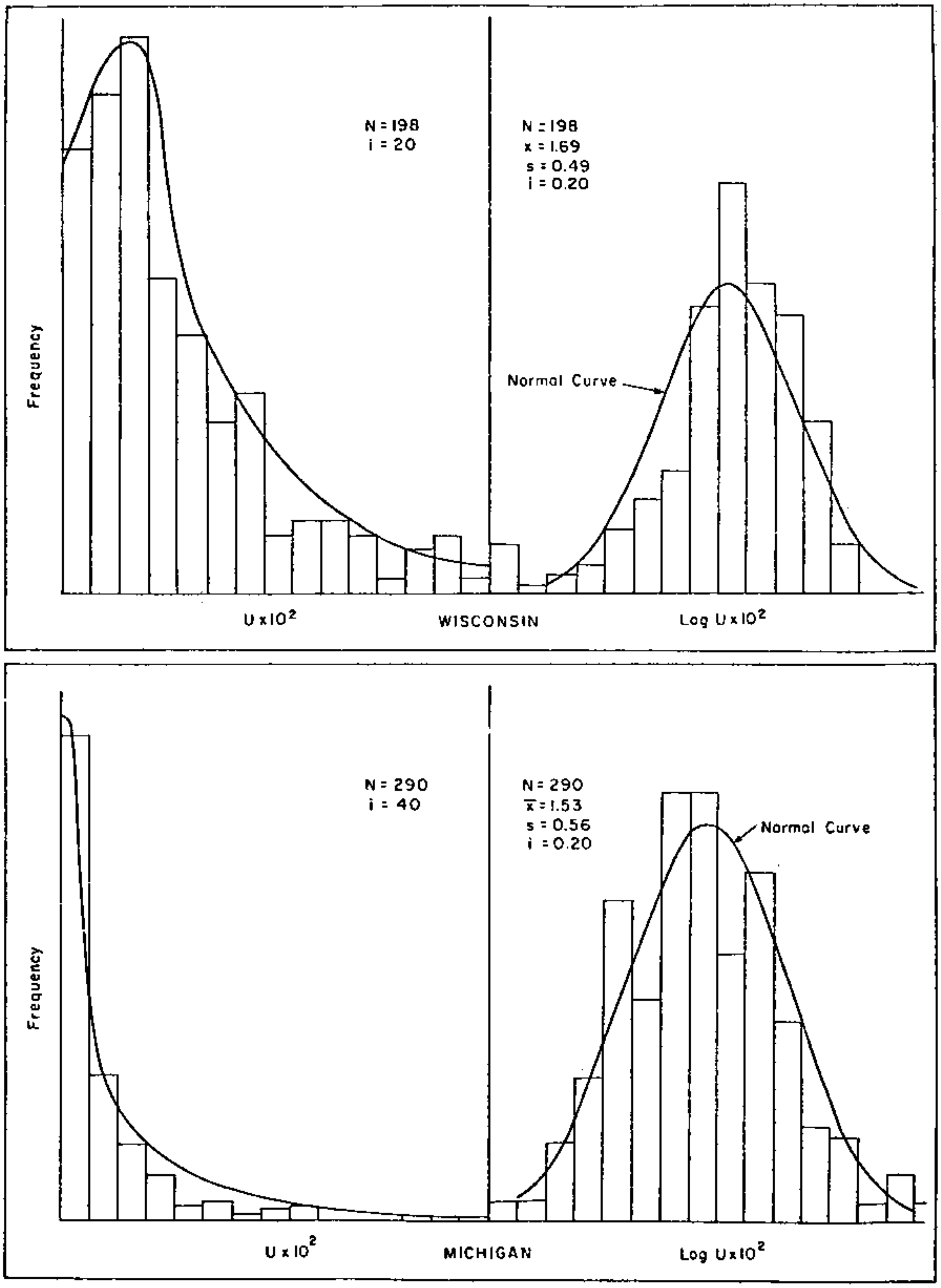

Figure 3. Frequency distribution of uranium for waters from northeastern Wisconsin and northern peninsula of Michigan

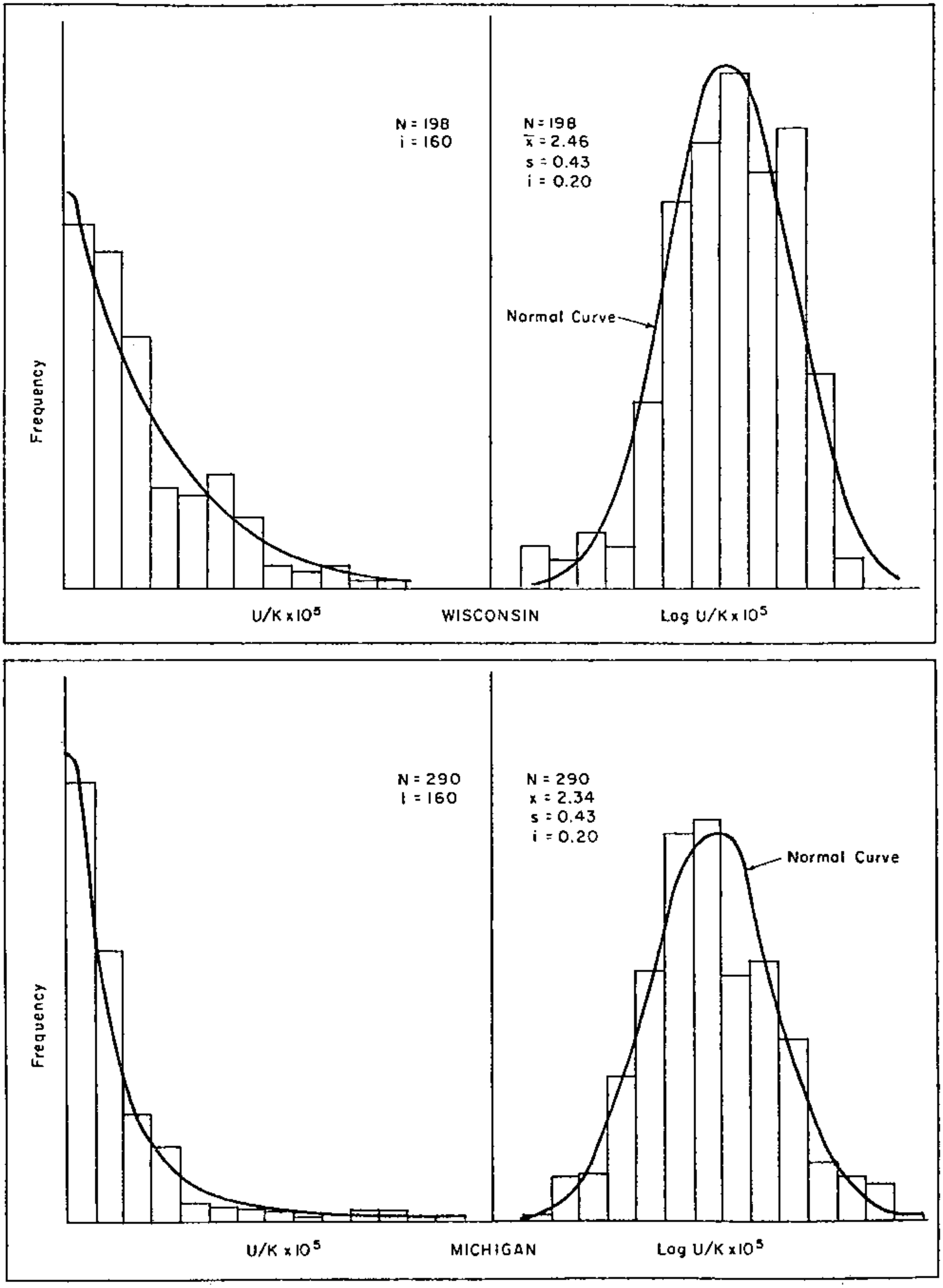

Figure 4. Frequency distribution of ratio (uranium/conductivity for waters from northeastern Wisconsin and northern peninsula of Michigan

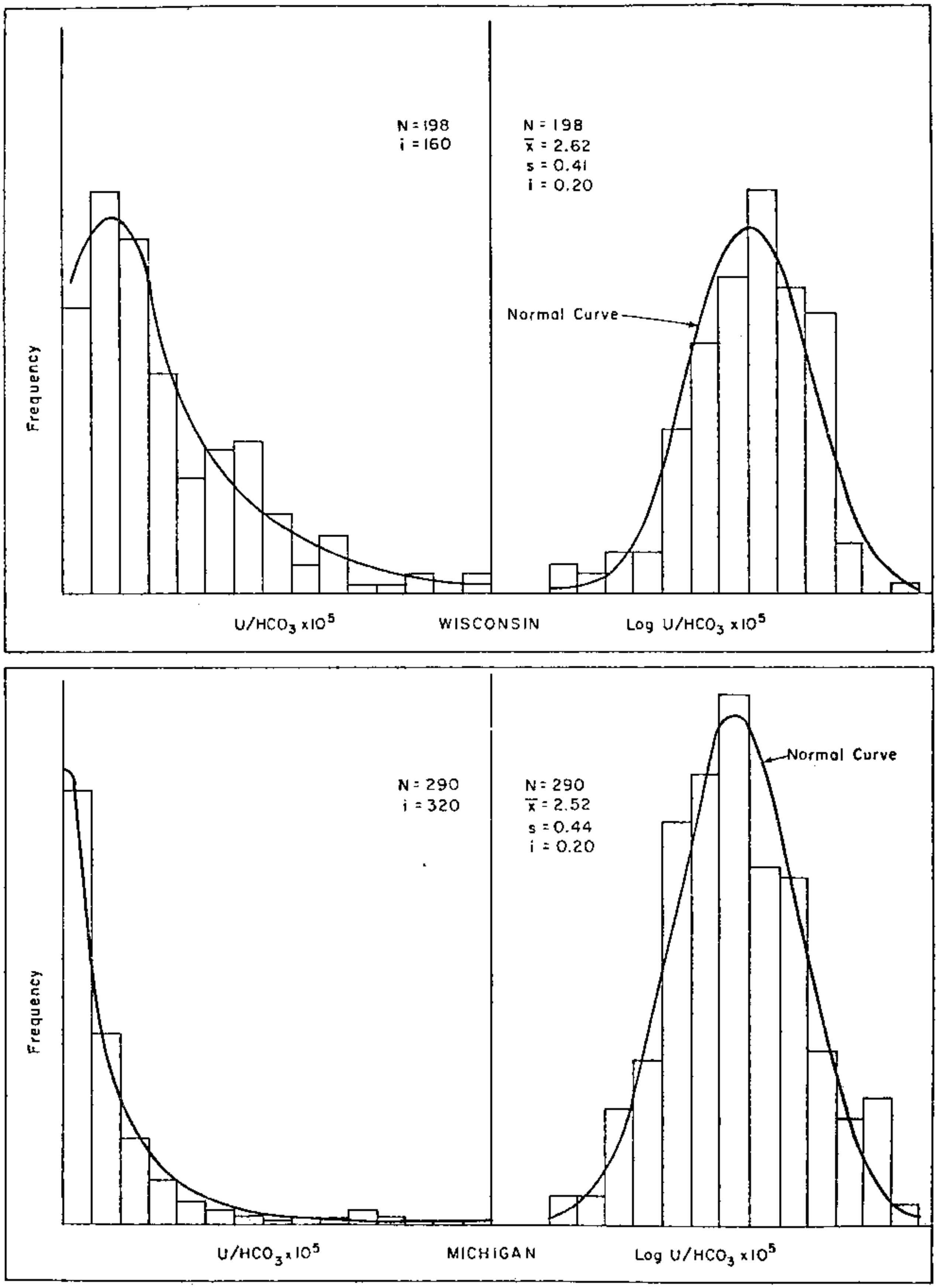

Figure 5. Frequency distribution of ratio (uranium/bicarbonate) for waters from northeastern Wisconsin and northern peninsula of Michigan

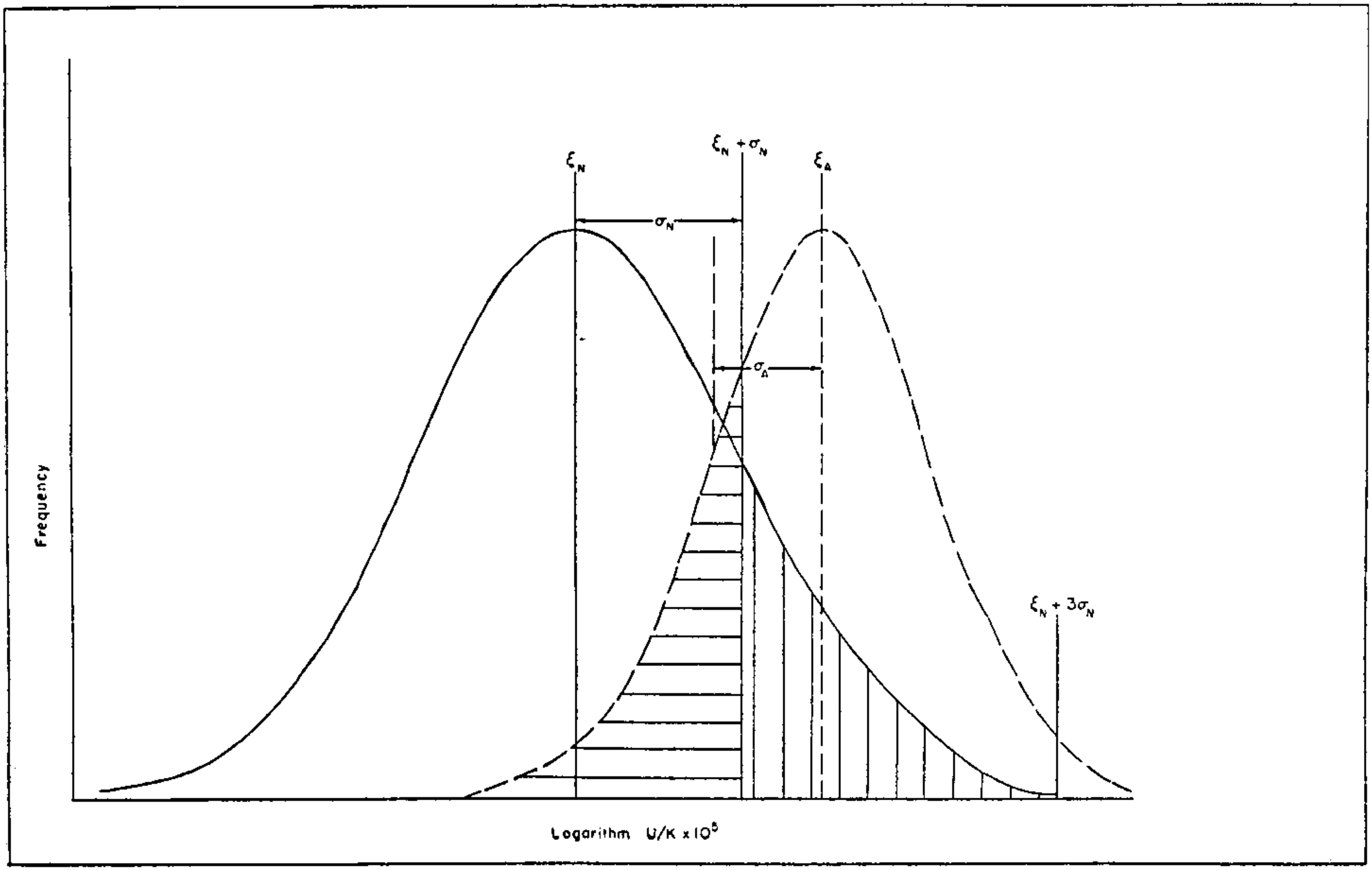

Figure 6. Log normal distribution curves for normal and anomalous waters from Mt. Spokane area, Washington

sample if 867. The remaining samples from this area contained on the average 0.17 ppb U_3O_8 with an average U/K ratio of 163.

Statistical Analysis of Data

The locations for all reconnaissance water samples are given in Plate 2. The distribution of the analytical data for the samples for Michigan and Wisconsin waters are shown in Figures 3, 4, and 5. It can be seen that the distribution of all the data are skewed. This type of distribution is usually encountered when dealing with geochemical data. Ahrens (1954) has shown that geochemical data will follow a log normal distribution to a good approximation. As can be seen in Figures 3, 4, and 5, the geochemical data for Michigan and Wisconsin waters approximate a log normal distribution.

Figure 4 shows the distribution of the ratio U/K x 10^5. Concerning the significance of this quantity, it is known that the conductivity of water is a fairly good measure of the amount of total dissolved solids in the water. Consequently the ratio U/K is a measure of the uranium concentration in the total dissolved solids. The normal range of uranium concentration in waters is usually from .05 to 2 ppb whereas the dissolved solids are present in amounts ranging from 50 to 300 ppm (parts per million)* The dissolved materials in the waters are derived from rocks and soils which contain from 0.1 to 20 parts per million of uranium. Waters coming in contact with large concentrations of uranium minerals will take up larger amounts of uranium but no unusual increase in the totals dissolved solids would be expected. This will result in an increase in the U/K ratio of the water. An increase in the uranium concentration with a

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* One part per million equals 10^{-6} grams per gram.

corresponding increase in the total dissolved solids would only indicate more efficient leaching of the rocks and soil by the solvent.

The value of the ratio U/K of the waters will depend upon the concentration of uranium in the rocks and soil and the ease with which the uranium can be leached by the water. Since many different rock types and soil types are present in the area, a wide variation of this quantity for the normal waters is to be expected. Reference to Figure 4 readily confirms this fact. Since the distribution of the U/K ratio is log normal, the data can be treated statistically in order to pick out those waters which may not belong to the background pattern.

Determination of Anomalies

approach to interp.

If normal waters in a given area have U/K ratios which show a log normal distribution, it might be expected that anomalous waters in the area would have U/K ratios which show a different log normal distribution. In the following discussion it is assumed that U/K ratios for anomalous waters follow a log normal distribution.

Data for 56 water samples from the Mt. Spokane, Washington area have been analyzed statistically. (Illsley, 1957). The mean and standard deviation for the log normal distribution of U/K are $\overline{x} = 2.58$ and $\sigma = 0.56$. Ten of these waters are known to be anomalous. The parameters for the assumed log normal distribution of the U/K ratio for the anomalous waters are $\overline{x} = 3.50$ and $\sigma = 0.38$. Using these parameters the distribution curves for both waters have been constructed and are shown in Figure 6. It can be seen that the distribution curves overlap. There is a range of U/K ratios which could belong to either the normal or the anomalous waters. In the Mt. Spokane area at least it is not possible to distinguish with certainty between normal and anomalous waters. The few water samples from Michigan which might be considered anomalous fall into the normal distribution pattern for the general area.

All but one of the anomalous waters from Mt. Spokane area and all of the known anomalous waters from Michigan have U/K values greater than $\bar{x} + \sigma$ for the normal waters, i.e. U/K ratios greater than antilog 2.56 + .56 = 1300 for the Mt. Spokane waters and antilog 2.34 + 0.43 = 590 for the Michigan waters. On this basis cutoff values for U/K were chosen as 590 for the Michigan waters and 780 for the Wisconsin waters. A more detailed discussion of the determination of anomalies is given in Appendix II.

It should be emphasized that the one-sigma cutoff mentioned above is suitable for only a reconnaissance program. Not all of the waters prove to be anomalous. The procedure can only be used to select areas or stream systems which merit closer study.

Michigan Anomalies

Figure 4 is the histogram obtained using 290 water samples. This represents nearly all of the surface water samples collected in Michigan. The one-sigma cutoff includes all waters with U/K ratios greater than 590. Table 1 lists all surface water samples whose U/K ratios exceed the cutoff value.

Wisconsin Anomalies

Note

Waters from Wisconsin have a higher background than the Michigan waters. Table 2 lists those waters sampled whose U/K ratio exceeds the cutoff of 760.

Tables 1 and 2 present data for all anomalous samples obtained in the areas. More detailed discussions of these areas are presented in a later section. Data for the whole area of interest are presented in Plate 3.

Reconnaissance of Northern Peninsula of Michigan on a One Sample per Township Basis

In the preceding sections, results of a statistical analysis of hydrogeochemical data obtained in Michigan and Wisconsin are presented. These data were gathered for the most part on the basis of two samples per township. For reasons of economy in a reconnaissance program, no more samples should be collected than are needed to give good coverage to the area.

In order to study the possibility of using a smaller sampling density a total of 108 samples were chosen at random from the Northern peninsula of Michigan. The parameters for the log normal distribution of U/K for these 108 samples were $\overline{x} = 2.22$ and $\sigma = 0.36$. The one-sigma cutoff is antilog 2.58 or 380. Table 3 gives the areas which would have been selected for further study based on 108 samples.

Several of the important areas would have been detected if a less dense sampling pattern of the following streams* had been carried out.

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* Referenced to the quadrangle and where appropriate the stream is enclosed by parentheses.

MICHIGAN WATER SAMPLES WITH ANOMALOUS U/K RATIOS

TABLE 1

Quadrangle and Stream	Sample No.	U/K	U (ppb)
National Mines Schweitzer Cr.	170	660	1.0
" " Ely Creek	171	610	1.6
" "	199	1890	3.5
" "	200	990	3.3
" "	207	980	1.5
" "	208	1180	2.2
" "	209	2270	3.4
" "	210	3020	5.5
" "	211	1520	2.7
" "	212	1890	3.3
" "	214	2000	1.9
" "	215	2570	4.3
" "	216	1120	3.1
" "	217	1180	3.2
" "	218	1120	3.2
" "	219	1320	4.6
" "	279S	1410	.8
Republic Bruce Creek	128	690	.2
Herman Plumbago Creek	184	870	.7
Ishpeming Green Creek	30	580	.6
" " "	31	660	.4
Skanee Huron River	7	660	.4
Republic Flatrock Creek	59	710	1.1
" " "	146	660	1.1
" " "	147	680	1.3
" " "	148	580	1.1
" " "	149	620	1.2
" " "	150	680	1.5
Witch Lake Michigan River	72	790	1.5
" " "	109	810	1.5
" " "	78	830	1.3
" Smith Creek	113	710	1.4
Ned Lake Deer River	244	660	1.1
" " " "	245	810	1.0
Norway Sturgeon River (at dam)	331	1230	5.2
" Pine Creek	344	650	2.2
" " "	370	710	2.2
" " "	371	710	2.2
" " "	372	2100	6.4
" " "	374S	1120	3.2
" " "	376	2820	10.2
" " "	378S	2630	9.7
" " "	379	2820	9.4
" " "	381	810	2.8

WISCONSIN SURFACE WATER SAMPLES WITH ANOMALOUS U/K RATIO

TABLE 2

Quadrangle and Stream		Sample No.	U/K	U (ppb)
Florence	Lunds Creek	122	780	1.8
"	LaMontagne Creek	123	790	1.7
"	Halls Creek	124	1660	2.6
"	" "	125	1440	2.8
Goodman	Sidney Creek	150	930	2.0
"	" "	153	1070	2.3
"	Shinn's Creek	154	1230	2.4
"	MacIntyre Creek	155	910	2.0
"	" "	163	1290	2.2
"	North Br. Harvey Creek	72	780	1.4
"	" " "	157	1820	2.5
"	" " "	158	1050	1.4
"	Trib to " "	160	830	1.4
"	North Br. Harvey Creek	161	780	1.3
"	Trib to " "	162	890	1.6
"	" " "	167	870	1.3
"	" Camp Creek	168	850	1.3
Wabeno	Colburn Creek	96	1000	1.1
"	" "	178	1050	1.8
"	Mexico Creek	176	910	1.6
"	Trib to Mexico Creek	177	830	1.3
"	Otter Creek	98	780	1.4
"	Trib to Otter Creek	179	1260	2.1
"	" " "	180	1440	2.7
"	" " "	181	1290	2.4
"	Inlet to Indian Lake	182	1510	2.8
Thunder Mt.	No. Br. Eagle Creek	171	810	1.2
" "	Homestead Lake Outlet	172	1180	2.0
" "	Oconto River	86	870	0.7
" "	" "	187	810	1.3
" "	Lake John Outlet	188	1050	1.7
" "	Trib to North Branch Oconto River	189	780	1.3
" "	No. Br. Oconto River	190	810	1.4
" "	Forbes Creek	191	1120	2.0
" "	" "	192	980	1.8
" "	Forbes Creek	193	1050	1.9

They are: 1. Ned Lake (Deer River), 2. Ishpeming (Ely Creek), 3. Norway (Pine Creek), 4. Republic (Flatrock), 5. Witch Lake (Mitchigan River), 6. Ishpeming (Green Creek). Republic (Bruce Creek), Herman and Skanee would probably not have been found owing to the limited distances that uranium is carried by stream waters in these areas. Randville, Sunset Lake and Iron River were not detected as areas of interest on the basis of a two samples per township reconnaissance program. Of these three areas, only the Randville area has been detailed and shown to be insignificant.

