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BOTTOM SEDIMENTS AND ORGANIC GEOCHEMICAL RESIDUES OF SOME MINNESOTA LAKES

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FOREWORD

Bottom Sediments and Organic Geochemical Residues of Some Minnesota Lakes, by F.M. Swain, Professor, Department of Geology and Geophysics, University of Minnesota, was first submitted to the Minnesota Geological Survey in early 1969. After several technical reviews, P.K. Sims, Director of the Survey at the time, approved the manuscript for publication on May 31, 1969. Sims intended to publish the report as part of the Geological Survey's Special Publication Series. For reasons long forgotten, the report languished in the files for several years. After a severe financial cutback in 1972, P. K. Sims resigned as Director; he was replaced by Matt S. Walton. Shortly after joining the Survey, Walton abolished the Special Publication Series as unnecessarily expensive. The manuscript was returned to Professor Swain. Although parts of it were published elsewhere, Professor Swain resubmitted the entire manuscript in 1991. Subsequent technical reviews under my direction established that parts of the manuscript were somewhat dated or had been superseded by subsequent studies. Nonetheless, the reviewers agreed that because the manuscript contained data unavailable elsewhere, it should be published in its entirety. For that reason, as well as to right an historic wrong, the current Director, Priscilla C. Grew, again authorized publication in May 1992, some twenty-three years after the original decision to publish the manuscript.

G.B. MOREY
Associate Director
and Chief Geologist

September 15, 1992

PREFACE

This compilation represents field and laboratory work done mainly in the 1960s; it includes previously unpublished data as well as further interpretation of results published by the author and graduate students. The laboratory procedures were primarily those used in the 1960s. However, the preparatory procedures, which were designed to alter the natural conditions of the sediment samples as little as possible, are still in use today.

The project supported the theses of several graduate students, as well as publications by the author that are listed in the References. Many excellent graduate thesis topics remain to be undertaken on Minnesota lake sediments.

ACKNOWLEDGMENTS

The Minnesota Department of Natural Resources provided valuable limnologic data, in particular the reports of John B. Moyle and John Dobie. The late Samuel Eddy provided much helpful information. Kendell A. Dickinson assisted with much of the field work. M. Alan Rogers, Harvey Meyer, Peter Fleischer, Mikola Malinowsky, Dennis Deischl, Gunta V. Pakalns, Inara Porietis, David Peterson, Judy M. Bratt, Patricia Bloomgren, and Shirley Kraemer, at the University of Minnesota, assisted with the field and laboratory work. The Graduate School, the Minnesota Geological Survey, and the Limnological Research Center, University of Minnesota, provided support for most of the work. Nicola Prokopovich assisted with much of the early work. The late Francis T. Ting, under a postdoctoral fellowship from Macalester College, performed some of the polysaccharide analyses. Steve Meger provided data on his studies of mercury in northeastern Minnesota lakes. An important modern work on Minnesota lake waters is that of Heiskary and Wilson (1990). Richard B. Darling drafted the illustrations. Holly Schoonover and Sue Linehan typed the manuscript.

BOTTOM SEDIMENTS AND ORGANIC GEOCHEMICAL RESIDUES OF SOME MINNESOTA LAKES

BY

F.M. SWAIN

ABSTRACT

Holocene lake sediments of Minnesota are represented by six facies: I) northeastern—allogenic littoral sand and gravel, and profundal clay and copropel, in Precambrian crystalline rocks, with low to high total carbohydrates, high and variable amino acids, low to moderate hydrocarbons, and low to high pigments; II) northwestern—mixed allogenic clastics, and authigenic copropel and marl, in calcareous glacial drift and Pleistocene lake beds, with moderate carbohydrates, low amino acids, and stratigraphically variable pigments; III) north-central—authigenic marl, copropel, and allogenic sediments in thick calcareous glacial drift, with moderate carbohydrates, low amino acids, and stratigraphically variable pigments; IV) east-central—authigenic copropel, marl, and allogenic clastics in calcareous and noncalcareous glacial drift, with high carbohydrates and amino acids, high hydrocarbons and polar lipids, high pigments, all stratigraphically variable; V) west-central and southwestern—allogenic silt, marl, and sapropel in calcareous glacial drift and gypsiferous Cretaceous shale, with high carbohydrates and amino acids, stratigraphically variable, high aromatic hydrocarbons; and VI) southeastern—allogenic fine clastics and copropel in Paleozoic clastic and carbonate rock and pre-Wisconsin drift, with known organic residues similar to those in Facies IV.