It should be noted that the Skanee and Herman areas contain anomalous waters due to several small isolated uranium occurrences whose locations were already known. The distance that the surface waters carry uranium in these areas is very short, commonly only a few tenths of a mile. Consequently, only a detailed sampling program would be certain to find them.

note length of dispersion halo

In the case of the present reconnaissance program throughout Michigan and Wisconsin it is not likely that a sample density greater than two per township would have detected a significantly greater number of anomalous areas than were reported. A sample density of one sample per township will probably find most anomalous areas if care is taken to sample major tributaries to streams in the area. The choice of sampling density is dependent to some extent on the availability and completeness of geologic and hydrologic information.

Apl 2

URANIUM TO CONDUCTIVITY RATIO FOR SELECTED MICHIGAN SURFACE WATERS

TABLE 3

Quadrangle and Stream		Sample No.	U/K
Republic	Flatrock Creek	59	700
"	" "	60	490
Norway	Pine Creek	312	440
"	" "	323	440
"	Sturgeon River	320	540
Ned Lake	Deer River	244	670
" "	" "	245	810
Ishpeming	Schweitzer Creek	30	530
"	" "	166	430
"	Ely Creek	171	610
"	Green Creek	35	470
Champion	Middle Br. Escanaba River	163	520
"	Mulligan Creek	141	530
Witch Lake	Fence River	73	460
" "	" "	248	530
" "	East Creek	110	430
Randville	Badwater Creek	311	440
Sunset Lake	Paint River	244	390
" "	" "	308	540
Iron River	Sunset Creek	300	380

DETAILED STUDIES OF ANOMALIES IN NORTHERN PENINSULA OF MICHIGAN

The major drainage systems in an area of approximately 4700 square miles in northern Michigan were sampled on the basis of two samples per township for reconnaissance purposes. Approximately 400 samples were collected and analyzed for uranium, bicarbonate and sulfate, and measurements were made of pH and conductivity.

Detailed sampling was done for several drainage areas based on geochemical anomalies detected by the initial reconnaissance sampling. Supplementary geophysical studies were made in an area on Ely Creek in an attempt to locate the source of anomalous uranium in waters. The Buckroe area, which was not detected in the initial reconnaissance and is not included in Table 1, was studied briefly because of interest generated by the occurrence of anomalous uranium and U/K values in well water from a Cambrian sandstone.

Note anomaly Ess H_2O's

National Mine-West Branch Ely Creek (Ishpeming Quadrangle)

A. Geology and Drainage

Schweitzer Creek and its minor branches are southeast-flowing tributaries of the East Branch Escanaba River, which drain the highlands along the southern margin of the Marquette synclinorium. The course of Schweitzer Creek lies entirely within Archean granite, gneiss and greenstone schist that border the iron mining district to the south.

Ely Creek drains a small area of Huronian rocks immediately south of Ishpeming, flows southward through the community of National Mine and thence to a confluence with Green Creek. (See Figure 7). It's total

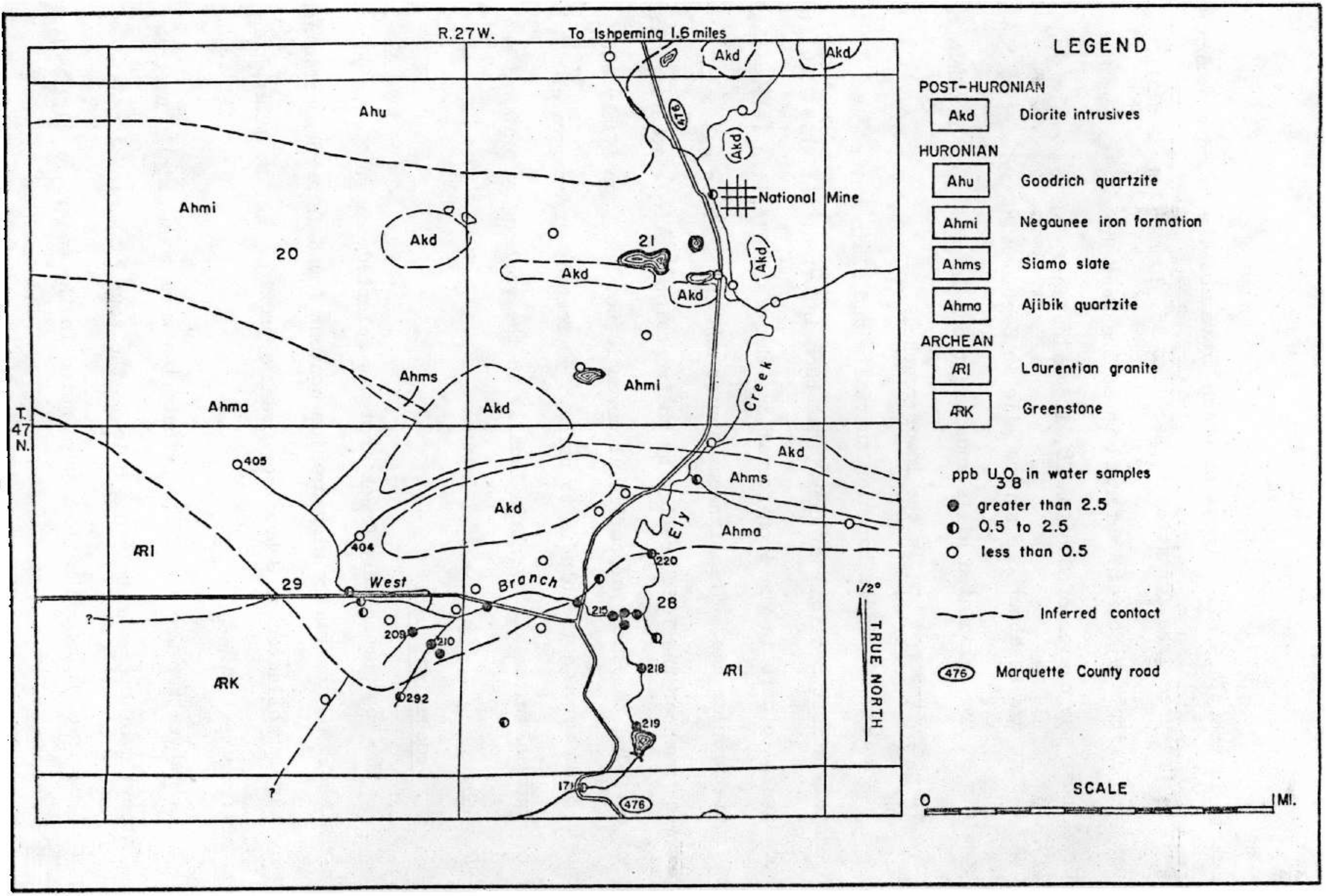

Figure 7. Sample location and geologic map, National Mine area, Marquette County, Michigan

length is about 4.5 miles, most of which traverses the broad southern belt of Negaunee iron formation in Sections 15, 16 and 21. A small, unmapped tributary, herein referred to as the West Branch, enters Ely Creek near the center of Section 28, 1.3 miles south of National Mine. This stream drains about one square mile in Sections 20, 28 and 29, which consists of low, glaciated hills and forest bog in the upper reaches, and an open sedge covered bog in the lower reaches.

A band of middle Huronian quartzite and slate which cuts arcuately across Sections 28 and 29 has been inferred. At this locality and several others in the iron formation, there are dioritic intrusives of post-Huronian age. This igneous series and the Archean basement provides much of the local relief by their resistance to weathering and erosion. The thickness of surficial cover is not known precisely but ranges from zero on the bluffs to perhaps 50 feet of stream gravel and finer outwash materials overlain locally in the valleys by peat and bog deposits.

B. Geochemical Data

The West Branch Ely Creek area was selected for further study on the basis of abnormally high uranium content found in a reconnaissance water sample collected on Schweitzer Creek approximately ten miles downstream from West Branch.

Schweitzer Creek and its tributaries were then sampled upstream at intervals of approximately one mile to the town of National Mine. Increasing uranium concentrations were noted in the waters of Ely Creek upstream to the West Branch but became abruptly lower above the West Branch confluence. Further sampling indicated that the apparent source of uranium was from a bog drained by West Branch in Sections 28 and 29. Samples 209, 210, 215, and 292 contained 3.43, 5.50, 4.30, and 1.51 ppm U_3O_8 respectively. The U/K ratio for these samples are 2270, 3020, 2560 and 1000.

anomalous H_2O's

Ten well water samples were collected in the immediate area of West Branch. Only two of these samples, both located adjacent to the bog were found to contain abnormally high amounts of uranium. None of the wells were in bedrock, and it can be assumed that most of the water was supplied from shallow (10-25 feet thick) surficial deposits.

At this point a geological investigation was carried out by AEC geologists from the Ishpeming Office to determine the nature of the bedrock of the area. The results of mapping are presented in Figure 7. It is noted that all water samples containing greater than 2.5 ppb uranium are concentrated near the inferred Archean granite - Ajibik quartzite contact.

A detailed soil sampling program was initiated. The results of this program are reported in the section entitled Uranium in Bog Soil.

C. Geophysical Investigations

In order to assist in evaluating the hydrogeochemical anomalies detected in the locale of the West Branch of Ely Creek (Section 29, T. 47 N., R. 27 W.), a series of geophysical investigations were made. The purpose of these investigations was:

1. To obtain information regarding the distribution of radioactive minerals in the surficial cover,
2. To relate the hydrogeochemical anomalies to a source of uranium, and
3. To determine the character and depth of the bedrock concealed by valley fill.

airborne survey

(a) Previous Reconnaissance Radiometric Work - Airborne radiometric surveys were made of the Ishpeming and adjacent quadrangles, including the local area of West Branch (Ely Creek), by the U.S. Geological Survey in 1955. No significant radiometric anomalies were detected over the Huronian or Archean rocks in the immediate vicinity of West Branch. The nearest airborne detected anomaly was located over Archean granite about 1.2 miles southeast of this area.

carborne survey

(b) Detailed Radiometric Investigations - A series of carborne radiometric traverses were made during the 1957 field season on all passable roads in the West Branch area using a sensitive recording scintillation counter. Several radiometric highs (1.5 to 2.0 times background) were detected adjacent to granitic outcrops a few hundred feet south of West Branch. Hand counter checks of these outcrops revealed small (1 to 3 feet diameter) pods of white, commonly bleached, feldspar-rich granite in which the radioactivity ranged from 6 to 10 times normal background value. All of the local high values were associated with granitic outcrops.

In an effort to localize more clearly the uranium which was detected in surface waters in the bog area, a 1400 foot long radiometric traverse was run parallel to the West Branch of Ely Creek in SE-1/4 Section 29. Two shorter radiometric traverses were run normal to the first. Hand scintillation counters were used to take readings of gamma ray intensity at 100 foot intervals along these traverses. Since the relative variation in these radiometric readings was less than the accuracy of the scintillation counters, none of the apparent anomalies were considered valid. Therefore it was concluded that radioactive minerals were quite uniformly distributed in the surficial cover in the bog area.

cover

(c) Electromagnetic Investigations - A series of parallel north-south electromagnetic traverses were run during the 1957 field season within the bog area of West Branch (SE-1/4 Section 29), and extending over the edges of the outcrops which surround the bog area. (See Figure 16) The electromagnetic equipment can detect material which has a high electrical conductivity compared to surrounding material, and which occurs within 200 feet of the surface. An example of material which can be detected by the electromagnetic method is rock which contains a high percentage of sulfide minerals. The age and geologic similarity of the rocks in this area with those of the Blind River uranium district of Ontario, Canada suggested the possibility that a zone of sulfide-bearing quartz-pebble conglomerate of lower or middle Huronian age might exist at some depth within the bog area and might be the source of the uranium which was detected by the hydrogeochemical assays. It was expected that the electromagnetic survey would detect such a unit if it existed within

200 feet of the surface. Since no electromagnetic anomalies were found in the bog area, it was decided to determine whether or not the equipment could detect the presence of such a unit (pyritiferous uranium-bearing quartz-pebble conglomerate) where it was know to exist in the Blind River mining district. The results of the electromagnetic tests in the Canadian locality are reported in a section entitled Geophysical Studies in Canada. The test results indicated that the concentration of pyrite in the quartz-pebble conglomerate in that area was too low to be detected by the electromagnetic equipment. It was concluded that the absence of electromagnetic anomalies in the West Branch area in Michigan did not preclude the existance of a unit of uranium-bearing quartz-pebble conglomerate similar to the Canadian ones studied.

note contrast & elec mag pyrite

(d) Self-Potential Investigations - A self-potential survey was run during the 1957 field season within the area shown in Figure 16. The equipment (porous cups, connecting cables, and a sensitive potentiometer) can detect self-potential anomalies which commonly result from vein type, high concentrations of sulfide minerals in rocks which occur in an enrivonment of differential oxidation. The objective of the self-potential survey was the same as that described under Electromagnetic Investigations above. Since no self-potential anomalies were found in the bog area, this method was also applied to the known Canadian deposits to obtain control information. The results of the Canadian tests indicated that the method was not effective in detecting the ore-body there. It was concluded that the absence of self-potential anomalies in the bog area

notes cond

in Michigan did not preclude the existence of a unit of pyritiferous uranium-bearing quartz-pebble conglomerate within the area covered by the self-potential survey.

(e) Magnetic Investigations - A series of parallel north-south magnetometer traverses were run during the 1957 field season within the West Branch bog area, and extending over the edges of outcrops which surround the bog. The magnetometer can detect differences in the magnetic susceptibility of rocks at considerable depths. Thus magnetometer surveys can be used to delineate the subsurface contact between two formations having different magnetic susceptibilities. Magnetometer surveys can also be used to estimate the depth of the basement rock if a magnetic susceptibility contrast exists between the basement rock and the overlying sediments and soil. Unfortunately, when magnetometer surveys were run in the West Branch area, it was found that the readings were severely affected by abundant erratic boulders of magnetic ferruginous slate which occurred in the glacial and alluvial cover. Since it was impossible to correct for this effect, it was also impossible to determine the character and depth of the bedrock within the bog area. The only definite conclusion which was drawn from the magnetometer survey was that a large mass of magnetic iron formation did not exist under the bog. If such a mass had existed, it could have been recognized because the resulting magnetic anomaly would have been much larger than the anomalies which resulted from the erratic boulders of ferruginous slate.

Bruce Creek Area (Republic Quadrangle)

A. Geology and Drainage

Bruce Creek is a small headwater tributary of the Middle Escanaba River, located in T. 46 and 47 N., R. 29 W., Marquette County, Michigan. Its length is about 6 miles, the upper 2/3 of which flows over spotty, till-covered "Republic granite" about 1 mile north of and parallel to the southeast-trending Republic trough.

The trough is occupied by Huronian sediments notably the Middle Huronian iron formation, the underlying Ajibik quartzite, and the overlying Michigamme slate. Lamey (1933) has reported contact metamorphic effects on the quartzite and iron member near Republic, and other structural features which suggest that the Republic granite is intrusive into Huronian beds.

The granite exposed along State Highway M-95 which crosses Bruce Creek north of Republic is dominately gray, coarsely granular and porphyritic. The feldspar phenocrysts are predominantly microcline, with lesser amounts of acid plagioclase. Quartz, biotite and miscovite are present although mica is not an abundant mineral. The abundance and identity of accessory minerals are not fully known although Lamey (ibid.) reported the presence of pyrite, pyrrhotite, chalcopyrite, magnetite, tourmaline, garnet, apatite, fluorite, zircon, and ilmenite in various samples of Republic granite. At Bruce Creek the granite is cut by large northwest-trending basic dikes, and some pegmatite veins. Throughout the area the granite shows abnormal radioactivity which has been noted in airborne surveys (Stead et.al., 1950) and various ground checks at the time of the present work.

B. Geochemical Data

A water sample collected from Bruce Creek at the bridge on Michigan Route 95 was found to contain 0.20 ppb U_3O_8. However, the conductivity of this sample was extremely low (29 micromhos) giving a U/K ratio of 690, which is greater than the statistical limits for normal waters.

Samples of the Republic granite were taken for laboratory study and the results which are discussed in a later section indicate that the rock contains sufficient leachable uranium to supply a source for surface waters.

Despite the low uranium concentration in the water a consideration of the geological geochemical environment and the U/K ratio for this sample suggests the need for additional water sampling along Bruce Creek.

Mitchigan River Area (Witch Lake Quadrangle)

A. Geology and Drainage

The Mitchigan River drains about 15 square miles of an elongated north-trending uplift in Precambrian rocks located in the eastern half of T. 46 N., R. 31 W., and the northeastern quarter of T. 45 N., R. 31 W., in Iron County, Michigan. (See Figure 8) The uplift comprises an inferred Archean core flanked by relatively steep dipping Middle Huronian beds including an iron formation. The bedrock is largely masked by Quaternary and Recent sediment, and the structure as shown on the Michigan Geologic Map (1936) has been recognized mainly by dipneedle surveys over the iron member.

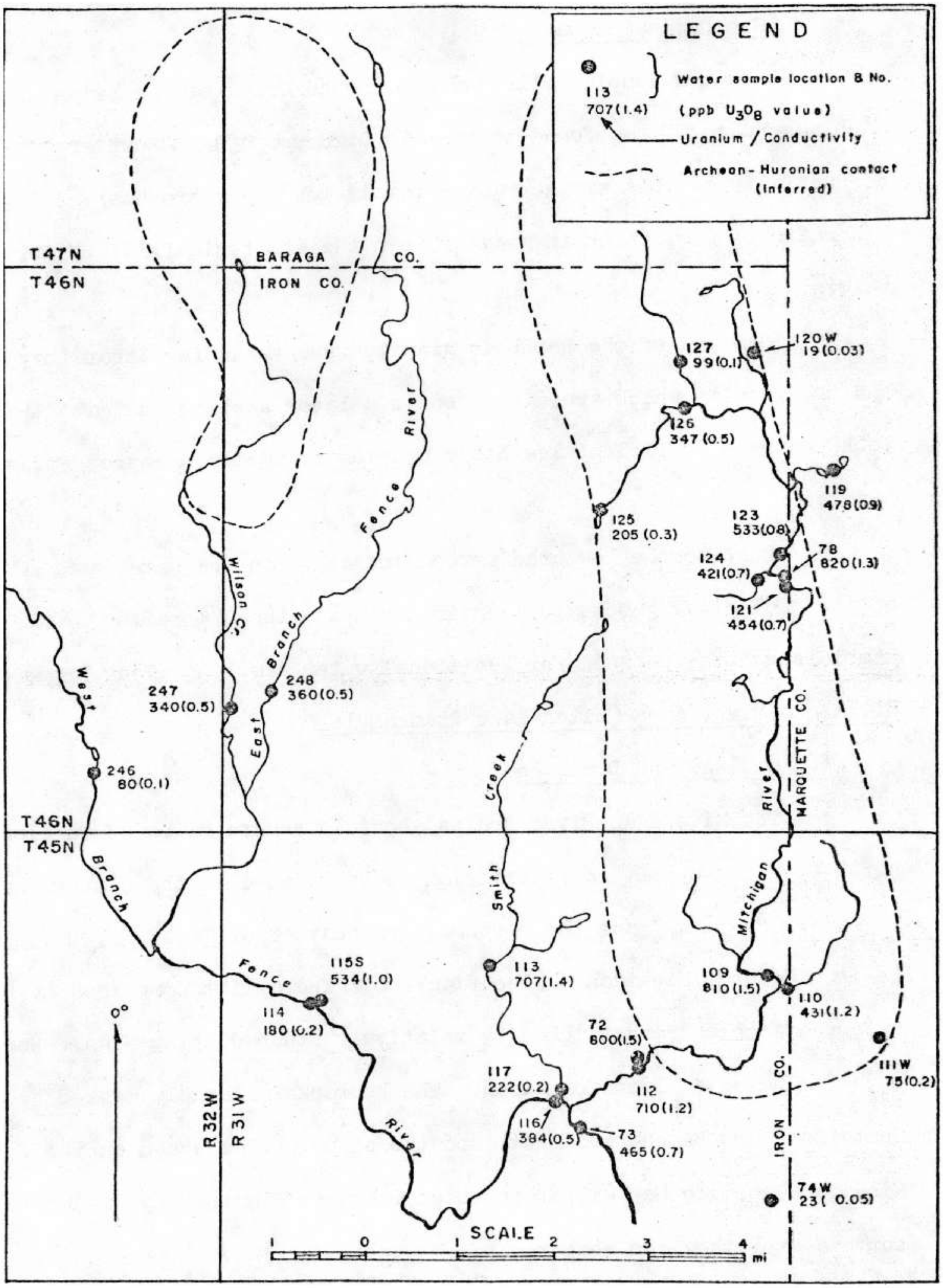

Figure 8. Water sample location map of Michigan and Fence River areas, Iron and Marquette counties, Michigan

The iron formation here is probably correlative with that in the Amasa Oval to the southwest, which Allen and Barrett (1915, p. 25-27) have correlated with the Negaunee iron formation of middle Huronian age in the Marquette district.

The river heads in a long, narrow swamp in SW-1/4, Sec. 14, T. 46 N., R. 31 W., which presumably lies near Huronian sediments on the western edge of the oval. It flows northeasterly across the Archean core to the eastern edge of Huronian beds, turns southward and runs parallel to the general metasedimentary contact for about 3 miles, then continues transversely over Archean rock to the southern margin of the structure where it crosses the obscured Huronian formations and discharges into the Fence River in the SE-1/4, Sec. 15, T. 45 N., R. 31 W.

The southwestern flank of the structure is drained by Smith Creek and data from this drainage are included below.

B. Geochemical Data

Ten water samples were collected from the Mitchigan River and its tributaries between its confluence with the Fence River and its headwaters in northeastern Iron County. Two samples were also taken from Smith Creek, 3 miles west of Mitchigan River.

The local background for uranium in water was determined to be 0.30 ppb U_3O_8. Seven samples from Mitchigan River and one from Smith Creek were found to contain uranium in amounts greater than twice background. However, normalizing these values by calculating the U/K ratios reveals that only two samples from the former and one from the latter are significant based on the limiting value for U/K of 590.

Although specific localization of uranium mineralization can not be established on the basis of the present work it may be worth noting that in general the U/K ratio and uranium concentrations continue at high levels and possibly increase with the downstream location of the samples. This is contrary to the carrying characteristics of surface waters which generally show a loss of uranium downstream through adsorption on organic and mineral debris and copreupitation by changes in solution pH, temperature or ionic concentration. The Mitchigan may be one of a few unique streams sampled in the Northern Peninsula of Michigan in that it appears to be acquiring uranium ions at a greater rate than losses are occurring. Possible sources are small unsampled tributary streams which cross the Huronian metasediments or which drain granite-rich till derived from the anomalously radioactive Republic granite. Additional detailed study would be necessary to establish the source or sources of uranium ions more precisely and to ascertain whether the uranium and U/K values remain consistently high in the unsampled portion of the river in the southern half of the structure.

Note unusual situation observed by Theme

note

anomalous stream

Deer River Area (Ned Lake Quadrangle)

A. Geology and Drainage

Deer River, a tributary of the Michigamme River system, drains the western and southern portions of the Amasa Oval in Twps. 44, 45, and 46 N., R. 32 W. Iron County, Michigan. The river heads in swamps located on Lower Huronian beds in the south half of T. 46 N., R. 32 W., but most of its length lies in till-covered metavolcanic rocks, slate and graywacke of the Hemlock formation which occupies a belt that completely surrounds the oval. Metarhyolites which are relatively rich in potash content have been reported near the base of this formation by Gair and Wier (1956). The other volcanics consist of greenstones and dark biotite, hornblends and epidote-bearing schists showing relict volcanic textures. Basic dikes intrude the Archean and Huronian rocks of the general area and a few quartz porphyry intrusives have been reported in the Kiernan quadrangle about 10 miles to the southeast. Gair and Weir (ibid) suggest the latter may be related to the acidic rocks of the Hemlock formation.

The ferruginous Fence River formation which overlies the Hemlock formation around the borders the oval is not crossed by the course of Deer River. Sandstone of Cambrian age was probably present in the area although its existence was not observed. However, boulders of a buff to red sandstone are present in the Kiernan Quadrangle at the southern end of the Amasa Oval (Gair and Wier, ibid). Glacial cover consists of moraines and outwash of varying thickness. That some of the material probably came from the area of Republic is shown by the presence of granite boulders whose lithologic and radioactive character closely resembles outcrops at Republic.

B. Geochemical Data

Two samples collected during the reconnaissance survey from Deer River contained 1.04 to 1.13 ppb U_3O_8 respectively. The U/K ratios for

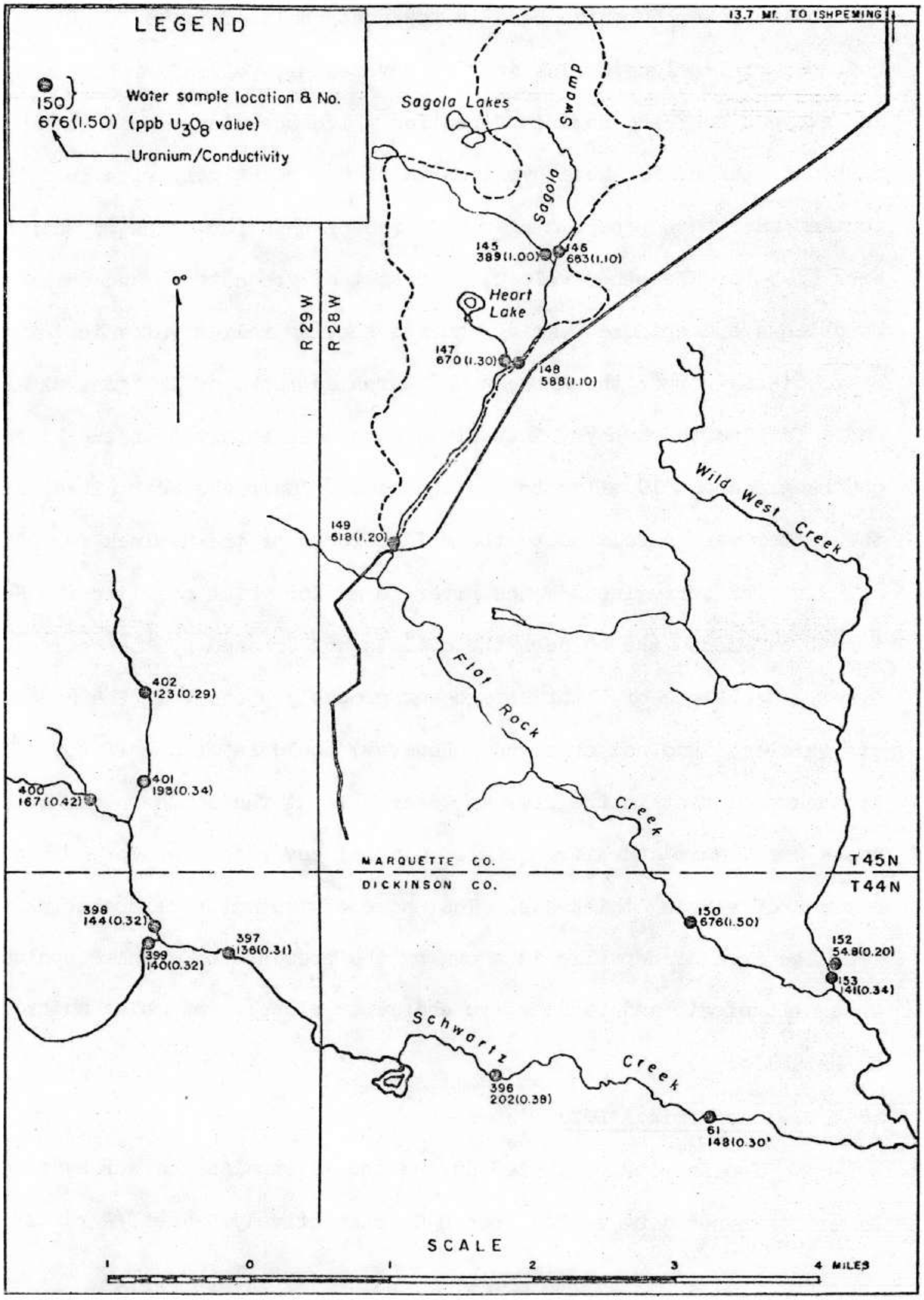

Figure 9. Water sample location map of Flat Rock–Schwartz Creek area, Marquette and Dickinson Counties, Michigan

these samples are 667 and 813, both of which are significant.

This area has had no detailed study. Additional geochemical work is needed before an evaluation of the area can be made.

Flat Rock Creek (Republic Quadrangle)

A. Geology and Drainage

Flat Rock Creek is a headwater tributary of West Branch Escanaba River and drains the Sagola swamp in Sections 5, 7, and 8, T. 45 N., R. 28 W., southern Marquette County, Michigan.

Surficial geology consists of moranies, glacial outwash, sandy till plains, and swamp deposits. Detail knowledge of the bedrock geology is limited but is indicated on the Michigan Centennial Geologic Map (1935) as granite. As a result of aerial and ground reconnaissance by the field party, several outcrops of massive, coarsely crystalline, locally porphyritic, gray granite were found along the creek in Sections 29, 30, 32 and 33. Radioactivity measurements of the granite outcrops averaged 0.012 mr/hr with highest values of 0.02 mr/hr noted at several locations. Several large, white pegmatitic dikes were observed from the air but were not accessible to ground study.

A brief, geologic study by Commission geologists of the Ishpeming Office revealed that in addition to the swamps, surficial materials in the northern 2/3 of T. 45 N., R. 28 W., consists mainly of sand with a few boulders of granite. Most of the southern third of the township is covered by sandy till in which there are many large boulders of granite. Soil background radioactivity in the area is about .003 mr/hr.

Radioactivity measurements of the large granitic boulders in place range from .006 to .015 mr/hr. It was estimated that at least 95 percent of the float in the area is coarsely crystalline, gray to pink granite which is abnormally radioactive. A few boulders of fine-grained, basic intrusive rock, and smaller cobbles of quartzite and dolomite were present. None of these was abnormally radioactive.

The swamp deposits occupy an elongate, south-trending plain which is dominantly forested with cedar, spruce, and lesser amounts of deciduous trees. Alders and other hydrophylic plants and shrubs are abundant along the watercourses. Small, treeless sedge covered areas are present only in Sections 8 and 19 near the creek. Thickness of the organic swamp deposits probably does not exceed a few feet inasmuch as a pit dug at the southern end of the swamp near county bridge in Section 19 exposed fine, stratified outwash sand and gravel at a depth of 18 inches.

The thickness of glacial cover ranges from nil at bedrock exposures along the creek to approximately 100 feet on the higher morainal ridges.

B. Geochemical Data

Sixteen stream water samples were taken from Flatrock Creek and its tributaries, Schwartz Creek and Wild West Creek. Only four of these samples, collected near the headwaters of Flatrock Creek in Sections 8 and 17, T. 45 N., R. 28 W., yielded both anomalous uranium concentrations and U/K ratios. (See Figure 9).

Localization of anomalies was established in upper drainage of stream in general area of Sagola Swamp. Possible sources of uranium cannot be determined because adequate geologic information of this area is not available. A geologic study of the highlands on the west side of Sagola Swamp where airborne radiometric highs were noted along the Range line common to R. 28 and 29W. would be useful in determining sources of uranium.

Pine Creek Area (Norway Quadrangle)

A. Geology and Drainage

Pine Creek is a major tributary to the Sturgeon River located in southern Dickinson County, Michigan. The stream follows a well-developed valley in lower Huronian bedrock, parallel to the Archean contact. The Geologic and sample location map (Figure 10) shows the bedrock geology as delineated by recent work by the U.S. Geological Survey (1957, Personal Communication). Nearly flat-lying outliers of Cambrian sandstone are shown as over print on bedrock geology.

The Archean granitic complex in the Pine Creek area is exposed as an elongate, northwest-trending, broken plateau about 15 miles in length. The rocks consist of weak to strongly foliated granite gneiss, containing locally more basic intrusions. Numerous pegmatite and quartz veins are present along the southern margin of the complex.

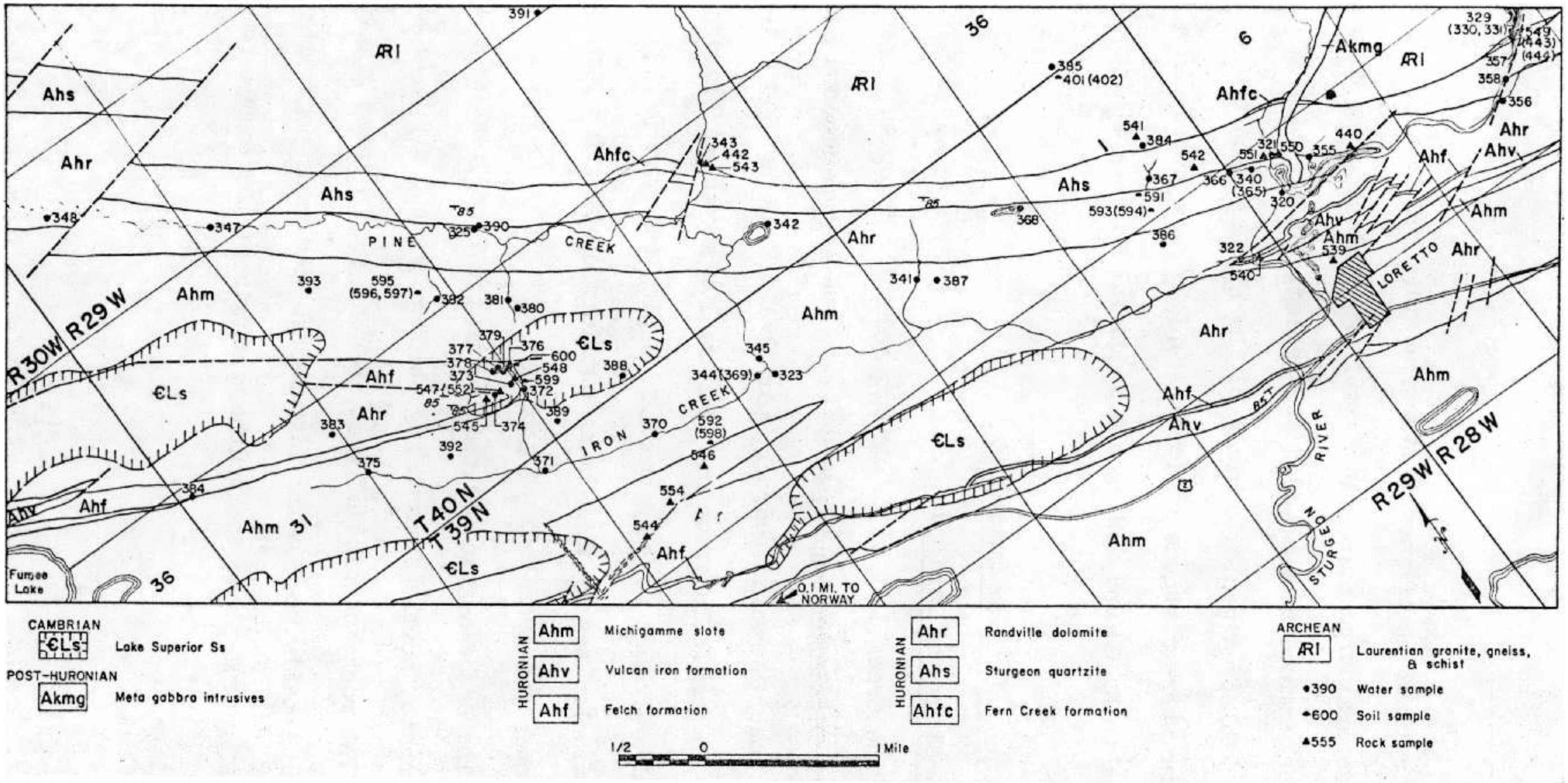

Figure 10. Sample location and geologic map of Pine Creek area, Dickinson County, Michigan

[illegible] gneiss

The contact of the Huronian with the granite gneiss is a highly tilted angular unconformity. Interposed between these two series at several localities are a basal conglomerate and argillite which Pettijohn (p. 397, 1943) has named the Fern Creek formation. The age of this formation is probably pre-Huronian.

Slight radioactivity was noted in a northeast trending shear zone that cuts this formation a few feet below the dam on the Sturgeon River in NE-1/4, Sec. 8, T. 39 N., R. 28 W. The shear zone contains sulfides and magnetite. Two samples (443 and 444) were analyzed and found to contain 0.89 and 0.44 ppm U_3O_8.

The Fern Creek formation is reported at four other localities along the Archean exposures; analysis of a composite sample of the formation at the Fern Creek area NE-1/4 Section 34, T. 40 N., R. 29 W. revealed no abnormal uranium content.

The overlying Huronian formations over which Pine Creek and Iron Creek flow are the Sturgeon quartzite, Randville dolomite, Felch formation and Michigamme slate.

The Sturgeon quartzite, unlike the other Huronian strata, is more resistant, and commonly forms a presistent, well-defined ridge which strikes about N. 40° W., and dips 80-85° southwest. The outcrop is displaced by several northeast trending faults along which the apparent movement of the northwestern block has been to the northeast.

No radioactivity was detected in the Sturgeon and chemical analysis for uranium indicated that only background amounts were present.

Exposures of Randville dolomite are rare and limited to small outcrops near Loretto and Iron Creek, north of Norway. All of these areas are structurally disturbed by faulting or intense folding. The formation consists of a series of beds in which dolomitic layers predominate. In the Iron Creek locality there are present also near the nose of the anticline in Section 32, T. 40 N., R. 29 W., dolomitic breccias, conglomerates, and cherty quartz breccias.

The cherty quartz breccias which crop out west of Iron Hill are found only at the top of the Randville (Bayley, p. 226, 1904). They are fine-grained vitreous, massive siliceous rock with gray, red or dark purple colors. The rock may be cut by anastomosing quartz veins, or it may be fractured and recemented by a mixture of fragmental and chemically deposited silica. Both processes produce breccias identical in appearance. They consist of sharply angular fragments of one color in a matrix of some other color, although the composition of matrix and fragments are essentially the same. Two samples of breccia were analyzed and found to contain 1.2 and 2.4 ppm U_3O_8.

Overlying the dolomite is a band of fine-grained mica schist which was named the Felch schist by Van Hise and Leith (p. 303, 1911). The age is probably middle Huronian. Recent mapping by the U.S. Geological Survey has indicated its presence in the Pine Creek area as indicated on the geologic map in Figure 10.

The Michigamme slate is poorly exposed in the area of interest along Iron Creek, but presumably consists of a thick series of black to gray, argillaceous and calcareous slates. No analyses for uranium were made on the formation in this locality.

B. Geochemical Data

Reconnaissance sampling of Pine Creek and the adjacent stretches of Sturgeon River indicated the presence of three possible anomalies. One of these was immediately eliminated after the apparent source material was located. Rocks at the base of the Sturgeon River dam were found to be radioactive and contained from 0.89 to 0.97 ppm U_3O_8.

A small tributary of Sturgeon River in the NW-1/4, NW-1/4, Section 7, T. 39 N., R. 28 W. was sampled at two locations. Additional sampling was not possible due to the lack of water in this small intermittent stream. The uppermost water sample had a uranium concentration of 1.75 ppb with the U/K ratio equal to 516. The results of analyses on stream sediment and sand samples, collected upstream from the water samples, are discussed in a later section.

Although several water samples from Pine Creek apparently contained anomalous amounts of uranium, i.e. greater than twice local background of 0.53 ppb, only one was found to have a possibly significant U/K ratio. The decision to investigate the area in more detail was governed more, however, by a comparison between this sample, 323 in the SW-1/4 SW-1/4, Section 2, T. 39 N., R. 29 W., and the next upstream sample, 345. The uranium concentration in Pine Creek dropped from 1.37 ppb to 0.62 ppb and the U/K ratio decreased proportionately. Attention was immediately focused on a tributary stream joining Pine Creek from the west between the two sample sites. This nameless tributary will be referred to as

Iron Creek because of its proximity to Iron Hill. Iron Creek originates in Section 31, T. 40 N., R. 29 W., passes through Section 32, where it is joined by a tributary flowing from the western base of Iron Hill, and continues through Sections 4 and 5, T. 39 N., R. 29 W., to the junction with Pine Creek in Section 3.

Four water samples were collected along Iron Creek at approximately one mile intervals. A fifth sample was collected from the north branch near Iron Hill. Sample locations are plotted on Figure 10. Although the uppermost sample on Iron Creek (375 in SE-1/4, NE-1/4, Section 31, T. 40 N., R. 29 W.) contained more than three times the local background amount of uranium, the major source of uranium is apparently the headwaters of the north branch in SE-1/4, NE-1/4 Section 32, T. 40 N., R. 29 W. Waters from three sources indicated by sample numbers 374S, 376S, and 378S were found to contain 3.20, 10.20, and 9.70 ppb U_3O_8 respectively.

The conductivity of all water samples collected from Iron Creek showed very little variation with a mean of 327 micromhos. The U/K ratios for the highest uranium-bearing waters give a mean of 2700, which is greater than the mean plus two standard deviations for the Michigan waters as a whole. These local increases in conductivity can be attributed to the measured increases in concentrations of calcium, magnesium, sulfate and bicarbonate.

The magnitude of the uranium concentration in the waters, however, indicates more than a general increase in total dissolved material. The source of the dissolved material must have an abnormally high concentration of leachable uranium. This source material, presumably rock in the area of uranium in water anomalies has not been located. Analyses of rock samples from the area showed no anomalous uranium concentrations and no radiometric anomalies were detected.

Sixteen well and spring water samples were collected in and around the Iron Hill area. Five samples were found to contain anomalous amounts of uranium. Three of these were from the area discussed above, one a spring flowing from the Cambrian basal conglomerate, one a well in the basement of the home of C. Treiber, and the third a water-filled prospect shaft on the same property as the well. The fourth anomalous sample (2.5 ppb U_3O_8) was taken from a well on the Olesky farm in the NW-1/4, NW-1/4, Section 31, T. 40 N., R. 29 W. The source of uranium in this 60 foot well, drilled in outwash sand and gravel, is not known. The remaining sample came from a deep (90 foot) drilled well in the Archean gneiss on the farm of Emil Johnson (SW-1/4, SE-1/4, Section 36, T. 41 N., R. 29 W.). The uranium concentration of this sample was 14.8 ppb U_3O_8, the highest value determined for any water sample collected in Michigan. Scattered radiometric anomalies have been detected in the surrounding areas (oral communication, E. P. Beroni).

C. Well Samples - Correlation with Formations

Twelve of the well and spring water samples were selected for general chemical analysis. In addition to the usual analyses, the concentrations of Ca, Mg, Na, K and Fe were determined. These samples were taken in areas underlain by the Randville dolomite, the Michigamme slate and the Felch formation. The results of the analyses indicate that waters from the Randville have the highest conductivity and the greatest amount of total dissolved solids, bicarbonate, sulfate, iron and sodium; the highest concentrations of calcium, magnesium and potassium were found in waters from areas of Michigamme slate; and the highest uranium concentration was found in waters apparently coming from the Felch formation.

Buckroe Area (Negaunee Quadrangle)

A. Geology and Drainage

The small community of Buckroe is located about 12 miles northwest of Marquette in Section 2, T. 49 N., R. 26 W., near the shore of Lake Superior.

Archean granite and greenstone from the mass of the rugged hills which parallel the lake shore from Marquette northward to Huron River. Along the shore the Archean is unconformably overlain by Lake Superior sandstone of Cambrian age in a band that extends inland from the beach for a distance of 1/4 to 3 miles.

Typical medium-bedded Lake Superior sandstone is exposed at Buckroe in a small wave-cut bluff as gently northeast-dipping, friable, reddish-brown sandstone and micaceous shales. The red sandstone is characteristically splotched with circular to elongate bleached zones 1/8 to several inches in diameter. A number of fractures which trend along the dip of the beds are strikingly outlined by gray, reduced zones whose widths are from a few inches to 18 inches. These features are present along the lake shore for a distance of 70 miles. Thin Pleistocene drift and soil obscure much of Cambrian sandstone above the shoreline.

The Garlic River and Big Garlic River are small streams that head in Archean greenstone and schist highlands a few miles north of the Dead River Basin in northern Marquette County. Their generally parallel eastward courses cross scattered drift on the rugged Archean schists and granite terrane in T. 49 N., R. 26 and 27 W. for a distance of about 7 miles. About one mile west of the lake shore, the streams cross the Archean-Cambrian contact, flowing thence over a sandy plain underlain by Lake Superior sandstone to their outlets on Lake Superior.

B. Geochemical Data

Five stream water samples collected in the immediate area of Buckroe were found to contain extremely low concentrations of uranium (< 0.05 ppb). Although these streams were sampled in the sandstone belt, the water sources are all to the southwest in the Archean basement complex.

Six water samples were collected from wells in the town of Buckroe within an area of about one half square mile. Four of these samples contained uranium in amounts greater than local background. Evaluation of the analytical data (U/HCO_3^- and U/K ratios) indicates that two samples containing 6.9 and 1.4 ppb U_3O_8 are probably anomalous.

The wells sampled are driven in the Lake Superior sandstone at depths between 14 and 110 feet. Seven samples of this sandstone were collected and analyzed for uranium. The mean uranium concentration was found to be 2.2 ppm with a maximum value of 5.2 ppm. The latter value was obtained with a sample of gray, micaceous sandstone collected near one of the wells which yielded water containing greater than background amounts of uranium. However, the bleached rock does not everywhere contain higher uranium values than the red material.

A portable scintillometer survey of the Cambrian sandstone at exposures along the beach near Buckroe and of recently excavated rock from a dug well located a few hundred yards west of the beach revealed very small, isolated radioactive anomalies in bleached zones containing trashy, micaceous sediments.

Subsurface water from the Cambrian sandstone near Buckroe contains larger amounts of uranium than are normally found in surface waters of the area north of the Marquette Mining District. The limited data suggests probable high uranium background for Cambrian sandstone, and possible occurrence of small anomalous areas associated with bleached zones.

DETAILED STUDIES OF ANOMALIES IN NORTHEASTERN WISCONSIN

The major drainage systems of northeastern Wisconsin were sampled on a two samples per township basis for reconnaissance purposes. One hundred and twenty water samples were collected as being representative samples of an area of approximately 2400 square miles.

The uranium, bicarbonate and sulfate concentrations of the samples were determined and the pH and conductivity was measured. The background uranium content of surface waters was determined to be 0.30 ppb. Statistical evaluation of the analytical results indicated the presence of four anomalous areas and eighty additional water samples were collected within these four areas.

Pine River-Popple River

A. Geology and Drainage

The Pine and Popple Rivers are east-flowing streams which drain an area mostly underlain by granitic rocks in northern Forest and western Florence Counties, Wisconsin. A section of Pine River crosses Precambrian sedimentary rocks on the southern edge of the Menominee iron range. Surficial cover consists of varying thickness of sandy till and occasional boulder till, with numerous swamp deposits along the stream courses.