INTRODUCTION

The sedimentary properties of Minnesota lake-bottom deposits, their succession with time, and their lateral and regional variations result from a combination of geologic, climatic, and biologic factors (Moyle, 1954; Swain, 1956, 1961; Eddy, 1963). Several major subdivisions of Minnesota can be identified on the basis of lake sediment properties: (1) northeastern Minnesota, with clayey, sandy, and gravelly sediments of low to moderate organic content, but locally higher organic content, as in Poplar Lake; (2) northwestern Minnesota, with silty, sandy sediments of moderate carbonate and organic content; (3) north-central Minnesota, with highly calcareous, in part, sandy and organic-rich sediments; (4) east-central Minnesota, with moderately calcareous and silty sediments of high organic content; (5) west-central and southwestern Minnesota, with highly silty sediments together with marl and copropel deposits; and (6) southeastern Minnesota, with clayey, sandy sediments and high organic content. Figure 1a shows the general distribution of sediment types.

This report discusses the sediments of several lakes in each subdivision in terms of the trophic development as reflected in the bottom deposits and other limnologic and geologic aspects. Previously published data, referred to briefly under each heading, is considered further in the discussion section.

FACES OF LAKE SEDIMENTS

A description of the principal sediment types and facies variations in lakes of the above six areas of Minnesota follows. For a discussion of coring procedures applicable to the study area see Wright (1980).

Northeastern Minnesota. The lakes studied in this area are: Silver Bay of Lake Superior, Lake County; Duluth Harbor, Lake Superior, St. Louis County; Poplar Lake (Fig. 2), Gunflint Lake (Fig. 3), and Seagull Lake (Fig. 4), Cook County; Snowbank Lake (Fig. 5), Lake County; Burntside Lake, Vermilion Lake, Pelican Lake, Crane Lake (Fig. 7), Lac la Croix (Fig. 8), Lake Kabetogama, and Rainy Lake, St. Louis County. The properties of the sediments of several of these lakes are summarized in Table 2; those of Silver Bay, Burntside Lake, Kabetogama Lake, Pelican Lake, and Rainy Lake were discussed previously (Swain and Prokopovich, 1957; Swain, 1956, 1961).

West-Central and Southwestern Minnesota. The lakes of this area lie in glacial drift that has been influenced by the high sulfate-content of the Cretaceous shales underlying the drift. Consequently, the sediments are variable but dominated by highly silty conditions together with marl, sand, clay, and mollusk-shell accumulations. Sapropelic oozes occur in some lakes. The lakes studied in this area are (Table 6) Cormorant Lake (Fig. 15), Becker County; Leek (Fig. 16), Big McDonald (Fig. 17), Otter Tail (Fig. 18), and East Battle Lakes (Fig. 19), Otter Tail County; Lake Miltona (Fig. 20), Douglas County; Reno Lake, and Lake Minnewaska, Pope County; Traverse Lake (Fig. 21), Traverse County; Big Stone Lake (Fig. 22), Big Stone County; Green Lake (Fig. 23) and Big Kandiyohi Lake (Fig. 24), Kandiyohi County; Lake Shetek (Fig. 25), Murray County; Turtle Lake and Hall Lake, Martin County; and Albert Lea Lake (Fig. 26), Freeborn County. Most of the lakes of this group lie in the Alexandria moraine belts of the Wadena Ice Lobe of early Wisconsin age. Those along the eastern and southern borders of the state are associated with drift of the Des Moines Ice Lobe of later Wisconsin age. The pH values of the upper sediments are somewhat alkaline and Eh values are moderately to strongly negative, showing that reducing conditions prevail in the sediments (Fig. 1b).