B. Geochemical Data

Several hydrogeochemical anomalies were detected in the Pine River-Popple River drainage basin in the south half of the Florence quadrangle. Samples 37 and 38, collected from Woods Creek (see Figure 11) were found to contain amounts of uranium significantly higher than background. A source of the uranium-rich water is probably in the immediate vicinity of Sample 37 because additional samples collected upstream from this tributary contained lower uranium content. Samples collected along La Montagne Creek indicate two possible source areas; one near Sample 122 in headwaters of the tributary Lunds Creek, and the other along La Montagne Creek between Samples 123 and 126. Sample 125 on Halls Creek containing 2.8 ppb uranium represented the largest hydrogeochemical value for uranium detected in Wisconsin. The location of the three anomalous samples 122, 123, and 125 suggests the presence of an elongate source area trending east northeast, in the east central part of

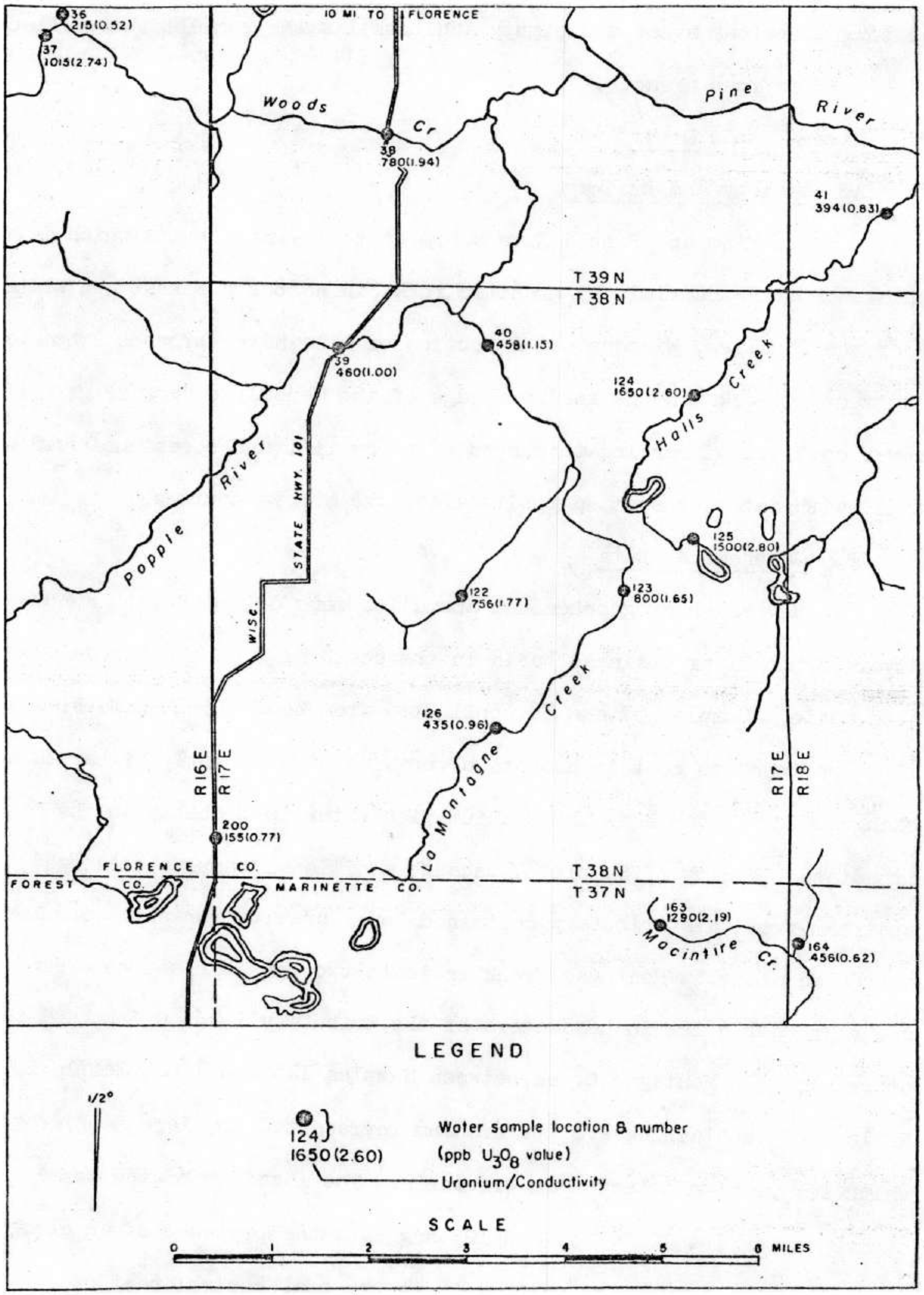

Figure 11. Water sample location map of Pine-Popple drainage, Wisconsin

T 39 N, R 17 E.

Sample 200W was from a farm well reported to be driven about 60 feet in glacial overburden and outwash deposits. The uranium content and the U/K ratio are the lowest encountered in this drainage area.

The abundance of glacial drift and other surficial deposits in this area of anomalous water samples suggests the need for further basic work on leaching and mobility of uranium in waters draining unconsolidated sediments and lacustrine environments. Additional water sampling and analysis of bedrock and soil samples are recommended in this area to establish relationship of uranium in streams to a mineralogic source.

Pike River - Goodman Area

A. Geology and Drainage

The North and South Branches of the Pike River drain a slight highland area between Goodman and Dunbar, in northwestern Marinette County. Areas of swamps and lakes are common in the headwater tributaries of both Branches.

Most of the area consists of low, rolling hills mantled with residual debris from the last glacial stage. Granite boulders derived from local bedrock are abundant in the drift, and occasional boulders of porphyritic gneiss and greenstone are present. The latter are probably derived from outcrops along Menominee River approximately 20 miles to the northeast.

The bedrock consists of glacially abraded knobs of acidic intrusives whose composition ranges from quartz diorite to granite. An exposure of gray, coarsely crystalline granite containing abundant sulfide and altered biotite was observed in SE-1/4, Section 36, T. 37 N., R. 18 E., approximately 4 miles east of sample 66 (Figure 11) and about 1 mile southwest of Dunbar. The rock was abnormally radioactive and several prospects had been recently opened. Analysis of a radioactive sample from a pit showed the rock contained 920 ppm or 0.09 percent U_3O_8. An autoradiograph of the sample revealed that the radioactivity occurred as small isolated blebs at the junction of crystal surfaces.

B. Geochemical Data

The uranium content of four water samples in the Goodman area suggested possible anomalous conditions. Twenty additional samples indicated the presence of three separate anomalous areas.

Samples collected along Sidney Creek showed an increase in uranium content to a maximum of 2.42 ppb at sample site 154. The U/K ratio for this sample (1240) is significant. The location of this sample and the data for adjacent samples are shown on Figure 12.

MacIntire Creek was sampled from its confluence with the North Branch Pike River to its headwaters. Two samples, 155 and 163, were found to contain anomalous uranium concentrations. The probable source of uranium-rich water is in the vicinity of Sample 163 shown on Figure 11.

Harvey Creek and its numerous tributaries drain the third anomalous area. Abnormally high uranium concentrations were detected in

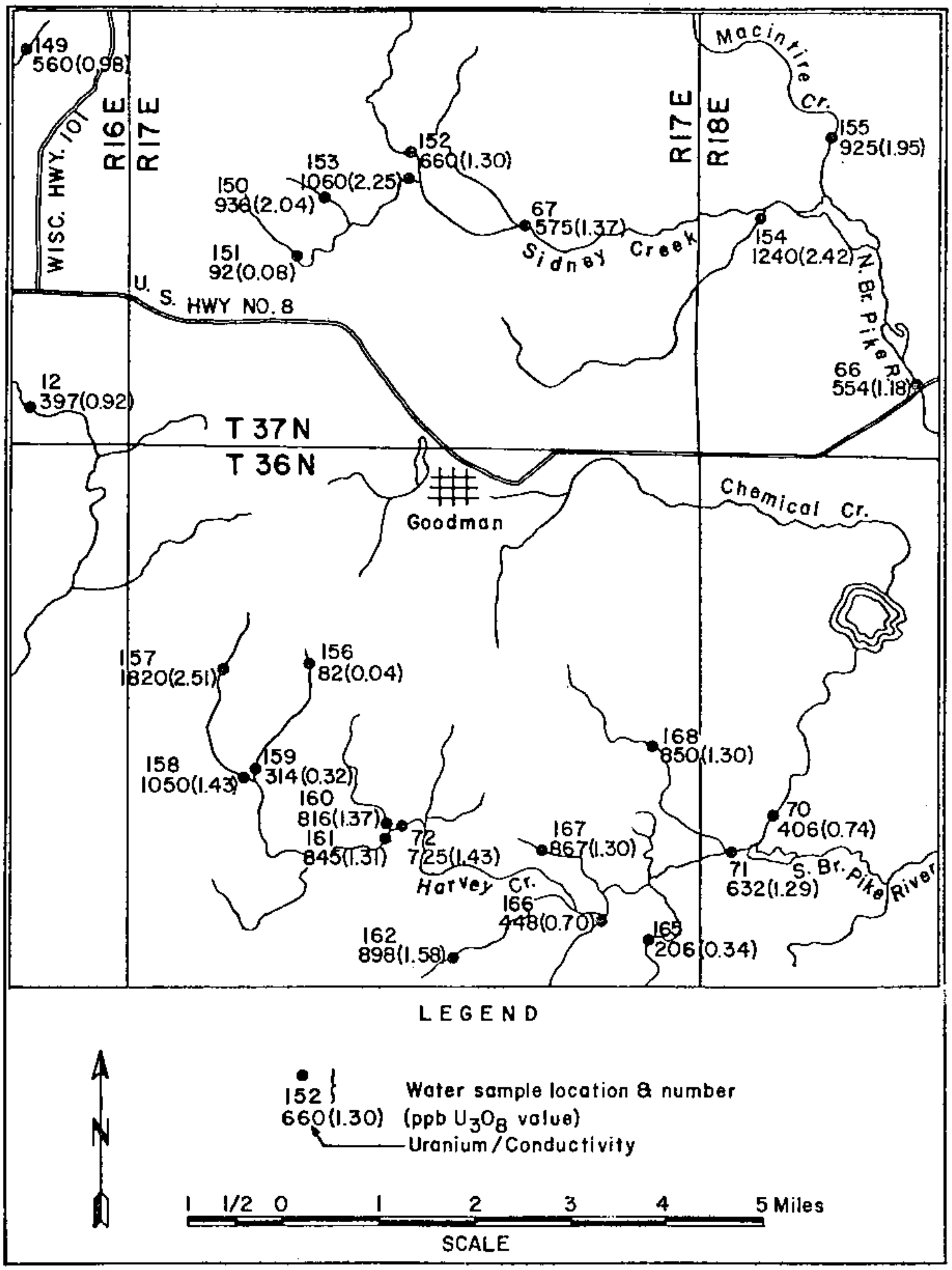

Figure 12.
Water sample location map of Pike River drainage, Wisconsin

water beginning at the junction of Harvey Creek and the South Branch Pike River. Camp Creek, the first north tributary contained considerable uranium close to the headwaters. The next tributary containing significant amounts of uranium was sample 167. A short distance upstream a tributary from the southwest was found to contain 1.58 ppb U_3O_8 (Sample 162). One other tributary sampled at the junction with Harvey Creek (Sample 160) contained anomalous amounts of uranium. The remaining water samples indicate a major source of uranium-rich water in the vicinity of Sample 157, where the maximum uranium concentration was detected (2.51 ppb U_3O_8). An organic sediment sample collected from the stream at water sample location 157 was found to contain 63 ppm U_3O_8, while another sample from the stream bed at 156 where the uranium content of water was 0.04 ppb, was found to contain only 1.3 ppm U_3O_8. This data suggests that uranium is migrating from an effectively leachable source in the immediate vicinity of 157.

Wabeno Area

A. Geology and Drainage

The Wabeno area is located approximately 5 miles east of Wabeno in the extreme southeastern corner of Forest County. Headwater tributaries of the North Branch Oconto River, Otter Creek and Rat River drain a highland that extends north of Wabeno to Laona.

Although most of the bedrock is concealed by glacial drift, it is presumed to be of granitic composition. Along the southern boundary of Forest County, an elongate east-trending belt of probable Huronian rocks extends from the vicinity of Ada Lake Lookout tower (Section 4, T. 33 N., R. 14 E.) eastward to the Peshtigo River, (Section 26, T. 34 N., R. 17 E.) within the Thunder Mountain area discussed below. Outcrops of dense, light gray, quartzite are present within this belt, notably in the vicinity of the Ada Lake, Carter and McCaslin Lookout towers. Diabase and granite are present at Carter Lookout, arkose near McCaslin Mountain, and porphyry between the last two localities just east of the Oconto River in Section 6, T. 33 N., R. 16 E.

B. Geochemical Data

Analytical results of two water samples taken in the Wabeno area during the reconnaissance phase indicated that both the Rat River and Otter Creek contained probable anomalous amounts of U_3O_8. Additional samples were collected from these drainage areas to confirm the presence of anomalies and localize a source area. The location of all water samples and analytical results are shown on Figure 13. The higher uranium values were detected in six samples (176, 177, 178, 179, 180, 181) most of which are located in the headwaters of tributaries to the two streams in an elongate, north-trending area about 5 miles long and 2 miles wide. These samples contained 1.63, 1.31, 1.78, 2.10, 2.70 and 2.40 ppb U_3O_8 respectively. A seventh sample, 182, from a tributary of the North Branch Oconto River arising in the same area contained 2.78 ppb U_3O_8 with a U/K ratio of 1500. Both values approach the maximum determined for Wisconsin water samples.

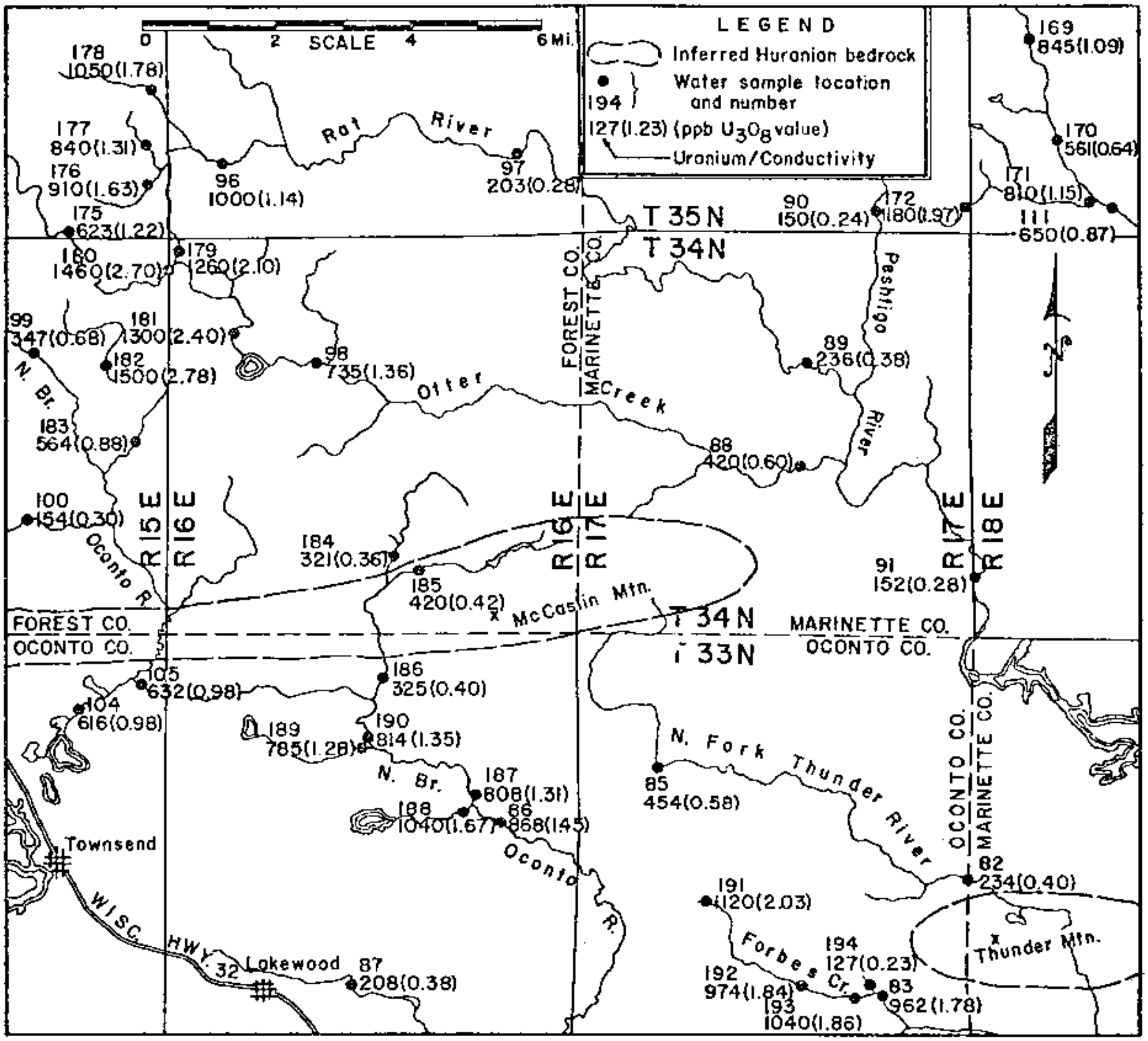

Figure 13.
Water sample location map of Wabeno and Thunder Mountian areas, Wisconsin

Thunder Mountain Area

A. Geology and Drainage

This area is located in the Thunder Mountain Quadrangle, near the common corner of Forest, Marinette and Oconto Counties. It comprises a broad J-shaped belt which lies south of the Huronian outcrop belt mentioned in the preceding section, and extends northward along the eastern range of townships of Figure 13.

Glacial cover is present in varying thickness and obscures most of the bedrock shown as granite on the Wisconsin geologic map (1911). A small inlier of Huronian meta sedimentary rocks is located in the SW-1/4 of T. 33 N., R. 18 E. at Thunder Mountain. Geologic information regarding these formations is scanty but presumably they are similar to those in the belt of the Carter-McCaslin Mountain area.

The northern part of the area is drained by Eagle Creek and the Peshtigo River; neither of these drainage systems are known to contact Huronian rocks. The southern part is drained by the North Branch Oconto River, North Fork Thunder River and Forbes Creek; of these only the first traverses the inferred Huronian outcrop belt.

B. Geochemical Data

The results of reconnaissance water sampling in the Thunder Mountain area suggested the presence of three anomalous areas. Subsequent detailed sampling confirmed the presence of three widely separated small areas drained by waters abnormally high in uranium. The analytical data for samples collected in the Thunder Mountain area are plotted on Figure 13.

Samples 169 and 172 from Eagle Creek in the northeastern corner of the area contained 1.09 and 1.97 ppb U_3O_8 indicating at least two source areas. Additional water sampling is needed to define the limits of this area more precisely, particularly in the upper drainage of Eagle Creek above sample 169.

Five water samples from the North Branch Oconto River and its tributaries in T. 33 N., R. 16 E. were found to contain anomalous amounts of uranium which suggests the presence of a source area just south of the inferred Huronian belt. The drainage areas represented by samples 188 and 189 are relatively small and well defined, but the source of the anomaly indicated by sample 190 is not precisely known. It must lie somewhere within the drainage of the Oconto River between samples 105 and 190 because the former sample does not reflect a significant increase over the values noted in the Oconto River of the Wabeno Area, nor does sample 186 from an unnamed tributary that crosses the inferred Huronian belt about two miles west of McCaslin Mountain contain anomalous amounts of uranium.

Forbes Creek, a tributary of Thunder River draining the southern part of T. 33 N., R. 17 E., was found to contain anomalous uranium concentrations. The uranium concent of the water increases upstream to sample 191 at the headwaters. Additional water samples along Forbes Creek might detect other sources but a surface examination and the collection of soil samples in the area surrounding sample location 191 is recommended for further delineating the source area.

The North Fork Thunder River and the Peshtigo River were not sampled in the detailed study in this area. The former stream heads along the southern flank of inferred Huronian rocks, and should receive additional attention but further sampling of the latter river in this area is not recommended because its large volume of flow tends to average out local anomalies contributed by lesser streams.

GEOPHYSICAL STUDIES IN CANADA

Introduction

The Geophysics and Geochemistry Branch of the U.S. Atomic Energy Commission carried out an experimental geophysics project in the Algoma uranium mining district near Blind River, Ontario, Canada, from September 9-12, 1957. The purpose of the project was to determine whether geophysical techniques could be used to locate similar-type deposits which might occur in the Michigan-Wisconsin area where a geochemical reconnaissance program was currently in progress. Field data were obtained in the vicinity of the Pronto Mine and the Algoma-Quirke mine using electromagnetic and spontaneous potential equipment. Figure 14 shows the location of these properties in relation to the Algoma Mining district.

Geology and Applicability of Geophysics

The uranium ore in the Blind River area occurs in the pyritiferous matrix of a quartz pebble conglomerate bed, 5 to 20 feet thick, near the base of the Mississagi quartzite of Huronian age which unconformably overlies Archean granite. The ore horizon strikes nearly east-west and dips 15^{o} to 30^{o} south of the vicinity of the two properties studied above. A rough positive correlation exists between uranium mineral concentration and pyrite concentration in the quartz pebble conglomerate. The presence of pyrite is the only unique physical characteristic associated with the ore horizon which was believed to be amenable to

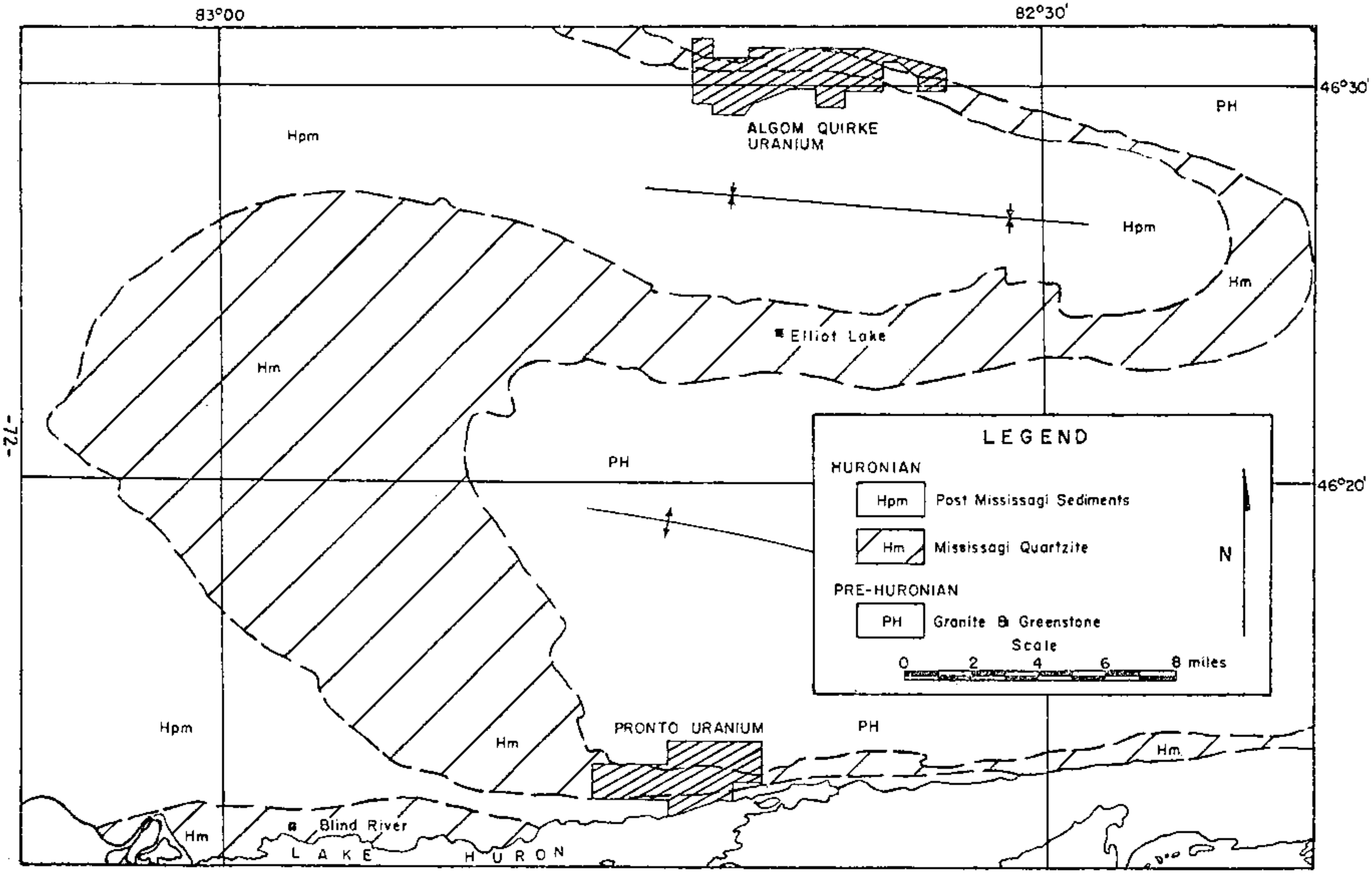

Figure 14. Index and outcrop map of Algona uranium district, Ontario

detection by geophysical methods. Pyrite concentrations in the rock can be detected by the electromagnetic and the spontaneous potential geophysical methods under favorable conditions. These conditions are:

1. Electromagnetic method: pyrite must be sufficiently continuous and sufficiently concentrated to distort the artificial electromagnetic field generated by the equipment.
2. Spontaneous potential method: pyrite must be in a state of oxidation, and must be sufficiently continuous, sufficiently concentrated, and sufficiently water saturated to generate a measurable potential.

pyrite contents & geophys methods here

The concentration of pyrite in the ore horizons at the Pronto and Algome-Quirke mines has been determined to range between 5 and 15 percent. These concentrations are considered to be very close to the lower limit of detectability of the electromagnetic and spontaneous potential methods. Since very little information was available concerning the other conditions listed above, actual field experiments, using electromagnetic and spontaneous potential equipment, were carried out to determine the feasibility of the geophysical methods.