Southeastern Minnesota. In this area the glacial drift is thin to absent and Paleozoic sandstone, shale, and carbonate rocks lie near the surface. The drift is generally not calcareous. The lakes studied in southeastern Minnesota are (Table 7) French Lake, Rice County (Fig. 24); Elysian Lake (Fig. 27), Waseca County; Lake Zumbro (Fig. 28), Wabasha and Olmsted Counties; and Lake Pepin (Fig. 29) in Mississippi River, between Goodhue and Wabasha Counties. The bottom sediments of these lakes are clayey copropelic silt and silty clay. The pH values are generally slightly alkaline to neutral and the Eh values are moderately to strongly negative (Fig. 1b).

Further details of lithologic variations can be found in Swain, 1956; Swain and Prokopovich, 1957; Swain, 1961; Swain, Venteris, and Ting, 1964; Swain, Paulsen, and Ting, 1964; Swain, 1965; and Swain, 1967.

Northwestern Minnesota. The lakes studied in this area are Lake of the Woods, Roseau and Lake of the Woods Counties (Swain, 1961); Upper and Lower Red Lake, Beltrami and Clearwater Counties (Swain, Paulsen, and Ting, 1964); and Maple Lake, Polk County. These lakes lie in Precambrian granite and schist on the north, and in calcareous glacial drift and Lake Agassiz clays on the south.

Properties and facies variations of these lakes are given in Table 3. All are in a mesotrophic to early eutrophic state of nutrient development; the resulting profundal sediments are silty, sandy, and diatomaceous pollen-bearing copropel and copropelic silts. The pH values are slightly alkaline, and Eh values are weakly negative to weakly positive in the upper sediments, indicating that the sediments are held in a slightly reduced state (Fig. 1b).

North-Central Minnesota. The lakes studied in this area are (Table 4) Lake Winnibigoshish and Moose Lake, Itasca County; Cass Lake, Beltrami and Cass Counties; Leech Lake (Fig. 10), Cass County; Lake Kabekona, Hubbard County; Lake Itasca and Long Lake, Clearwater County; and Shell Lake (Fig. 11), Becker County. These lakes lie in an area of calcareous drift; their profundal sediments are silty to non-silty, diatomaceous marl, whereas the littoral sediments are sand, peaty marl, and peat. The pH values are slightly acidic to slightly or moderately alkaline, and the Eh values are moderately to slightly negative in the surface profundal sediments (Fig. 1b). These values are somewhat more variable in the littoral sediments but the latter are generally in the reduced state.

East-Central Minnesota. Many of the lakes studied lie in the mixed gray and red glacial drifts of the Superior and Wadena ice lobes. They are (Table 5): Whitefish (Fig. 12) and Pelican Fig. 13) Lakes, Crow Wing County; Mille Lacs Lake (Fig. 14), Crow Wing, Aitkin, and Mille Lacs Counties; South Stanchfield, Spectacle, Green, and Fannie Lakes, Isanti County; Rush Lake and Green Lake, Chisago County; Clear Lake and Eagle Lake, Sherburne County; Lake Johanna, Ramsey County; Lake Minnetonka, Hennepin County; Prior Lake, Scott County; and Cedar Lake, Wright County. These lakes are eutrophic to dystrophic or hypereutrophic in development. Their bottom sediments are copropel and sapropel, marl, and diatomacous copropel and copropelic marl. The pH values of these upper sediments range from slightly acidic to slightly alkaline, and Eh values are somewhat positive to moderately negative (Fig. 1b). The sediments are held in a reduced state, despite the positive Eh values in some sediment samples, because of the large amount of organic matter.

Chemical Analyses of Lake Sediments. Chemical analyses of the bottom sediments of several Minnesota lakes published in an earlier study (Swain, 1961) are reproduced in Table l.

Rainy Lake, Kabetogama Lake, and Pelican Lake, St. Louis County, are in northeastern Minnesota. Lake of the Woods, Roseau and Lake of the Woods Counties, is in northwestern Minnesota. Kabekona Lake, Hubbard County, is in north-central Minnesota. Rush Lake, Chisago County; Prior Lake, Scott County; Lake Minnetonka, Hennepin County; and Cedar Lake, Wright County, are in east-central Minnesota. Green Lake, Kandiyohi County, is in west-central Minnesota.