Equipment

The electromagnetic equipment was a Slingram, self-contained, portable unit which was operated by 3 men. The equipment consisted of a transmitting and a receiving coil, an oscillator, a compensator-amplifier unit, and connecting cables. The coils were oriented horizontally and were spaced 32.5 and 65 meters apart. Frequencies of 440 and 1760 cycles per second were used.

The spontaneous potential equipment consisted of two porous pots filled with copper sulfate, connecting cables, and a null-reading potentiometer.

Geophysical Surveys - Description of Results

The location of geophysical stations on both mine properties was limited to areas where the ore horizon had not been mined out previously, and to areas where there were no electric power lines, the proximity of which causes interference in electromagnetic measurements. At the Pronto mine, the presence of a large tailings pond further limited the positioning of geophysical stations. However, five electromagnetic and two spontaneous potential profile locations were selected which avoided these hinderances. The profiles varied from 300 to 600 feet in length and crossed the ore-bearing horizon in a direction perpendicular to its strike.

A. Electromagnetic

None of the electromagnetic results are considered anomalous. A good electromagnetic anomaly resulting from pyrite concentrations would be typified by negative imaginary component readings accompanied by low real component readings on Slingram equipment. Inspection of the plotted curves show that these two conditions do not occur simultaneously. The relatively large variations of the real component readings can be attributed to elevation differences between the transmitting and receiving coils. The small variations of the imaginary readings do not exceed the limits of accuracy of the instruments. The results of the electromagnetic tests indicated that this geophysical technique could not be used successfully to locate uranium ore bodies of the Blind River type.

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B. Spontaneous Potential

A small spontaneous potential anomaly occurred on one of the S.P. profiles in the vicinity of the ore horizon. However, the other S.P. profile, only 50 feet away and parallel to the first profile, did not show a similar anomaly. Therefore, it is questionably whether the anomaly was caused by the pyrite in the ore zone, and very probable that it was the result of random spontaneous potential variation. Since much of the area traveresed by the S.P. profiles consisted of bare outcrops of impervious quartzite or granite, it was impossible to obtain good electrical contact for many of the readings. For this reason, the readings are not considered very dependable. The results of the spontaneous potential tests indicated that this geophysical technique could not be used reliably to locate uranium ore bodies of the Blind River type.

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C. Conclusions

The field data obtained from the experimental geophysical project in the Blind River, Canada uranium mining area indicated that neither the electromagnetic nor the spontaneous potential method could be used successfully in the Michigan-Wisconsin area to locate similar uranium ore deposits unless the pyrite occurrences were more favorable.

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geophysics unreliable in pE detection of cgl u deps

URANIUM CONTENT OF ROCK TYPES AND SURFICIAL DEPOSITS

Introduction

The background uranium content of ground and surface waters is derived from three primary source materials: bedrock, glacial deposits, and other surficial deposits. Because proper evaluation of both hydrogeochemical anomalies and the ore potential of an area depend, in part, on quantitative knowledge of the uranium content of rock and soil materials, a brief study was made of its occurrence in rock and soil materials common to the water reconnaissance area.

Rock Types

Considerable emphasis has been placed by numerous authors on the widespread association of uranium in the Palezoic black shale formations present in the midwestern United States. The uranium content for three European and eight American black shales of Paleozoic age were summarized by Bates and Strahl (1958). Table 4 contains the average values for uranium in the Paleozoic black shales of the United States from data complied by those authors. The weighted mean for these samples is 31.2 ppm U_3O_8; for all samples excluding the Chattanooga shale the weighted mean is 6.8 ppm U_3O_8.

Because of the widespread distribution of dark slates in the Huronian sequence of the Northern Peninsula area some interest had been developed in these rocks as possible source materials for uranium. Table 5 summarized the present data on the abundance of uranium in five Precambrian and one Cambrian rock types of Northern Michigan and Wisconsin. The results of analyses on more than 30 samples of Precambrian slate do not show significant uranium concentrations. On the average, slate contains more

Note (U) & slates

uranium than quartzite, dolomite and schist but less than granite. In general, the impermeable nature of the metamorphic formations such as slate, quartzite and schist prevents large scale solution of uranium by ground and surface waters. Conversely, certain granites and sandstones may contribute relatively larger amounts of uranium to the hydrologic system because of their permeability and generally higher uranium contents.

It should be noted that the compilation in Table 5 includes several samples which were analyzed for uranium only because they were radioactive. The average uranium content in such rock types as the granite and slate probably will be less than the average values indicated in Table 5.

TABLE 4

URANIUM CONTENT OF BLACK SHALES*

Shale	Location	Age	No. Samples	Average Uranium Content (ppm)
Reedsville	Pennsylvania	Ordovician	4	4
Chattanooga	Tennessee	Devonian	317	62
Ohio	Ohio	Devonian	220	10
Woodford	New Mexico	Devonian	116	9
Hamilton	Pennsylvania	Devonian	6	6
Chemung	Pennsylvania	Devonian	4	3
Allegheny	Pennsylvania	Pennsylvanian	34	4
Kansas	Kansas	Pennsylvanian	21	16

(*After Bates and Strahl, (1958) Mineralogy and Chemistry of Uranium-Bearing Black Shales, 2nd. UN International Conference on Peaceful Uses of Atomic Energy, p. 1910)

TABLE 5

URANIUM CONTENT OF ROCKS IN NORTHERN MICHIGAN AND WISCONSIN

Rock Type	Age	No. Samples	Uranium Content (ppm) Range	Mean
Granite	Archean	27	3-40	16
Slate *	Mid Huronian	34	1-10	3
Schist	Huronian	10	1-20	2
Sandstone	Cambrian	9	1-5	2
Quartzite	Lower Huronian	15	0.2-3.5	1.2
Dolomite	Lower Huronian	6	0.5-5.0	1.5

Surficial Deposits

In an attempt to relate hydrogeochemically detected uranium to source areas the problem of uranium contribution by Quaternary sediment was considered. Owing to the prevalence of glacial drift over which flow most of the streams of Northern Michigan and Wisconsin, samples of various glacial deposits were collected for analysis of uranium. While it was believed that anomalous amounts of uranium would not be found in glacial deposits, the amount of uranium present should reflect the type of materials from which the surficial deposits were derived.

The surface map of Northern Michigan (Leverett, 1911) indicates three major types of glacial deposits represented in Dickinson, Marquette and western Menominee Counties, Michigan: moraines, outwash plains, and drumlins. The clastic material of these deposits has been derived from both Archean granitic rocks, and early Paleozoic sedimentary rocks which border Lake Michigan and Lake Superior to the northeast.

Twenty-seven samples were collected from the moraines and outwash plains in southern Dickinson and western Menominee Counties. Samples

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* Some data from U.S.G.S. Report No. TDS-867, April 1, 1954 for Carl Dutton requested by R. C. Vickers.

were collected at intervals of about 3 miles on a traverse extending east from Randville along State Highway 69 to Foster City, south on county roads to Waucedah, and west on secondary roads to the vicinity of Iron Hill. The samples consist mainly of sand with varying amounts of coarser clastic materials ranging up to occasional fragments 3 to 5 inches in greatest dimension.

The samples were crushed, quartered, pulverized, dried and assayed for uranium by the fluorimetric method. The uranium content of these samples varied from 0.3 to 10.4 ppm U_3O_8 with a mean of 1.3 ppm, and appears to have a log normal distribution. The only sample which falls outside the limits set by the mean plus two standard deviations (odds against are 43 to 1) is the one containing 10.4 ppm. This sample consisted of reddish sand containing some clay, many small pebbles and a few larger granitic rocks. The sample was collected from a road cut in Michigan Highway No. 69 located in the east central part of Section 33, T. 42 N., R. 29 W., Dickinson County. No attempt was made to relate this sample to bedrock of the area.

Twelve soil samples were collected in six adjacent townships of southeastern Florence County and northern Marinette Counties from areas of moderately thick glacial drift consisting of moraine and outwash material. Four additional samples of outwash sand were obtained from two townships in northeastern Florence County. The latter samples were obtained from localities which had shown anomalous radiometric values by carborne and portable scintillometer surveys. The limited bedrock exposures in these areas consisted mainly of greenstone and granite which gave radiometric readings only slightly above background value of 0.003 mr per hr. with a portable scintillation counter.

The samples were treated as indicated in the preceding paragraph and analyses made for uranium. The uranium content of the Wisconsin soil samples varied from 0.2 to 1.5 ppm U_3O_8 with a mean of 1.0 ppm.

Although the results of the soil analyses do not indicate the presence of significant uranium concentrations in the materials sampled, the highest U_3O_8 value noted in the Michigan samples is about two thirds of the mean value for all granitic rocks of the area. The mean uranium content of the unconsolidated surficial deposits is less than most rock types in Michigan and Wisconsin. Because these deposits are rather permeable and comminuted the surface area per unit volume of material is greatly increased. Consequently, solution of uranium and other ions by natural waters might result in elevated background values for uranium and conductivity in this media which could obscure those parameters derived from bedrock or mineralized zones. With the limited studies made it was not possible to establish whether indurated rock materials or the surficial deposits contribute uranium equally or disproportionately to natural waters.

perhaps
the other
1/3 or 33%
has leached by
weathering climate
WC9, etc ??

URANIUM IN BOG SOIL

Introduction

Many of the water samples which contain anomalous amounts of uranium were taken from streams that originate in or flow through swamps. Similar environments exist for many streams which contain only background uranium so it is unlikely that the swamp per se causes anomalous amounts

NOTE
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U & bogs
or swamps

NOTE,
opinion

of uranium in waters. In a few instances samples taken only a few yards apart just above and below an impounded stream showed a marked decrease in the lower sample. It is thought equally likely that the waters may introduce uranium into the peaty materials of the bog. Consequently, a knowledge of the distribution of uranium in the peat and organic rich soil could give useful information concerning the uranium concentration and mobility of ground and surface waters.

National Mine (West Branch Ely Creek)

Twenty-nine organic-rich soil samples were collected within or near a small bog deposit drained by the West Branch of Ely Creek near National Mine, Michigan. The surface samples were collected by removing and discarding the upper 2 to 3 inches of living vegetation including crown and roots of sedge and other plants. The next 4 to 6 inches of soil were taken as the sample. These samples were dried, ignited, and analyzed for uranium.

A scatter diagram of the U_3O_8 in surface samples versus the loss on ignition for twenty-five of the samples is given in Figure 15a. It is seen that a reasonably good correlation exists between U_3O_8 content and loss on ignition. Since the loss of weight is due mostly to combustion of the organic material, the loss on ignition should represent a good estimation of the organic content of the sample. The ratio gm U/gm organic material should be independent of the organic content of the sample and will reflect the influence of other factors. Figure 16 shows the areal distribution of this parameter for surface samples collected from bog near National Mine.

[U] vs LOI CORR

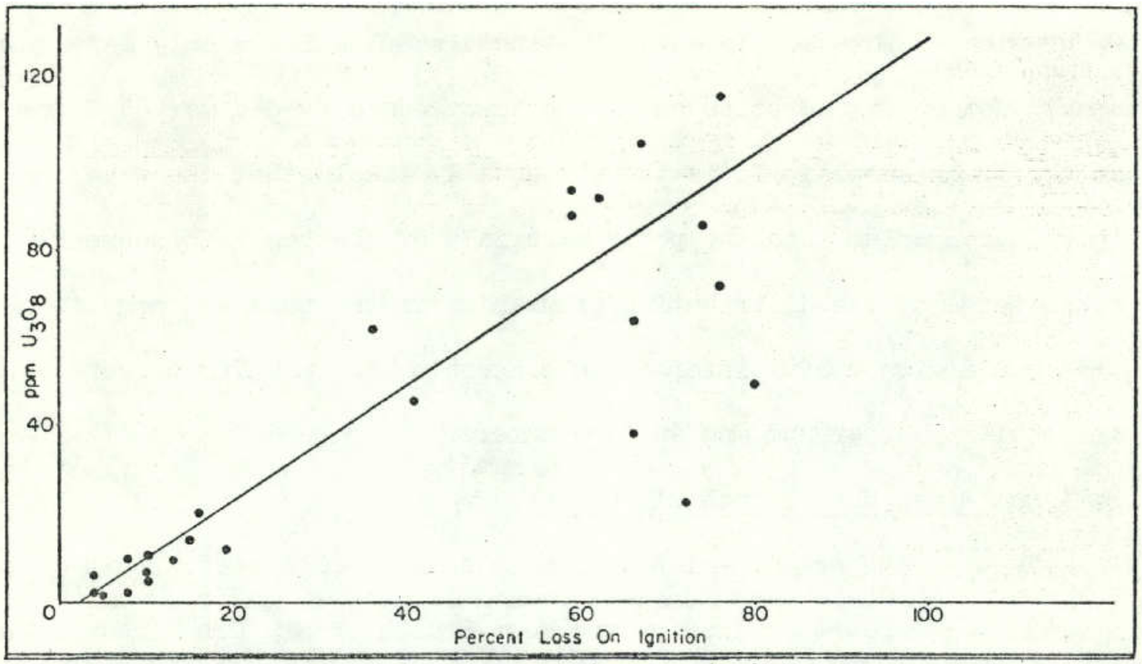

Figure 15a. U_3O_8 in sample vs. present loss or ignition (National Mine, Mich)

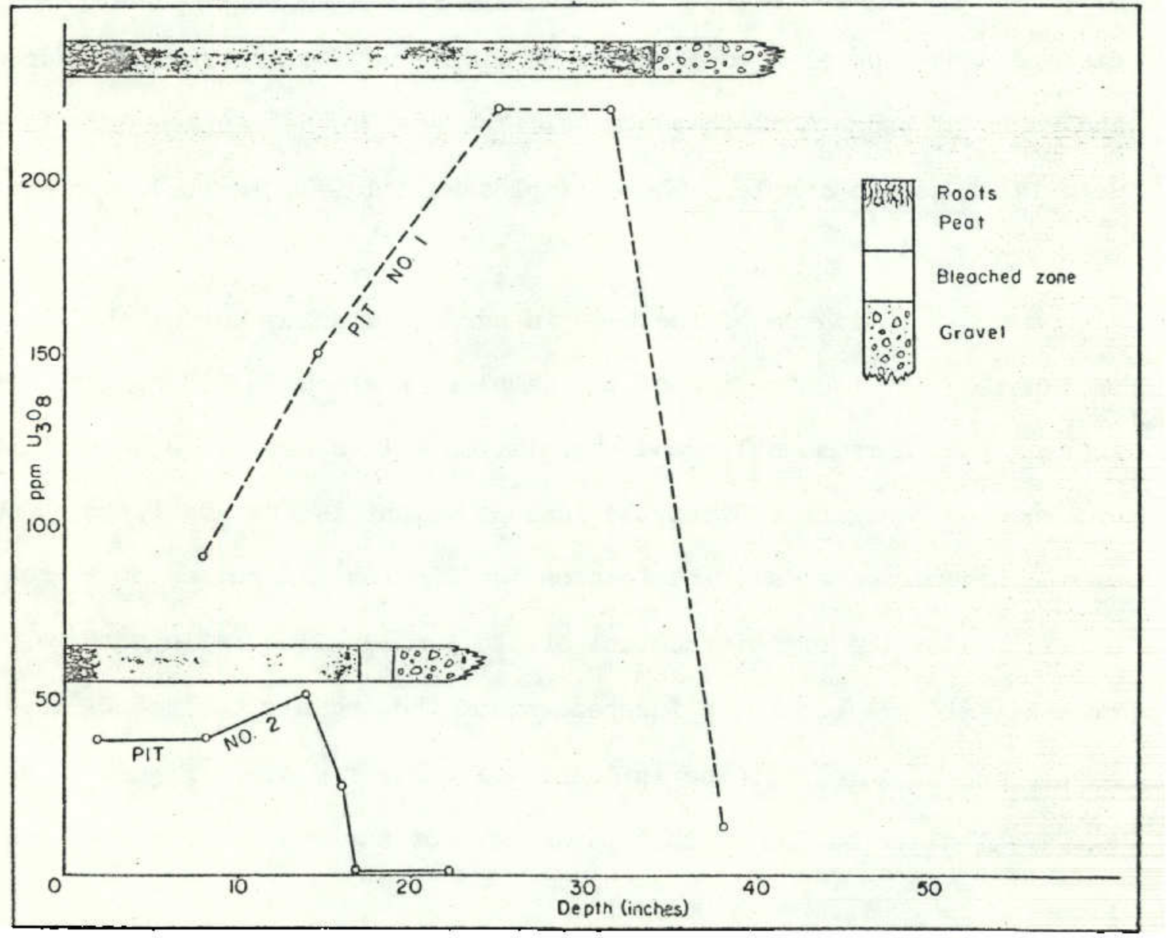

Figure 15b. Relation of uranium in log material with depth (National Mine, Mich)

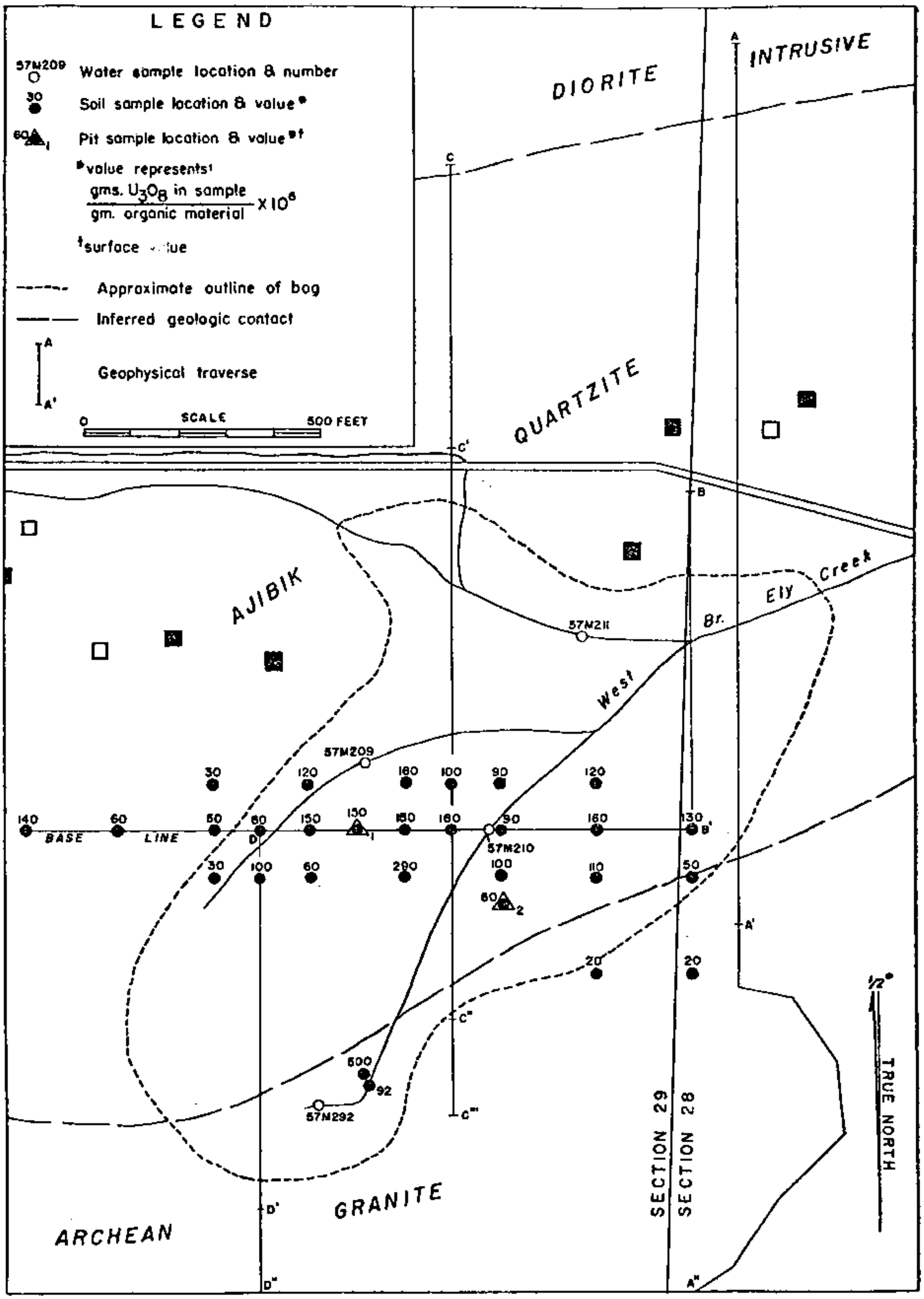

Figure 16. Sample and geologic map, West Branch Ely Creek
Marquette County, Michigan

In addition to the surface samples, two shallow pits were dug (Figure 15b) and samples collected at various depths below the surface. The surface layer excluding growing plant material contained a considerable amount of partially decomposed organic debris and a few pebbles. The organic-rich material below the surface layers consisted of a fine, black soil which gave a light tan, very fine silty residue after the organic material was oxidized. In pit 2 a bleached layer consisting of a 2 to 4 inch thickness of very fine silt was found just below the organic layers at a depth of about 18 inches. Underlying the fine grained layer was sand and gravel of unknown thickness. The results of a pebble count made on a sample from this layer by H. K. Holen (1957, Personal communication) are given in Table 6. Nineteen of the 33 pebbles were of calcareous composition capable of supplying bicarbonate ion to the subsurface waters of the bog.

Figure 15b shows the results of analyses on depth samples from the two pits. The variation of uranium content with depth shows that most of the uranium occurs in the zone of organic material. In general, surface samples and samples at greater depths will show lower uranium content than samples taken at intermediate depths. The lowest values are found in the organic-free clastic sediments on which the bog is deposited.

The origin of the anomalous waters is probably related to the bedrock of the surrounding low hills and underlying the swamp. Two granite samples collected from the south end of the swamp contained 17 (F48573) and 6 (F48574) ppm of U_3O_8. Demineralized water which had been in contact with these granite samples for several days in the laboratory contained 0.38 and 2.8 ppb U_3O_8. When water containing 100 ppm of sodium bicarbonate was used as a solvent, the uranium concentrations increased to 3.8 and 7.0 ppb, respectively. It is of interest to note that the amount of uranium leached from granite by waters is not directly dependent upon the amount of uranium in the granite. The leachable uranium is also related to many variables of the solvent, one important one being the bicarbonate content.

NOTE factors affecting leaching

TABLE 6

PEBBLE COUNT IN PIT NO. 2 NATIONAL MINE AREA, MICHIGAN

Rock Type	No. of Pebbles
Limestone	6
Limestone (fossiliferous)	5
Dolomite	4
Dolomite (fossiliferous)	4
Granitic	5
Fine grained basic igneous	4
Pink Quartzite	2
Gray Chert	2
Sandstone, Jacobsville	1
	33

A possible source of the uranium in the natural waters of the bog is believed to be from the Archean granite which approximates the southern border of the bog. The presence of calcareous pebbles in the gravel under the bog suggests a correlative abundance of additional fine calcareous clastics which would tend to make this water a good solvent for uranium in the underlying and adjacent granitic rocks.

Another bog sample was collected at the headwaters of West Branch Ely Creek (Figure 7) near water sample 405. The bog area here consists of a poorly drained cedar swamp overlying Ajibik quartzite and about 0.2 miles from the inferred Archean granite contact. In spite of a high organic content, this sample contained only 10 ppm of uranium. The sample of water flowing through the swamp contained less than 0.05 ppb of uranium.

Sagola Swamp (Flatrock Creek)

The headwaters of Flatrock Creek arise in the Sagola Swamp of southern Marquette County. Geologic information indicate that radioactive granite is exposed on the west side of the swamp and probably underlies the entire area. Four water samples from the stream and upper tributaries during the reconnaissance study were considered anomalous.

TABLE 7

ANALYSIS OF BOG MATERIAL IN SAGOLA SWAMP

Sample	Description	Loss on Ignition, %	U (ppm)	gm U x 10^6/ gm organic
415	Top 6" collected near water sample 149	14.0	15	110
418	Black organic muck just below dense grass root system. Sample 6-8 inches deep.	54.8	20	38
417	Lowermost black organic muck above sand. Sample 4" thick. Bottom of sample 17" below surface.	19.4	14	68
416	Fine grained silty sand from a pit near water sample 148. Sample collected 30 inches below surface.	4.2	4.2	100

A surface soil sample near water sample 149 and samples from a pit dug near water sample 148 were collected in the Sagola Swamp at the headwaters of Flatrock Creek (Figure 9). The data which are summarized in Table 7 reinforce the conclusions drawn from the bog samples taken at National Mine with respect to vertical distribution of uranium and relation to organic matter.

Inasmuch as the inferred bedrock is Archean granite and the glacial cover is composed largely of these materials, which commonly show abnormal radioactivity and uranium content, it is suspected that the anomalous bog deposits and waters are related to this Archean source.

West Branch Harvey Creek

An interesting contrast is shown by results of analyses on two sediment samples collected from Harvey Creek in the South Branch Pike River drainage (Figure 12) of Marinette County, Wisconsin. Two streams originate in separate swamps which are about one mile apart. Water sample 157 from the North Branch of Harvey Creek contained 2.5 ppb U_3O_8 and the sediment contained 40 ppm U_3O_8 and had an LOI of 34 percent. Water sample 156 from a small tributary stream one mile to the east contained less than 0.05 ppb U_3O_8 and the stream sediment contained 1 ppm U_3O_8 and had an LOI of 70 percent. Although the geology is not well known, the area is probably underlain by porphyritic granite and granite gneiss. Numerous boulders of this rock, many of which are radioactive, are present in both streams. A more detailed study of this or similar areas might provide useful information about the factors which influence the uranium concentration and enrichment in waters and stream sediments.

EVALUATION OF HYDROGEOCHEMICAL METHOD

Hydrogeochemical methods have been used in prospecting for many metallic elements including uranium, but seldom has the application been directed to the reconnaissance for uranium on such a large scale in an area whose favorability was so incompletely known. The few isolated occurrences of uranium in Michigan were used advantageously in the orientation studies (p. 19-21) to determine that measureable quantities of uranium and significant uranium to conductivity ratios could be established in the hydrologic environment. With this assurance, reconnaissance water sampling was initiated in the area around Ishpeming and extended northward to Lake Superior and Channing. Ideally, two samples were selected from streams in each township, but depending on ease of access the number of water samples taken per township varied from zero to three. Approximately 120 samples were taken which were adequate to establish background uranium (U_3O_8) and conductivity (K) values for waters draining this area of 60 townships. Before this phase was completed it became apparent that the background value of uranium was quite low, being generally less than 0.1 ppb.

Water samples taken from Archean terrane north of the Marquette iron range (Figure 2) generally contained less than 0.05 ppb uranium, the lower detectable limit of the fluorimetric method used in the field laboratory. At the southern margin of the Marquette range, and extending south and southwest across the Republic granite of probable post-Huronian age, the uranium background of water is about 0.2 ppb. Within the Menominee iron district near Iron Mountain, the uranium background of

Pine Creek has a value of about 0.5 ppb. The trend of elevated background values southward from Lake Superior continues into northeastern Wisconsin. The uranium background of Wisconsin waters is generally higher than in Michigan but does not show the extremes encountered in the latter.

The U/K values for Michigan anomalies show a greater dispersion than those in Wisconsin. Cf. Tables 1 and 2. The most significant values in Michigan are found near the Huronian-Archean contact of the Marquette range (National Mines locality) and Menominee range (Pine Creek locality).

Plate 3 is a uranium to conductivity contour map of part of northeastern Wisconsin and northern peninsula of Michigan based on results of detailed sampling in this area. Although slightly different contour intervals were used in each state significant patterns are developed which merit discussion. As noted in the section on Statistical Analysis of Data page 26, normalizing the uranium content by means of the U/K ratio provides a means of evaluating the probable anomalies in areas of varying background.

With few exceptions, the higher U/K values in Michigan waters appear to be associated with metasedimentary rocks of early and middle Huronian age or with the contact of these rocks and certain younger granitic rocks. The lower values are associated with Archean granites, greenstones and basic rocks and with the thick metasedimentary shale sequence of Late Huronian age.

In Wisconsin where the bedrock geology is not well known, the pattern of U/K ratios cannot be related to bedrock with certainty. Most of the higher U/K values are believed to represent highland drainage areas in granitic rocks. Only in the area east of Lakewood may the ratios reflect the influence of possible Huronian rocks.

No orientation studies were done in Wisconsin because of the lack of known uranium occurrences. After the detailed sampling was well advanced, report of a single uranium prospect near Dunbar, was received (see page 63). This locality on Sec. 36, T. 36 N., R. 17 E. is within the 400 to 800 interval and about one township removed from an area of highest U/K values. It is believed that similar low grade uranium occurrence may exist throughout the granitic highland area of northeastern Wisconsin but further detailed investigation would be required to verify their existence.

The use of hydrogeochemical techniques has shown that areas of favorability can be prognosticated and most likely contouring of geochemical parameters can establish a useable, if somewhat unrefined, method for selecting target areas for further work.

COMPARISON OF AIRBORNE RADIOMETRIC AND HYDROGEOCHEMICAL WORK IN PART OF NORTHERN MICHIGAN

Introduction

The area covered by airborne radiometric work was a block of 36 townships with Ishpeming, Michigan at the approximate center. The flight lines (N-S at 0.5 mile intervals) were flown in 1955 by the U. S. Geological Survey at an average height of 200 feet above the ground surface. Seventy-two geochemical water samples were taken from streams and wells in this same area during the summer of 1957 by the Geophysics and Geochemistry Branch. These samples were analyzed for uranium (U) and conductivity (K), and the U/K values were contoured as shown in Figure 17. The preparation of the U/K map and the correlation which exists between this map and the contour map of averaged radiometric values obtained from the airborne work are discussed below.

Construction of Radiometric Contour Map

Anomalies were picked from airborne radiometric strip charts and plotted on topographic sheets. These anomalies were assigned values according to a scale of arbitrary radiometric intensity which ranged from 0 (background) to a maximum of 7. No attempt was made to pick the intensity to greater than integer accuracy, so that if an anomaly was assigned a value of 2, for example, the exact value was between 1 and 2. This arbitrary scale was initially established by H. K. Holen of the Ishpeming Office.

After the anomalies had been plotted on the topographic sheets, all of the anomalies of various radiometric intensities which occurred in each section were summed up, and the sum was written in the center

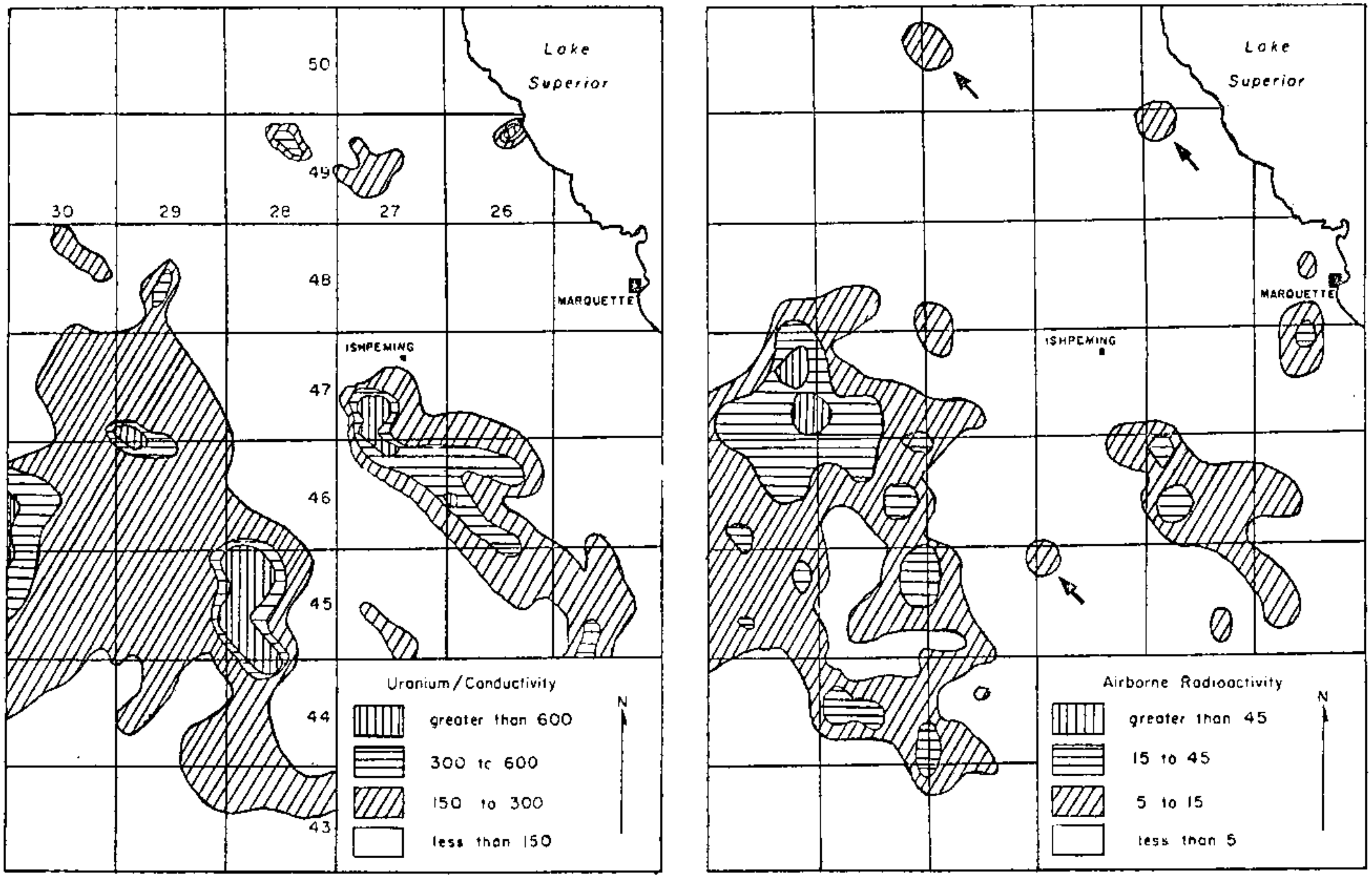

Figure 17. Geochemical anomaly and radio activity map of portion of Marquette County, Michigan

of each section. For example, if 3 anomalies occurred in a section, and their intensities were 2, 5 and 3, the number 10 was written in the center of that section. Then, for each square block of 4 sections, these numbers were added together and their sum was plotted at the center of the block. This, in effect, was an averaging system. When this stage of the work was completed, a number (N) which represented the sum of the anomalies of various intensities ($N = \Sigma ai$) within an area of 4 square miles appeared at each intersection of N-S and E-W section lines. Contours were then drawn on these numbers at geometrically progressing intervals of 5, 15 and 45.

Comparison of Airborne Radiometric and Ground Hydrogeochemical Contour Maps

By referring to Figure 17 it can be seen that the two areas outlined by a heavy line on both the large radiometric and hydrogeochemical anomaly maps are roughly coincidental, although the boundaries and magnitudes are not identical. Three of the small radiometric anomalies (marked with an arrow) are in the same drainage systems of small hydrogeochemical anomalies, but are displaced upstream. Four other small radiometric anomalies have no hydrogeochemical counterparts, and two small hydrogeochemical anomalies have no radiometric counterparts. One high-level hydrogeochemical anomaly resulted from water obtained from wells (in the vicinity of Buckroe). This anomaly was not detected by the airborne radiometric method.

Conclusions

Anomalies which are large in area (more than one township) can be detected both by radiometric flying and hydrogeochemical reconnaissance in this area, although the two methods do not result in anomalies having identical magnitudes and boundaries. The cost of radiometric flying is smaller than the cost of hydrogeochemical work by a ratio of about 4 to 7. Thus a great deal of expense could be saved by first flying radiometric control over a large area, and then doing hydrogeochemical work in the radiometrically anomalous area. If the objective of a large scale reconnaissance (such as the one conducted in Michigan) is only to locate anomalies which are large in area, this technique would work well. However, some small hydrogeochemical anomalies would have been overlooked if this had been done in Michigan. Therefore, if hydrogeochemical anomalies which are relatively small in area are the objective of a reconnaissance, radiometric flying will not contribute information which can be depended upon in every case. Furthermore, if buried sources of uranium are suspected in an area, the chances of detecting them by the airborne radiometric method are remote, whereas the chances of detecting them by the hydrogeochemical (well water) method are much better.

Note relative economic advantage of airborne survey over hydrogeochem survey

Good pts adv. of hydrogeochem

CONCLUSIONS

Considering the scope of the problems encountered, and the limitations imposed by the data acquired in this reconnaissance investigation, the following conclusions are offered at this writing.

Low Order of Uranium in Waters

In comparison with other areas investigated for uranium by hydrogeochemical methods in the Western Interior regions of the United States, the uranium content and the dissolved soild content of waters in Michigan and northeastern Wisconsin is quite low. The low uranium background values suggest that geochemical anomalies in waters will likewise be of a low order because of conditions inherent to the area studied: (1) limited bedrock permeability in metamorphic terrane; (2) dilution effect of surface water runoff; and (3) rapid "fadeout" or inability of many streams to carry trace amounts of uranium over extensive distances.

low amplitude anomalies to be expected

some reasons

Uranium in Bedrock and Surficial Cover

Metasedimentary rocks generally contain from 1 to 20 ppm U_3O_8, but isolated pods of the upper iron member and a few mineralized zones of the Michigamme slate may contain as much as a few hundred ppm. Granitic rocks consistently carry uranium values ranging from 3 to 40 ppm. Surficial cover, with the exception of certain bogs contains from 0.3 to 6.0 ppm uranium. The U_3O_8 content of bog soils may range up to 300 ppm. The mean uranium content of sandy glacial till based on a limited number of samples in Michigan and Wisconsin is about 1.0 ppm, although individual samples may contain as much as 10 ppm.

Relation of Anomalous Waters to Bedrock

The bedrock in the area of interest can be divided into three general types: (1) granite, (2) Huronian metasediments, and (3) Cambrian sandstone. In the following discussion it is convenient to divide the granites into two types: (Lamey 1933).

1. "Archean" in Baraga County and the part of Marquette County north of a line between Champion and Negaunee, and
2. Post-Huronian "Republic" granite in Iron, Dickinson and the southern part of Marquette County.

Waters associated with terrane underlain by Archean granite and upper Huronian bedrock tend not to be anomalous. Most waters which flow over middle Huronian beds tend to be anomalous. There are exceptions to the above generalizations: (1) The waters of the Huron River and Plumbago Creek cross terrane of Upper Huronian rocks but the anomalies found are of limited areal extent and are due to small uranium deposits. (2) The waters of Flat Rock Creek apparently flow over granitic bedrock, although there is a possibility that middle Huronian beds minus the iron formation are buried under the till in this area. (3) The waters flowing over middle Huronian beds on the southern flank of the "Republic" granite exposures in the area between Randville and Felch are not anomalous.

In general, anomalous waters are associated with the contact between the Republic granite and middle Huronian beds. None of the anomalous waters were associated with the contact between middle Huronian beds and Archean granite exposed north of the Marquette range.

The rocks of the middle Huronian age contain less uranium than is found in granite, and probably do not add unusually large amounts of background uranium to the waters. The possible association of abnormal concentrations of uranium with the contact between the "Republic" granite and the middle Huronian rocks is worthy of further study.

any part fluvial or strictly marine?

Uranium content of well waters from the Cambrian sandstones is greater than surface waters for the area. Considerably more sampling is needed before the data from subsurface waters can be interpreted in a manner comparable with surface waters discussed above.

any downdip potential & any reduced facies?

Evaluation of Geophysical Studies

eval & concl

Limited experiments with surface magnetic and electrical methods in Michigan and Canada indicated that these geophysical methods could not be applied satisfactorily to locating ore deposits of the Blind River type.

Evaluation of Hydrogeochemical Reconnaissance

log normal distribu.

Over a large area the concentration of uranium in surface waters and the solids dissolved in these waters exhibit considerable variation. The distribution of these concentrations is approximately lognormal, and this fact is useful in interpreting hydrogeochemical data. Limited information from the Michigan area and the Mt. Spokane area of Washington suggests that waters having concentrations of uranium in their dissolved solids greater than the mean plus the standard deviation of their lognormal distribution may be associated with uranium mineralization. A more precise evaluation of the usefulness of the one-sigma cutoff limit must await concrete evidence as to the presence or absence of uranium mineralization associated with the anomalous waters. Within a broad reconnaissance area, the hydrogeochemical method has demonstrated its utility for delineating specific areas of favorability.

RECOMMENDATIONS FOR FURTHER STUDY

As in any investigation of this nature, answers to many problems were not obtainable within the limitations imposed by time, and other problems developed for which answers should be sought.

Recommendations for further study are categorized in two general groups: (1) Those related to areas having enhanced favorability for uranium mineral occurrences based on the detection of anomalies in water, and (2) supporting studies of a theoretical nature.

Areas of Anomalous Water

For areas of favorability in Michigan associated with the Republic granite-Middle Huronian contact it is recommended that two or more areas be selected for further detailed study to determine the source of uranium in the waters. An effort should be made to develop knowledge concerning the mode of uranium enrichment and its possible genetic relation to the granitic intrusive.

Coincident with the study of marginal relationships, the areas of anomalous waters wholly within the granitic body should be investigated. A suitable drainage area for this study is Flat Rock Creek, where it is recommended that a detailed study be made of uranium in water and solids in the area of the Sagola Swamp, including the highland drainage area to the west.

No further work is recommended for areas of high favorability in Wisconsin until data from the preceding studies can be evaluated.

Study of limited areas of favorability in Cambrian sandstone on the south shore of Lake Superior should be deferred. However, consideration should be given this formation as possible host rock for low grade uranium deposits in the event that a need should develop for long range potential investigations in the area.

Supporting Studies

It is recommended that further statistical studies be directed especially toward determining the distribution of uranium in waters of the investigated area. Such studies should include the statistical treatment of other parameters such as U/K, U/HCO_3, U/SO_4 for waters of the region to determine whether anomalous waters obey a lognormal distribution, and show a significant contrast with waters which are not anomalous.

It is recommended that a complete investigation be made on the character and ion exchange capacity of brown waters, i.e., those which are associated with swamp and peat deposits and which contain polyacids of the humic or fulvic type. The study should determine the effect of such acids on the mobility of uranium, bicarbonate and other diognostic ions in natural waters, and provide an understanding of the interference which the organic complex exerts on analytical procedures for trace amounts of uranium.

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APPENDIX I

ANALYTICAL PROCEDURES

Fluorimetric Determination of Uranium in Geochemical Samples

Introduction

The analyses of different types of geochemical samples containing minute quantities of uranium pose many problems. The primary requisite for trace analysis is a sensitive detection method, because the concentration of uranium in these materials may be as low as a few tenths of one part per billion. In order to solve these problems, a certain amount of basic information is needed on the different steps and procedures required in the determination of trace amounts of uranium.

Two general methods have been widely used to determine small amounts of uranium in earth materials. The first or colorimetric method uses various reagents such as ammonium thiocyanate, ascorbic acid or hydrogen peroxide (in either alkaline or slightly acid solution) to obtain a solution of uranium suitable for optical measurements at an appropriate wavelength. Such methods, while adequate for detection of uranium in the range of 5×10^{-5} to 2×10^{-2} grams, are not sufficiently sensitive for the parts per million or parts per billion ranges encountered in hydrogeochemical studies.

The preferred and more sensitive method for determining uranium is based on the uranium activated fluoresence of sodium fluoride under ultraviolet light. A melt is obtained by fusing uranium minerals with an alkali carbonate-fluoride flux and the fluoresence of the melt is determined with a sensitive fluorimeter. The intensity of the fluoresence is proportional to the amount of uranium present; 10^{-10} grams of uranium are detectable by this method. The following sections are devoted to studies of various phases of the fluorimetric determination of uranium.

The determination of uranium in geochemical samples can be divided into three phases:

1. Decomposition of sample and solution of uranium.
2. Isolation of uranium in a relatively pure fraction.
3. Incorporating uranium into a flux pellet and determining fluoresence of the resulting disc.

All three phases must be considered in the analysis of rock and soil, but only the last two phases are required for analysis of uranium in waters.

Decomposition of Sample and Solution of Uranium

The rock and soil samples, ignited if they contain organic material, can be decomposed by heating with a small amount of sulfuric acid to dryness. The amount of sulfuric acid used is that necessary to moisten the sample. One or two drops of nitric acid may be added to insure the removal of traces of organic material. If manganese is suspected after the residue has fumed, add 5 ml of 10% H_2SO_4 and 0.2 gm $NaHSO_4$. Otherwise take up with 10% H_2SO_4 and filter into small volumetric flasks and dilute to mark with water. This decomposition procedure is adequate for nearly all samples which contain uranium in the parts per billion range. A comparison between granite samples analyzed using sulfuric acid decomposition and with HF-HNO_3 procedures of Grimaldi, et al, (1954) is given below.

	U_3O_8 Found (ppm)	
Sample No.	(H_2SO_4)	($HF-HNO_3$)
48513	11	17
48514	5	6
48515	28	25
48526	12	16
48527	20	22
48528	9	10

Granite samples are a most difficult type to decompose with sulfuric acid probably because some of the uranium is present in minerals which resist the action of sulfuric acid. The precision of the method is such that the discrepancies noted in the above table are hardly significant. One advantage of using the H_2SO_4 method, despite its slightly lower efficiency, is that the extractive procedures using ion exchange resin are carried out in a weak sulfate solution.

Isolation of Uranium from Sample

Ostle (1954) gives a procedure for removing uranium from a sulfate solution using Amberlite IRA-400 resin in the hydroxide form. The resin should be nearly chloride free and attaining it by repeated washing with base is a tedious chore. Since sodium bisulfate is added to the sample before analysis, the resin will be largely converted to the sulfate form before all of the sample has passed through the resin column. Consequently, the resin should be just as effective in the sulfate form as in the hydroxyl form. This was confirmed by converting the resin to the sulfate form and checking the recovery of known amounts of uranium.

Amberlite IRA-400 resin was converted to the sulfate form by washing a column of the resin with 10% sulfuric acid until the effluent was free of chloride ion. The excess sulfuric acid was removed by washing with demineralized water. The resin was stored under demineralized water.

In addition to being easier to prepare, the sulfate form of the resin has one major advantage over the hydroxyl form. The hydroxyl form adheres strongly to the resin column until it was dried, but the sulfate form of the resin can be washed from the column with a stream of water from a wash bottle.

Resin columns were prepared from a length of 5/16 inch O.D. tygon tubing 3.5 inches long. One end of the tubing was closed with a pinch-cock clamp while the other end was slipped over the stem of a 125 ml separatory funnel. It was found that a resin column 1.5 inches deep would remove as much as 0.005 mg U_3O_8 from a 100 ml water sample at a flow rate of 5 ml/min. In all subsequent studies a minimum resin bed thickness of 1.5 inches was used with a flow rate not in excess of 3 ml per minute.