The lakes lie in Precambrian schist, granite, basalt, and reddish-brown glacial drift and are mostly oligotrophic or early eutrophic in development. The littoral sediment facies range from coarse gravels and sands along exposed shores to peat in bays and stream entrances. The profundal sediment facies typically are brown and red silty oxidized clays at shallower depths, down to 32-50 ft, and pollen-bearing gray and tan clays in a nonoxidized state at greater depths. In Lake Superior the red clays extend into deeper water, 700-800 ft or more. Profundal humic matter and copropel in some of the lakes, such as Poplar, Vermilion, and Kabetogama, may be related to drainage from deforested tracts as well as to the onset of trophication.

Nodules and crusts of earthy ferric oxide and manganese oxide, probably of bacterial origin, are common in lakes with strong current flows along the bottom, such as Lac la Croix, Crane Lake, and Rainy Lake. This is one of the few areas of the state where varved sediments are present in the modern lake deposits; silty, light-colored layers alternate with slightly darker-red clayey laminae in Lake Superior, Rainy Lake, Kabetogama Lake, and others, except in the upper 1.5 ft or so, where the varves seem not to have developed or to have been destroyed by burrowing organisms. A change toward more copropelic bottom sediments from the 1950s to 1983 has been recorded in Crane Lake (Meger, 1983).

The pH values of upper lake sediments in this area are typically neutral or slightly acidic and Eh values slightly to moderately positive, indicating weakly to moderately oxidizing conditions; pH may become alkaline and Eh negative downward in the sediments.

Rainy Lake has Lake Agassiz-age varved clays along its margins and perhaps beneath the lake itself. These crop out east of Ranier, Minnesota.