It was not necessary to add sodium bisulfate or sulfuric acid to the water sample to obtain complete removal of uranium. A study of the effect of adding sulfuric acid to the sample before it was passed through the resin was made. The results are summarized below.

		Gm x 10^{-6} U_3O_8	
Ml 10% H_2SO_4 Added	Sample Volume	Added	Found
0	100 ml	0.25	0.25
1	100	0.25	0.25
3	100	0.25	0.26
5	100	0.25	0.23
7	100	0.25	0.21
10	100	0.25	0.22

It can be seen that the amount of acid added had no effect on the recovery if no more than 3 ml of 10% H_2SO_4 per 100 ml of sample was used.

The resin containing the uranium was washed out of the column into a platinum dish which is used to prepare the pellet for the floresence measurement. The excess water is evaporated under an infra-red lamp and the resin ignited leaving the uranium in the ash. Two grams of flux were added to the dish. After fusion and annealing the fluoresence of the pellet is read.

Incorporation of Uranium into Flux Pellet and Determination of Fluoresence

A homogeneous fusion mixture containing fluoride is necessary to provide reproducible phosphors for the determination of fluoresence by instrumental means. One problem inherent in preparing such a flux is in obtaining mixtures which have a sufficiently low uranium content. The need for reagent grade reagents and scrupulously clean vessels is essential.

Preparation of Flux

The procedure recommended by Grimaldi, et al (1954) is to heat in a platinum dish a mixture consisting of 9 gm sodium fluoride, 45.5 gm sodium carbonate and 45.5 gm potassium carbonate by weight, at a temperature of 650°C for 15 or 20 minutes or until most of the material has fused. As many 100 gm lots are fused as desired. After the melt has cooled, the cakes are broken up in a large mortar with a pestle until all of the material will pass through a 5-mesh screen. The lumps of flux are then tumbled in a dry ball mill until the mixture will pass through a 65-mesh screen. The balls are removed and tumbling is continued for several hours.

This elaborate procedure was found to be unnecessary since adequate mixing was obtained by manually mixing the proper amounts of reagent grade components in a closed quart glass jar or by placing the jar and its contents on the rollers of a ball mill for an hour or two. Tests of the flux indicated that homogeneous, low background material was obtained by either method. Small lots of flux prepared in this manner were quite uniform from lot to lot and within lots and could be blended to make larger amounts of flux with a uniform blank.

Ordinarily the fluoresence of the flux corresponded to a reading of 0.017 to 0.020 micro-amperes on a Jarrell-Ash fluorimeter. The reading increased 0.001 micro-amperes for each 0.001 micro-gram of uranium in a flux pellet weighing two grams. The fluoresence of a two gram pellet varied linearly with the amount of uranium in the pellet up to, at least, 10 micrograms of uranium. If small amounts of certain impurities which quench the fluoresence are present, the linear relation is no longer valid.

Determination of Fluoresence

Depending on the uranium content, an aliquot of the solution of the decomposed sample or the water sample is filtered and the uranium extracted with a resin column. Two resin blanks are treated with demineralized water and also carried through the following steps given in RME-131 (Illsley and Kinnaman, 1959). The resin is washed from the tube into a low platinum dish of about 10 ml capacity and the excess water withdrawn by means of a medicine dropper. The resin is dried in the dish under infrared heat. When dry, the dish is heated in a fume lood to burn off the resin. Ignition is continued until only white ash remains.

To the ash in the dish are added 2.00 grams of carbonate fluoride flux which is heated to fusion and maintained in a melt for 4 minutes while swirling the dish, to assume homogeneity of uranium in flux. The melt is then allowed to solidify and annealed at 150° to 200°C for 10 minutes, then cooled to room temperature and removed from the dish by inverting over an asbestos board or other clean surface.

The fluoresence of the cooled discs is measured with a reflection type fluorimeter. The average value of the readings of the two blanks is subtracted from the reading of the sample. The amount of U_3O_8 present in the sample in micrograms (μg) is determined from a standard curve prepared according to the procedure given in RME-131 p.21 (Illsley and Kinnaman).

Quenching Studies

Price, Ferretti, and Schwartz (1945) have studied the theoretical aspects of the quenching process and checked the theory against experimental results using a sodium fluoride flux. They found that the percent quenching was a function of the concentration of quencher in the flux and was independent of the amount of uranium present over a wide range of uranium concentrations. Since a different flux was used in this laboratory (containing sodium and potassium carbonate in addition to sodium fluoride), a study was made of the quenching by iron, manganese, and thorium in this particular flux.

Solutions containing 0.25 micrograms of U_3O_8 and varying amounts of quencher were transferred to platinum dishes and heated to dryness.

Two grams of flux were added to each dish. After fusion and annealing the fluoresence of the pellets was measured. The following table gives the quenching as a function of concentration of quencher in the flux for the three quenching impurities where C = micrograms of quencher/gm of flux and

$$\phi = \frac{\text{Reading-Blank (with quencher)}}{\text{Reading-Blank (without quencher)}}$$

C	ϕ		
	Manganese	Iron	Thorium
0	1.00	1.00	1.00
2.5	0.80	0.98	0.92
5.0	0.71	0.91	0.57
12.5	0.54	0.88	0.44
17.5	0.46	0.86	0.41
25	0.36	0.88	0.41

Reference to the above table indicates that thorium and iron behave as if they had a limited solubility in the flux. Iron would not cause an error of more than 10 percent if a coating of the oxide does not cover the surface. Thorium can cause a greater error but it is not commonly found in most samples in quantities great enough to cause serious interference. Manganese is sometimes found in stream sediments in quantities large enough to cause serious interference. Unlike iron and thorium, it is quite soluble in the flux. This is due to the formation of manganates which are stable in alkaline media. Manganese will give the flux pellet a bluish green cast if its concentration is as low as 5×10^{-6} gm/gm of flux so that the presence of manganese in a sample is readily detected.

Removal of Impurities

A series of studies were made to test the removal of quenching impurities using Amberlite IRA 400 resin. Synthetic solutions containing 0.25×10^{-6} grams U_3O_8 and 50×10^{-6} grams of quencher were prepared. One hundred ml samples of the solutions to which 1, 2, 3, 4, or 5 ml of 10 percent sulfuric acid was added were passed through the resin. The results indicated that iron and manganese were not absorbed on the resin. The following table shows the results obtained with thorium.

Ml 10% H_2SO_4 Added	$\phi = \frac{\text{(Reading-Blank) Thorium Added}}{\text{(Reading-Blank) No Thorium Added}}$	$\frac{\text{gm} \times 10^{-6}\ U_3O_8 \text{ Recov'd.}}{\text{gm} \times 10^{-6}\ U_3O_8 \text{ Added}}$
1	0.57	0.54
3	0.68	0.66
5	0.84	0.78
7	0.91	0.84
10	0.83	0.80

The poor recovery for the samples to which 1 to 3 ml of 10 percent sulfuric acid were added was due to the quenching by thorium absorbed by the resin. The amount of quenching decreased as more acid was added to the sample but at the same time the uranium adsorbed by the resin decreased.

The amount of thorium adsorbed by the resin can be estimated by the amount of quenching observed in the pellet. The value of ϕ when 1 ml of acid was added was 0.57. This value of ϕ was observed previously when 10×10^{-6} gm of Th were present in the pellet. Thus approximately $\frac{10 \times 10^{-6} \times 100}{50 \times 10^{-6}} = 20\%$ of the thorium was retained on the resin.

In the analysis of rock and soil samples the effect of quenching impurities in the sample can be greatly reduced or eliminated by limiting the amount of quencher in the pellet. This is usually accomplished by putting a sample into solution, diluting to a large volume and analyzing a small aliquot for uranium. Such a procedure is not successful if the uranium content of the sample is small or if the sample contains large amounts of the quencher, because the aliquot necessary to eliminate quenching does not contain enough uranium to analyze. A larger aliquot can be used if it is first diluted to 100 ml and analyzed using the procedure for water samples. The interference of manganese is easily eliminated by this procedure. Large amounts of iron interfer, but the quenching of iron is not serious if the sodium and potassium carbonate-sodium fluoride flux is used. As noted in the previous section, the removal of large amounts of thorium is not possible using this procedure.

Sulfate Determination

Introduction

One of the purposes of the field program in Michigan was to locate uranium ores associated with pyrite. It was anticipated that the sulfate ion concentration in surface and well waters might be a guide to the location of pyrite concentrations. A rapid method for determining small amounts of sulfate has been described by Fritz and Yamamura (1955). Enough laboratory work was done to verify and adapt the method for use in determining sulfate concentrations in the field with an accuracy of ± 4 ppm.

Field Procedure for Determining $SO_4^{=}$ in Natural Waters which are Free of Phosphate

Chemicals and Equipment

Barium perchlorate $\left[Ba(ClO_4)_2 \cdot 3H_2O \right]$ available from G. Frederich Smith Chemical Company, Columbus, Ohio
Isopropyl alcohol
Ethyl or methyl alcohol (Absolute)

Thorin indicator O (2-hydroxy-3, 6-disulfo-1-napthylazo) benzenearsonic
acid, disodium salt, 0.2 persent water solution
Hydrochloric acid, 10 percent solution
Ion exchange resin, Amberlite IR-120 (H+) Analytical Grade
Kimble Opticlear vials 5 dram K-5 No. 7600
Medicine dropper
Pyrex glass wool
Glass or plastic tube ca 25 mm (diameter), 6 inches long
Rubber stoppers to fit tube
Pinchock clamp

1. Preparation of thorin indicator

   Weigh 0.20 gm of thorin indicator and dissolve in 25 ml of distilled water. Dilute to 100 ml.

2. Preparation of barium perchlorate solution

   Weigh 5.00 grams of barium perchlorate, $Ba(ClO_4)_2 \cdot 3\ H_2O$. Dissolve in 50 ml of distilled water. Dilute to 500 ml. Transfer 20 ml of barium perchlorate solution to a 100 ml volumetric flask. Dilute to 100 ml with isopropyl alcohol. Adjust pH to 3.2 with 10 percent hydrochloric acid. Standardize against 0.005 H_2SO_4 solution using following procedure:

   a. Prepare 0.005 N sulfuric acid by diluting 5.00 ml of N/10 sulfuric acid to 100 ml.

   b. Pipet 10 ml of 0.005 N sulfuric acid to 50 ml Erlenmeyer flask. Add 40 ml of absolute methyl alcohol (ethyl alcohol), and two drops of thorin indicator solution.

   c. Titrate with barium perchlorate solution to a yellow or pink color change.

   d. Calculate mg $SO_4^{=}$/ml of $Ba(ClO_4)_2$ solution $= \dfrac{\text{Normality of } H_2SO_4 \times 480}{\text{ml of } Ba(ClO_4)_2}$

3. Preparation of ion exchange column.

   Bore a hole in rubber stopper so that the glass tube of a medicine dropper can be inserted. Insert the glass tube. Slip a short length of rubber tubing over the glass tube and close with a pinchcock clamp. Insert the stopper in one end of the 25 mm x 6" glass or plastic tube. Place a pad of pyrex glass wool over the stopper outlet and fill the tube half full with distilled water. Add Amberlite IR 120 (H+) ion exchange resin until a bed 3 inches deep has been formed. Place a pad of pyrex glass wool on top of the resin. Add clean sand or glass beads to hold down the glass wool pad. Fill the column with water and close with a rubber stopper. The resin column should never be allowed to drain dry.

4. Calibration of medicine dropper.

   Using the medicine dropper, add 150 drops to a tared liquid weighing bottle. Determine the weight of the water to the nearest 0.01 gm. Calculate gm x 10^{-6} of $SO_4^=$/drop of $Ba(ClO_4)_2$ solution:

$$\text{gm} \times 10^{-6}\ SO_4^{=}/\text{drop} = \frac{\text{Mg } SO_4^{=}/\text{ml of } Ba(ClO_4)_2 \text{ solution} \times 150000}{\text{Wt. of Water (in grams)}}$$

Field Procedure:

1. Pass 150 ml of water sample through resin column. Discard.
2. Pass an additional 10-15 ml of water sample through the resin. Pipet 2.0 ml of the water into a 5 dram Kimball Opticlear vial. Add 8 ml of absolute methyl (ethyl) alcohol and 1 drop of thorin solution. If the color of the solution is not yellow, add 10 percent HCl dropwise until the color changes to yellow.
3. Add standard $Ba(ClO_4)_2$ solution until the color of the solution changes

from yellow to pink. Count the number of drops added.

$$\text{ppm } SO_4^{=} = \frac{\text{gm} \times 10^{-6}\ SO_4^{=}/\text{drop} \times \text{no. of drops}}{2}$$

Note 1. Each drop of $Ba(ClO_4)_2$ solution is equivalent to approximately 4 ppm of SO_4 if a 2 ml sample is used.

Note 2. Larger samples may be used if enough alcohol is added to make the final solution contain 80 percent by volume of alcohol.

Preparation of Resin Column and Determination of Sample Size Necessary to Flush the Resin Column

The resin column consisted of a piece of glass tubing 25 mm O.D. and 6 inches long. It was closed at the bottom with a one hole rubber stopper through which a piece of 8 mm glass tubing was inserted. A piece of rubber tubing was slipped over the glass tubing. The rubber tubing was closed with a pinchcock clamp. A small pad of pyrex glass wool was placed over the column outlet. The column was then half filled with water and Amberlite IR-120 (H+) ion exchange resin was added until a bed 3 inches deep had been formed. A piece of pyrex glass wool was placed on the top of the resin bed and enough 30 mesh Ottawa sand was added to form a bed 1-1/2 inches deep.

A sodium sulfate solution containing 0.0592 mg $SO_4^{=}$ was passed through the column which contained demineralized water. Fractions of the effluent were collected and analyzed for $SO_4^{=}$ by titrating with standard $Ba(ClO_4)_2$ solution (0.422 mg $SO_4^{=}$/ml). The results are summarized below.

Fraction Collected	Ml of Sample	Ml $Ba(ClO_4)_2$ Solution	Mg $SO_4^{=}$ / Ml of Sample
0 - 50 ml	10.0	.42	0.018
50 - 75 ml	10.0	.88	0.039
75 - 100 ml	10.0	1.22	0.054
100 - 110 ml	10.0	1.36	0.060

Since the sulfate concentration of the feed solution was 0.059 mg/ml, it was concluded that 100 ml was sufficient to flush the previous solution from the resin column.

Performance of Field Method for Sulfate in Waters

Sodium sulfate solutions containing 10, 20, 40, 60, 80 and 100 ppm of sulfate were prepared. Sample of 150 ml of solution were passed through the resin column. The first 125 ml were discarded and the remaining 25 ml were collected. Two 2 ml samples of each solution were analyzed. The results which are summarized below are well within acceptable limits required of precision and accuracy for field application.

ppm SO_4	Drops $Ba(ClO_4)_2$ Added (4 ppm/drop)	ppm Found	Average
10	3	12	
10	3	12	12
20	6	24	
20	5	20	22
40	11	45	
40	11	45	45
60	16	66	
60	15	62	61
80	19	78	
80	19	78	78
100	24	98	
100	25	102	100

Carbonate and Bicarbonate Determination

Introduction

Although pH of water samples was normally determined at the collecting site with a portable meter, a re-determination was made on each sample prior to determining the alkalinity in the laboratory. Knowledge of the pH was necessary to establish the presence of carbonate ion in waters; if the pH was greater than 8.2 carbonate is present and must be determined before an analysis can be made for bicarbonate.

Procedure

The procedure as adapted from Faber H. A., et al (1955) is based on a volumetric determination using standardized H_2SO_4. The reagents are prepared as follows:

Standard sulfuric acid, 0.020 N. Prepare a stock solution approximately 0.2 N by diluting 6 ml conc: H_2SO_4 to 1 liter. Standardize against pure anhydrous Na_2CO_3. Dilute an exact quantity of the stock solution to 1 liter to prepare the 0.020 N solution.

Phenolthalein indicator - Dissolve 0.5 gm phenolthalein in 50 ml ethyl alcohol and then add 50 ml demineralized water. Add 0.02 N NaOH dropwise until a faint pink color appears. Store in a glass bottle.

Methyl orange indicator - Dissolve 0.05 gm methyl orange in 100 ml demineralized water.

The procedure for determination of carbonate and bicarbonate follows: Transfer 50 ml of filtered water sample to a pyrex beaker and measure pH. If pH is greater than 8.2, add 0.2 ml phenalphthalein indicator and titrate with 0.02 N H_2SO_4 dropwise until pH is lowered to 8.2. Solution should have just lost pink coloration and become pale yellow. Record volume of acid used (Ta_1).

If pH is less than 8.2, or after completing above titration add 5 drops of methyl orange solution and titrate with dropwise addition of 0.20 N H_2SO_4 until indicator changes to pink at pH 4.0. Record volume of acid used Ta_2.

Calculations

$$\text{ppm } CO_3 = \frac{\text{N acid} \times 2\ Ta_1 \times 1000 \times \text{meq wt } CO_3^{=}}{\text{ml Sample}}$$

$$= \frac{0.02 \times 2\ Ta \times 1000 \times 60}{50}$$

$$= 48\ Ta$$

$$\text{ppm } HCO_3^{-} = \frac{\text{N acid} \times 2\ Ta_2 \times 1000 \times \text{meq wt } HCO_3}{\text{ml Sample}}$$

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APPENDIX II

STATISTICAL ANALYSIS OF HYDROGEOCHEMICAL DATA

Introduction

In prospecting for minerals with geochemical techniques, soil or water samples are collected and analyzed for some diagnostic property of the mineral being sought. For example, if the search is for copper ores, the concentration of copper in soils or waters is the diagnostic property which is determined. In the hydrogeochemical search for uranium ores the ratio of uranium concentration to conductivity (U/K) of water samples has been used as a diagnostic parameter. Reasons for using the ratio U/K are discussed in the following paragraphs.

In general, if measurements of some diagnostic property are usually low and close to the average value unless influenced by contact with mineralized zones, no difficulties are encountered in detecting anomalies. Unfortunately the U/K values for surface waters do not always fit into such a pattern because in a large geographic area they commonly vary over a wide range. The distribution of these values is approximately log normal, i.e. the distribution of the quantity log U/K is normal. In some areas waters known to be anomalous may have U/K values which are lower than the usual background value.

Uranium is present in almost all rock types in amounts usually ranging between 0.05 to 50 parts per million. The amount of uranium dissolved by waters which come in contact with these rocks will depend upon many factors, e.g. the surface area of rock with which a given volume of water makes contact, the chemical nature of the waters, the uranium content of the rock and the ease with which the uranium is leached, etc. It can be seen that numerous combinations of circumstances are possible which affect the amount of uranium taken up by natural waters.

In general waters which come into intimate contact with rock type containing trace or larger amounts of uranium would be expected to dissolve more uranium than waters which have only limited contact with the same rock type. By the same token if more uranium is dissolved by water, more of the other rock constituents such as Na^+, K^+, Ca^{++} and Mg^{++} will also be dissolved. The alkali and alkaline earth metals in solution can be estimated from the conductivity, K, of the water and the ratio of U/K should, to a certain extent, be independent of the intimacy of contact between rock and water.

In well indurated, impermeable rocks containing greater than background concentrations of uranium minerals the area of contact between the rock constituents and ground waters is limited. The degree of contact between ground waters and any zones of uranium mineral concentrations in the rock would also be limited. However owing to the generally higher uranium content of the rock the amount of uranium dissolved compared to the amount of other metals dissolved should be greater. Even though the concentration of uranium in these "anomalous" waters might not be large, the ratio U/K would be higher than the U/K ratio of other waters which contain higher concentrations of uranium and other ions.

The distribution of the ratio U/K for surface waters is found to be log normal, that is, the log U/K is normally distributed. This statement must be qualified with respect to the number of samples from a given stream or stream system which are used. Obviously one cannot include twenty samples from one stream and two samples from each of 20 other streams and expect an unbiased picture of the variation of U/K in the waters of the area. Since the variations in U/K for the normal waters cannot be directly related to environmental factors, it seemed advisable to determine if a statistical analysis of the data could be used to delineate anomalous waters from background values.

Information Obtained From a Statistical Analysis

If a set of data exhibit a normal distribution, this distribution can be described by two parameters; the mean, μ, and the standard deviation σ. The mean is a measure of the central tendency of the data while the standard deviation is a measure of the spread of the data. For a more detailed discussion of these quantities the reader should consult standard texts on statistics such as Mode (1951) or Dixon and Massey (1951).

When the parameters of a normal distribution are known it is possible to predict the fraction of the data which fall within a certain range of values. If a normal population has a mean, $\mu = 10$, and a standard deviation, $\sigma = 2$, the value of 12 is said to exceed the mean by one standard deviation. For a normal distribution 15,8 percent of the values can be expected to exceed the mean plus one standard deviation $(\mu + \sigma)$. Stated in another way the odds against obtaining a value as great as or greater than $\mu + \sigma$ are about 5 to 1. Table 1 gives more information concerning the fraction of the values which exceed the mean by multiples of the standard deviation.

TABLE I

$X = \mu + n\sigma$	% of values greater than X	Odds against obtaining a value greater than X
$\mu + \sigma$	15.87	5.30 to 1
$\mu + 1.34\ \sigma$	9.01	10.1 to 1
$\mu + 1.5\ \sigma$	6.68	14.0 to 1
$\mu + 2\ \sigma$	2.27	43.1 to 1
$\mu + 2.33\ \sigma$	0.99	100 to 1
$\mu + 2.5\ \sigma$	0.62	160 to 1
$\mu + 3\ \sigma$	0.13	770 to 1
$\mu + 3.5\ \sigma$	0.002	50,000 to 1

In evaluating the results of a hydrogeochemical reconnaissance program, two types of errors are possible. The first type of error is to describe a water sample as anomalous when in fact it is not. The second type of error is to describe a water sample as part of the normal environment when actually it represents water which has been in contact with an ore zone. The above statements imply that both the normal and the anomalous waters from an area fit into separate distributions. It has been shown that distribution of a geochemical property of normal waters from an area is log normal, but data indicating the type of distribution for anomalous waters are very meager. Assuming that the anomalous waters also show a log normal distribution, it is possible to examine some of the available data with respect to these errors.

The U/K ratios of 56 water samples from an area near Mt. Spokane, Washington were examined statistically. The distribution of U/K x 10^6 is log normal with a mean, $\bar{x} = 2.58$, and standard deviation $s = 0.56$.

Ten of these samples are known to be anomalous because the water originates in or flows through zones of known uranium deposits. Assuming a log normal distribution for the anomalous samples, the mean and standard deviations are $\bar{x} = 3.46$ and $s = 0.40$. Although 10 is not a very large number of samples to use for calculating $\bar{x}$ and s, the value for s is reasonable when compared to the values obtained from other areas.

Figure 6 is a plot of the theoretical distribution curves for the normal and anomalous waters. Referring to Figure 6, it can be seen that the theoretical distribution curves exhibit considerable overlap. There is a range of U/K values which could belong to either distribution. Because there is a large overlap, it is not possible to set a high cutoff such as $\bar{x} + 2.5$ s or $\bar{x} + 3$ s, without eliminating most of the anomalies. In the Spokane area a cutoff of $\bar{x} + s$ would detect all but one of the anomalies. The one standard deviation cutoff would also include approximately 15% of the normal waters as anomalous. This means that if $\bar{x} + s$ were used as a cutoff to guide an exploration program a total of 18-20 streams would be investigated in detail and about one-half of them would turn out to be anomalous.

In Michigan the known anomalous waters have U/K ratios which are only slightly greater than the one-standard-deviation cutoff determined from the log U/K distribution. The almost complete lack of knowledge of uranium deposits in the Northern Peninsula of Michigan and Northeastern Wisconsin makes it very difficult to establish a valid cutoff for U/K. The cutoff values chosen are arbitrary and are subject to change as more information becomes available.

Calculation of Parameters

To calculate the parameters for the log normal distribution the data are first transformed to logarithms and the mean and standard deviation of the logarithms are calculated in the usual manner. If the number of samples is large, it is simpler to divide the raw data into intervals so that the ratio of the maximum value to the minimum value for each interval is a constant and to calculate the parameters using the grouped data. This method is described in more detail in the following paragraphs.

The data are divided into groups: group 1 contains all values between x_0 and x_2, group 2 between x_1 and x_2......group n contains all values between xn_{-1} and x_n. x_0 and x_n are the minimum and the maximum values appearing in the raw data. The different values of x are related by the equation:

$$\frac{x_1}{x_0} = \frac{x_2}{x_1} = \frac{x_3}{x_2} = \ldots\ldots \frac{x_n}{x_{n-1}} = \text{Constant}$$

This procedure insures that $(\log x_1 - \log x_0) = (\log x_2 - \log x_1) = \ldots\ldots = (\log x_n - \log x_{n-1}) = \frac{1}{n}(\log x - \log x_0)$. The proper average value for the intervals is the geometric mean of the end points or $\sqrt{x_0 x_1}$, $\sqrt{x_1 x_2}$, ..., $\sqrt{x_{n-1}\, x_n}$.

The procedure to be used in the calculation is summarized below:

1. Determine the maximum and minimum values which appear in the data, e.g. 10 and 1000.
2. Find the logarithms of these values. (log 10 = 1, log 1000 = 3). Calculate log (max. value) - log (min. value). (log 1000 - log 10 = 2).
3. Choose the number of intervals into which the data are to be divided so that the average number of values in each interval is between 5 and 25. If the set of data is composed of 200 values

it could be divided into 10 groups containing an average of 20 values per group. (Or into 8 groups containing an average of 25 values per group). Determine k by dividing log (maximum value) minus log (minimum value) by 2 times the number of groups and determine the anti-logarithm of the results.

$\frac{(\log 1000 - \log 10)}{2X10} = \frac{2}{20} = .1000$; k = antilog .1000 = 1.259).

4. Multiply minimum value by k to get the mid-point of group 1. Multiply this result by k to get the minimum value of group 2. Repeat to get the mid-point and minimum values of each group.

   Minimum value group 1 = 10 k = 1.259

   Mid-point group 1 = 10 x 1.259 = 12.59 or 12.6.

   Minimum value group 2 = 1.259 x 12.59 - 15.85 or 15.8.

   Mid-point group 2 = 19.96 or 20.0

   Minimum value group 3 = 25.13 or 25.1, etc.

5. Determine the number of values which fall within the range of values for each group. (Number of values between 10 and 15.7, between 15.8 and 24.9, etc.).

6. Calculate the mean, $\bar{x}$, and the standard deviation s from the grouped data. The calculations are illustrated in the following tabulation:

Group	Range $(x_n - x_{n-1})$	Midpoint x_i	Frequency f_n	Log x_i	f log x_i	f(log $x_i)^2$
1	10-15.7	12.6	1	1.1004	1.1004	1.2109
2	15.8-25.0	20.0	6	1.3010	7.8060	10.1556
3	25.1-39.7	31.6	19	1.4997	28.4943	42.7329
4	39.8-63.0	50.1	23	1.6998	39.0954	66.4544
5	63.1-100.0	79.5	50	1.0004	95.0200	180.5760
6	100.0-158.5	126	47	2.1004	98.7188	207.3490
7	158.6-251.3	200	30	2.3010	69.0300	158.8380
8	251.4-398.4	316	16	2.4997	39.9952	99.9760
9	398.5-631.5	501	6	2.6998	16.1988	43.7335
10	631.6-1000	795	2	2.9004	5.8008	16.8246
			200		401.2597	827.8509

$\Sigma(f_n) = 200$

$\Sigma(f_n \log x) = 401.2597$

$\Sigma(f_n (\log x)^2) = 827.8509$

$$\bar{x} = \frac{\Sigma(f_n \log x)}{\Sigma(f_n)} = \frac{401.2597}{200} = 2.0063$$

$$S^2 = \frac{\Sigma(f_n (\log x)^2)}{\Sigma(f_n)} - \bar{x}^2 = \frac{827.8509}{200} - (2.0063)^2 = 4.1393 - 4.0252 = .1141$$

$S = .3378$

The grouped data used in the above table were derived from a log normal population with $\bar{x} = 2.000$ and $S = 0.3333$.

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APPENDIX III

EFFECTS OF ORGANIC MATERIALS ON URANIUM IN NATURAL WATERS

Introduction

Most of the surface waters in the Northern Peninsula of Michigan originate within or pass through a swamp environment. Consequently nearly all of the waters have an opportunity to contact decaying organic debris. Many of these waters are stained brown by a material probably derived from this organic debris. Information concerning the behavior of uranium in the presence of peat, indicates that the constituents of a bog or swamp terrain may exert some influence upon the uranium present in the surface waters. Experiments performed by Szalay (1954) indicated that humic acids readily take up uranium from solution. Manskaia, et al (1956) has shown that peat can absorb uranium from nitrate solution. His work indicates that much of this uranium can be recovered by treating the peat with an alkaline leaching solution to release humic and fulvic "acids" from the peat. These organic "acid" fractions are considered by Manskaia to be an important factor determining the ability of natural waters to carry uranium.

This section reports some experimental studies designed to investigate the behavior of uranium in the presence of organic debris.

Leaching of Uranium from Organic Debris of Bog Material

One stream of interest in Marquette County, Michigan is West Branch of Ely Creek which flows through a bog near its junction with Ely Creek. The upper two or three feet of the bog is composed of an interlayered mixture of decayed organic debris and very fine, silty sand which is known to contain uranium.

A sample of the bog material, No. 48413, consisting of upper six inch layer was selected for study. Ten samples weighing approximately 0.25 gms were transferred to beakers and leached with 15 ml of an alkaline leach solution for a period of two hours. One of two drops of isoamyl alcohol was added as wetting agent. The slurry was filtered and washed with water. The combined filtrates and wash liquors were diluted to 100 ml and 25 ml aliquots were analyzed for uranium. The residues were ignited and also analyzed for uranium. The results are summarized below.

Sample No.	Wt. of Sample	Leach Solution	gm $U_3O_8 \times 10^{-6}$ Leached	gm $U_3O_8 \times 10^{-6}$ in Residue	% U_3O_8 Leached gm $U_3O_8 \times 10^{-6}$
1	0.250	10% NH_4OH	0.82	3.4	20
2	0.252	10% NH_4OH	0.70	3.2	18
3	0.254	5% NH_4OH	0.78	3.0	21
4	0.250	5% NH_4OH	0.85	2.7	24
5	0.252	1% NH_4OH	0.68	2.8	19
6	0.254	1% NH_4OH	0.20	2.8	7
7	0.250	5% Na_2CO_3	3.9	0.45	90
8	0.251	5% Na_2CO_3	4.0	0.22	95
9	0.253	1% Na_2CO_3	4.0	0.28	93
10	0.252	1% Na_2CO_3	4.0	0.35	92

Considerably more effective leaching of uranium is accomplished by sodium carbonate solutions than with ammonia. When the carbonate leach solutions are acidified, dark brown humic acid precipitates, leaving the light yellow colored fulvic acids in solution. The fulvic acids have a similar appearance to the ammonia leach solutions.

Another experiment was conducted using Sample 48418 collected at a depth of 6 to 8 inches in a bog at the headwaters of Flatrock Creek in southern Marquette County, Michigan. One-half gram samples of the material were leached with demineralized water and solutions containing various amounts of sodium carbonate. Results are summarized in the following table.

Sample	pH	CO_3 ppm	HCO_3 ppm	U_3O_8 ppb
1	6.2	0	13	0.5
2	8.2	0	102	2.1
3	9.8	175	430	23
4	10.2	430	808	30

Again it can be seen that the presence of carbonate ions in the solution has a marked effect on the amount of uranium leached by the solution. The color of the leach liquor became much darker as the carbonate concentration was increased. It seems likely that most of the uranium in the organic layers is bound with the so-called humic "acid" fraction.

Investigation of Brown Coloring Material in Waters

In a recent article, Shapiro (1957) reported the results of some studies related to the brown colored material in lake waters. He was able to isolate a fraction which was a true acid having a molecular weight of 450 and an equivalent weight of 228. This fraction, consisting of a mixture of many diabasic acids, some of which were not colored, he termed humolimnic acids.

Shapiro's procedure for isolating these acids involved (1) concentration by vacuum evaporation, ion exchange or freezing (2) extracting acids from concentrated sample with ethylacetate (3) extracting acid from ethyl acetate with an alkaline solution (4) re-extraction from acidified alkaline solution with ethyl acetate and evaporation of ethyl acetate.

A limited amount of work was done to see if the humolimnic acids were present in peat and in natural waters of Michigan and Wisconsin. A sample of peat was leached with a 5% NaOH solution. The humic "acid" fraction was removed by acidifying the extract and filtering. The fulvic "acid" fraction was concentrated on a steam bath. Part of this fraction could be extracted into ethyl acetate. A sample of this material weighing 0.0313 gms was dissolved in water and titrated with 0.05 N sulfuric acid and was neutralized at a pH of about 7.5. The titration curve obtained was what one would expect for a fairly strong acid. The equivalent weight of the material was approximately 250. Further tests revealed that this yellow colored material could be leached from peat with acidified ethanol or even with demineralized water. A fraction of the material leached with acidified ethanol had an equivalent weight of 280. Isoamyl alcohol and tributyl phosphate can also be used to extract the acids from aqueous solutions.

A composite sample of stream waters collected in northeastern Wisconsin was concentrated by freezing. This technique is quite effective for this purpose and will be described in the following section. A small amount of material was extracted by ethyl acetate from the concentrated waters. Unfortunately the amount obtained was too small to obtain an accurate value for its equivalent weight.

All work reported above was of an exploratory value. One major limitation to any work in this field is the complete lack of any convenient and reliable analytical methods for identifying and measuring the amounts of these materials present in a sample.

A Procedure for Concentrating Trace Amounts of Impurities in Water Sample by Freezing

The method employed to concentrate the coloring matter in natural waters may be of some use in other investigations. If the material present in water is destroyed or altered by heat, it cannot be concentrated by boiling off the excess water. In this case it might be convenient to use freezing as a method of concentrating the impurity.

A portion of the sample is poured into a tray used to make ice cubes. The tray is placed in the freezing compartment of an refrigerator until the sample has been converted to ice cubes. Another fraction of the sample is chilled and then added to a Waring Blendor. Three or four of the sample ice cubes are added to the Blendor. The Blendor is started and allowed to run until these cubes have been completely crushed. The slurry is filtered with suction. Most of the material to be concentrated will be found in the filtrate.

This procedure can be used where there is need to concentrate a large volume of sample to less than one liter. It cannot be used if all of the material must be recovered.

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APPENDIX IV

LEACHING OF URANIUM FROM GRANITE BY WATER

Introduction

Background uranium concentrations in surface and ground waters is derived from the rock and soil with which the water came in contract. Very little information concerning the action of water in leaching uranium from rock is available. This preliminary study was designed to determine the important variables which control the removal of uranium from rocks and soils and its entry into natural waters.

Preliminary Rate Studies

Attempts were made to study the rate of solution of uranium from granite by treating weighed amounts of crushed granite with water. A column was prepared from a 2-inch I.D. plastic tube 17.5 inches long. The bottom of the column was closed with a one-hole rubber stopper through which was inserted a short section of glass tubing. A piece of rubber tubing fitted over the glass tubing and a pinchcock clamp were used to control the flow of water through the column.

The column was filled to a depth of 15 inches with about 900 grams of crushed unweathered granite. Demineralized water was added to the column and allowed to stand for different periods of time. The column was drained and the water analyzed for uranium.

This procedure was used with three granite samples from Marquette County, Michigan. The results are given below.

U_3O_8 in Water Leach (ppb)

Sample	Time (Hours) 1	2	16	19	72	96
48513	0.28		0.86	0.71	0.84	0.84, 1.0
48514	1.8	1.2	5.4	3.0	6.1	5.6, 4.8
48526	0.86	3.0	6.1	6.4	23	30, 30

The results are somewhat erratic but do indicate that eventually the concentration of uranium in water becomes essentially constant. The conductivity of the water samples for the 96 hour run was measured and the ratio (U_3O_8/K) x 10^5 was calculated. Results are tabulated below.

Sample	U_3O_8 in Water (ppb)	Conductivity (μmho)	U/K x 10^5
48513	0.84	39.5	2100
48513	1.0	39.5	2500
48514	5.6	16.0	35000
48514	4.8	16.7	29000
48526	30	63.1	47500
48526	30	65.1	46000

The water from leaching of granite sample 48514 had a reddish cast which suggested the presence of colloidal ferric hydroxide.

Effect of Bicarbonate

An experiment similar to the preceding experiments was conducted to study the effect of bicarbonate ions on the leaching of uranium from granite. The granite was leached for three hours with demineralized water and with water containing 100 mg of sodium bicarbonate per liter. The results are given in the following tabulation.

U_3O_8 in Leach Solution (ppb)

Sample	Demineralized Water	Bicarbonate Solution
48513	0.6	1.8
48513	0.3	2.2
48514	1.3	1.6
48514	1.0	6.6
48526	3.8	10
48526	2.4	12

Variance analysis of the data given above indicate that the odds are greater than 19 to 1 that bicarbonate caused an effect on samples 48513 and 48526. The data for sample 48514 are not precise enough to say whether or not bicarbonate has any effect. However, in view of the results for the other two samples it is safe to assume that the effect of bicarbonate is the same for all three samples.

The experiment was repeated except the leaching time was 115 hours with the following results.

U_3O_8 in Leach Solution (ppb)

Sample	Demineralized Water	Bicarbonate Solution
48513	0.38	3.8
48514	2.8	7.0
48526	12	44

The above data again confirms that bicarbonate significantly enhances the amount of uranium leached from granite by water.

U/K Ratio for Dolomite Leach

A sample of dolomite (Sample No. 48539 Dickinson County, SW-1/4, Sec. 7, T. 39 N., R. 28 W.) was crushed and stirred in water for one hour and allowed to stand overnight. Uranium analysis of four samples gave 0.07, 0.08, 0.08, and 0.10 ppb or an average of about 0.07 ppb. The conductivity of the water was 20.1 micromhos giving a (U/K) x 10^5 ratio of 400.

Discussion of Results

The amount of uranium in two of the three granite leach waters is quite large when compared with normal surface waters in the Northern Peninsula of Michigan. The ratio of U/K x 10^5 which is roughly proportional to the uranium in the total solids dissolved in the water is much greater than that found in surface waters.

It is to be expected that surface waters flowing over granite bedrock might exhibit a higher uranium background than those flowing over dolomite bedrock. The same behavior should apply to the influence of the rock type of boulders in till on the background uranium in the surface waters. Judging from the results of the leaching experiments, wide variations in the normal uranium concent of waters from areas of granite can be expected.

The reasons for the large variation in the amount of uranium leached from granites by water are not known. That it is not related to the total uranium concent of the granite can be seem from the following data.

Sample	U_3O_8 in Granite	(U_3O_8 in Leach Water) 96 hours
48513	17	0.9
48515	6	5.4
48526	16	30.

This type of behavior can be explained by assuming that the granite contains two types of uranium minerals; soluble and insoluble. The uranium in granite which is present in minerals such as euxenite, fergusonite, and other rare earth columbium-tantalum minerals would not be expected to be water soluble. The uranium present in less stable minerals (with respect to the action of water) is the fraction which is responsible for the normal uranium content of waters. The background uranium concentrations in surface waters are thus a more significant reflection of the "leachable" uranium in the granite.

Sample 48526 was collected near a diabase dike, which might account for the large amount of leachable uranium in this particular granite. Unfortunately, no other samples of this type granite were available for leaching studies.

It should be mentioned that the conductivity of granite and dolomite leach waters is much lower than the conductivity of most of the natural surface waters from the Northern Peninsula of Michigan. This suggests that other factors also influence the composition of the surface waters.

Conclusions

Considerable amounts of uranium can be leached from granite by water. The ease with which uranium can be leached from granite by water is not related to the total uranium in the granite.

The usefulness of hydrogeochemical methods for detecting uranium ore deposits depends ultimately upon a knowledge of the influences of geologic environment and the geochemical characteristics of natural media. Such basic knowledge is only incompletely available at the present time. Further study should be made to obtain this necessary information in order that more meaningful evaluation of hydrogeochemical data can be accomplished.

PLATE 1
GEOLOGIC FORMATIONS IN UPPER PENINSULA MICHIGAN - NORTHEASTERN WISCONSIN+

				MARQUETTE RANGE AND SOUTH SHORE			MENOMINEE RANGE			NORTHEASTERN WISCONSIN		
SYSTEM		SERIES		FORMATION OR UNIT	ROCK TYPE	THICKNESS (FEET)	FORMATION OR UNIT	ROCK TYPE	THICKNESS (FEET)	FORMATION OR UNIT	ROCK TYPE	THICKNESS (FEET)
QUATERNARY		RECENT		Alluvium, swamp lake deposits	Silt, clay, sand, gravel, muck, marl, peat, bog	0-30	Alluvium, swamp lake deposits	Silt, sand, gravel muck, marl, peat	0-30	Alluvium, swamp lake deposits	Silt, sand, gravel, muck, marl, peat bog	0-20 +
		PLEISTOCENE		Glacial drift	Till, outwash, lacustrine	0-250	Glacial drift	Sand and boulder till outwash	0-300	Glacial drift	Sand and boulder till outwash	0-300
				Unconformity			Unconformity					
PALEOZOIC		CAMBRIAN		Lake Superior sandstone	Sandstone, dolomitic, shale and sandstone conglomerate	0-100?	Lake Superior sandstone	Sandstone, calcareous often with basal conglomerate	0-300	Lake Superior sandstone	Sandstone, siltstone (eastern border of area only)	0-200
				Unconformity			Unconformity			Unconformity		
PRECAMBRIAN	ALGONKIAN	KILLARNEY GRANITE* KEWEENAWAN		Acidic intrusives	Granite	-	Acidic intrusive	Quartz sericite	-			
				Basic intrusive	Diabase and basalt (diorite)	-	Basic intrusive	Metagabbro dikes	-			
				Unconformity			Unconformity			Unconformity		
		HURONIAN	UPPER	Michigamme slate	Slate and mica schist thin beds Bijiki iron formation	1000-2000	Michigamme slate	Dark gray to black graphitic slate, calcareous slate and ferruginous cherty iron	10000±	Upper sedimentary group	Conglomerate, quartzitic, slate (?)	–
				Clarksburg volcanics	Greenstone & conglomerate (cut by diabase and basalt)	Several 1000	Quinnesec greenstone	Volcanic flows	–			
										Unconformity		
				Greenwood iron formation	Grunerite schist, sideritic slate, specular hematite	50						
				Goodrich quartzite	Quartzite and conglomerate	1500	Goodrich quartzite	Ferruginous cherty quartzite occasionally conglomeratic (locally absent)	0-500	Acidic intrusive		
				Unconformity			Unconformity					
			MIDDLE	Negaunee iron formation	Siderite slate, grunerite-magnetite schist, ferruginous slate and chert, and jaspilite	1500	Vulcan iron formation	Hematite, jaspilite ferruginous slates	650	Vulcan iron formation	Hematite, siderite, ferruginous chert, magnetic and gruneritic slates	–
				Siamo slate	Slate, graywacke and quartzite	650						
				Ajibik quartzite	Quartzite (with slate graywacke, and basal conglomerate)	700-900	Greenstone	Volcanic flow, tuffs and agglomerates	–	Basic intrusives		
				Unconformity			Unconformity			Unconformity		
			LOWER	Wewe slate	Slate with graywacke conglomerate and mica slate and schist	100-1050	Felch formation	Graywacke and schist	0-150±	Lower Sedimentary Group	Quartzite, slates, and graywacke	–
				Kona dolomite	Cherty dolomite (with slate, graywacke and quartzite)	700-1400?	Randville dolomite	Dolomite, dolomitic slate, quartzose dolomite, talcose schist	1800±			
				Mesnard quartzite	Quartzite, clean to sericitic (with basal conglomerate)	150-670	Sturgeon quartzite	Clean to sericitic quartzite grading to dolomitic schist	1000±			
							Fern Creek formation	Argillite, conglomerate, arkose	0-300			
				Unconformity			Unconformity					
ARCHEAN		LAURENIAN		Granite	Granite, gneiss, syenite	-	Granite, gneiss		-	Granite, gneiss		–
		KEEWATIN		Kitchic schist	Basic schist and greenstone	-	Schist			Schist		–
				Mona schist	Basic and acidic schist	-						RME-1099

*Stratigraphic position doubtful.
+Modified after Bayley (1904), Leith, Lund and Leith (1935), Pettijohn (1953) and others.

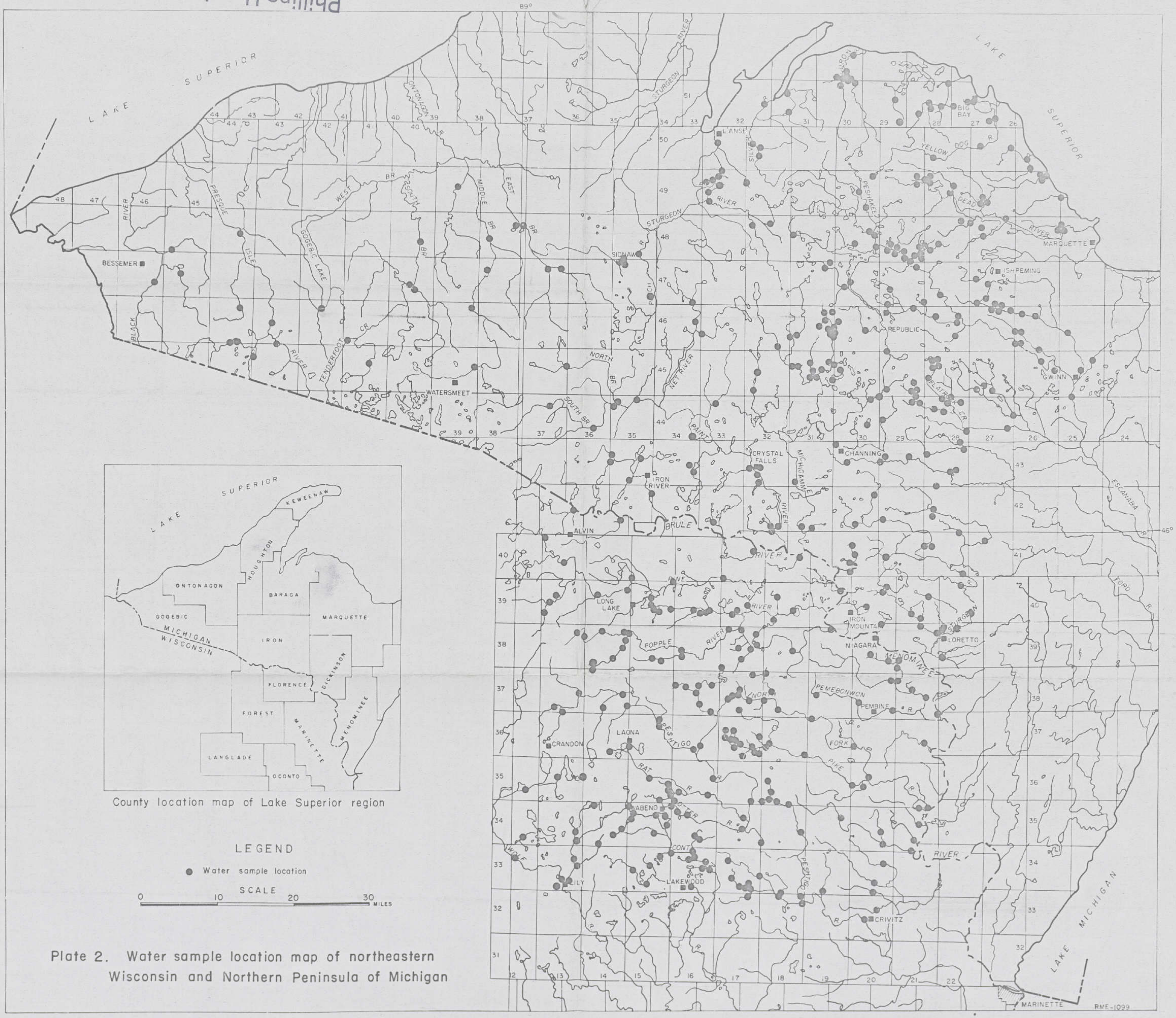

Plate 2. Water sample location map of northeastern Wisconsin and Northern Peninsula of Michigan

Plate 3. Uranium/conductivity contour map of northeastern Wisconsin and Northern Peninsula of Michigan