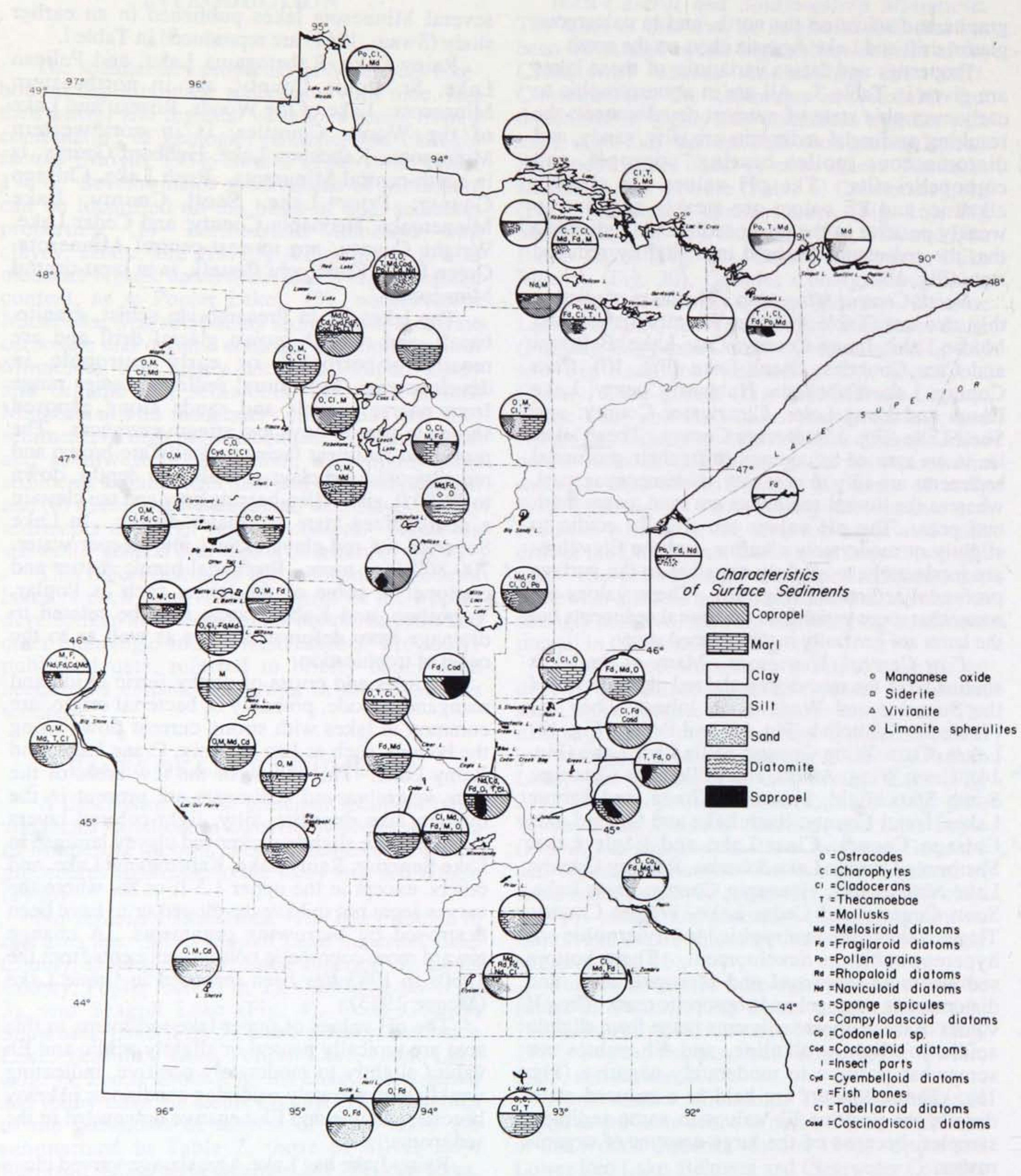


Figure 1a. Characteristics of surface sediments.

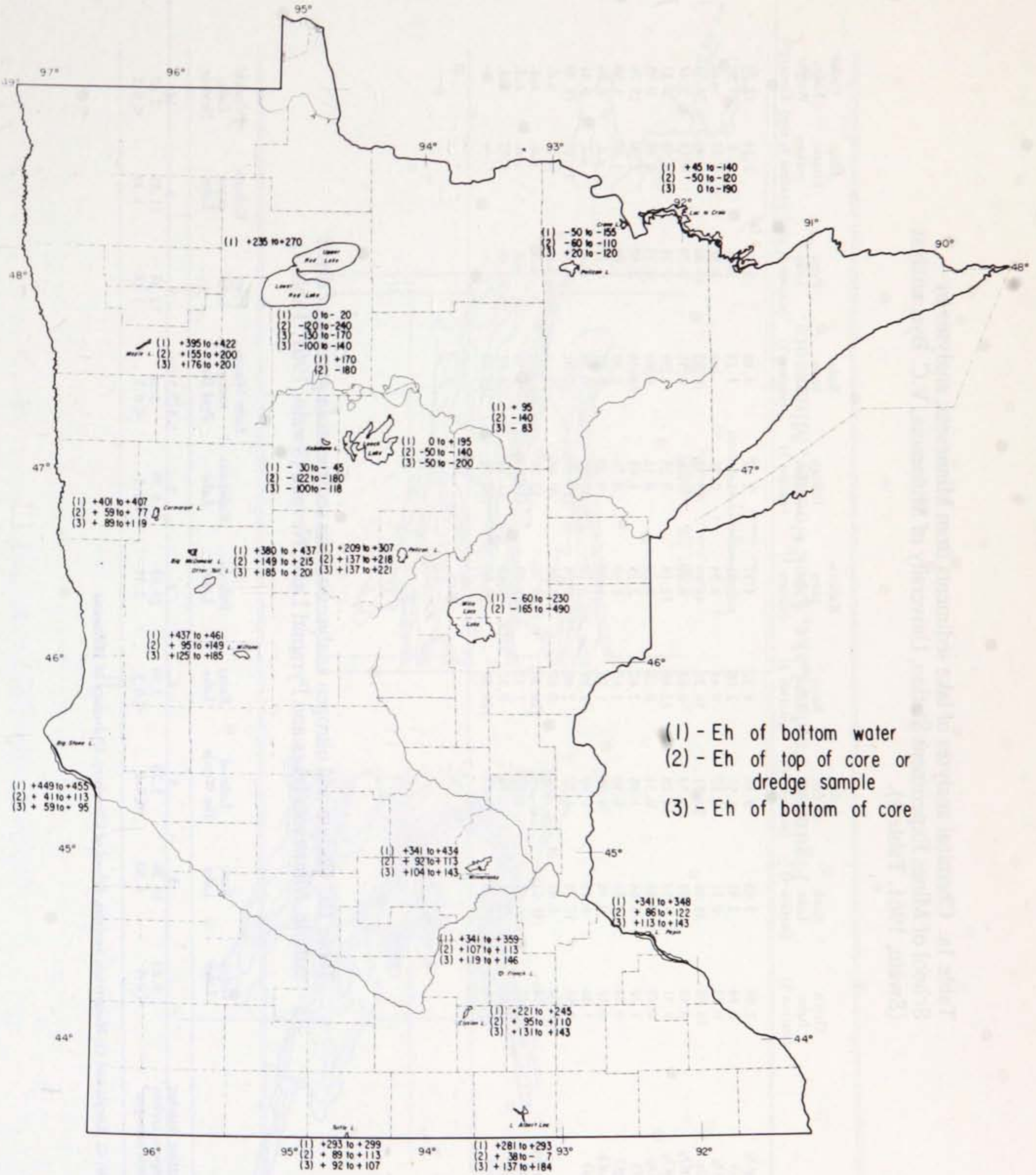


Figure 1b. Oxidation potentials in bottom waters and sediments.

Table 1a. Chemical analyses of lake sediments from Minnesota; analyses by School of Mines Experiment Station, University of Minnesota, V.C. Bye, analyst (Swain, 1961, Table 1).

	Green Lake (station 5)	Rush Lake (station 4)	Lake of the Woods (station 14)	Rainy Lake (station 3)	Kabetogama Lake (station 3)	Pelican Lake (station 3)	Kabekona Lake (station 5)	Prior Lake (station 1, top)	Lake Minnetonka (station 3, top)	Cedar Lake, Wright County
Fe_2O_3	2.66	3.63	9.86	8.37	4.17	2.32	4.68	5.77	7.14	12.20
FeO	0.84	2.41	1.57	2.08	3.51	1.24	1.23	n.d.	n.d.	3.94
P_2O_5	0.23	0.71	0.47	0.44	0.54	0.35	—	0.37	0.52	n.d.
SiO_2	76.58	38.66	52.51	56.24	48.19	33.92	10.92	45.66	46.42	26.78
MnO_2	0.46	0.74	0.54	0.62	0.41	0.36	0.51	0.79	0.11	2.47
Al_2O_3	9.31	4.52	14.28	12.86	12.18	5.25	1.58	9.21	8.58	2.37
TiO_2	0.15	0.16	0.34	0.28	0.26	0.12	0.04	0.53	0.45	0.05
CaO	1.78	5.64	1.86	2.62	2.25	1.63	38.26	2.50	7.00	15.78
MgO	0.54	1.33	0.50	2.67	2.30	0.76	0.99	1.00	3.80	1.00
Na_2O	2.17	0.46	0.95	1.72	1.06	0.29	0.05	0.278	n.d.	0.10
K_2O	1.36	0.75	1.99	1.95	1.79	1.32	0.50	n.d.	n.d.	0.41
C	0.56	17.78	4.57	2.40	9.76	(25.45)	5.01	10.79	11.25	15.39
S	0.08	0.65	—	0.07	0.35	(0.66)	—	n.d.	0.19	n.d.
Ign. loss	(2.04)	(41.63)	—	(10.20)	(24.36)	52.80	n.d.	n.d.	n.d.	n.d.
H_2O	2.47	16.92	9.31	7.17	12.20	(19.74)	6.56	n.d.	n.d.	n.d.
CO_2	0.47	3.84	0.40	0.51	0.68	(1.34)	29.67	2.06	4.57	n.d.
Total	99.66	98.20	99.15	100.00	99.65	100.36	100.00	—	—	—

Table 1b. Carbon and nitrogen analyses of lake sediments in percent of dried sample, Minnesota lakes and Pyramid Lake, Nevada (Swain, 1961, Table 2).

	Green Lake	Rush Lake	Lake of the Woods	Rainy Lake	Pelican Lake	Kabekona Lake	Lake Minnetonka Peat Bog	Prior Lake	Kabetogama Lake	Pyramid Lake, Nevada
Station number	5	8	3	2	1	5	1.5–2.5 feet	5	3	18
Organic carbon*	0.63	16.24	5.73	3.09	14.03	5.79	2.12	12.54	11.35	2.67
Total nitrogen*	<0.5	1.80	<0.5	<0.5	2.15	<0.5	<0.5	1.16	1.39	<0.5

*W. C. Kuryla and O. Hamerston, analysts, School of Chemistry, University of Minnesota

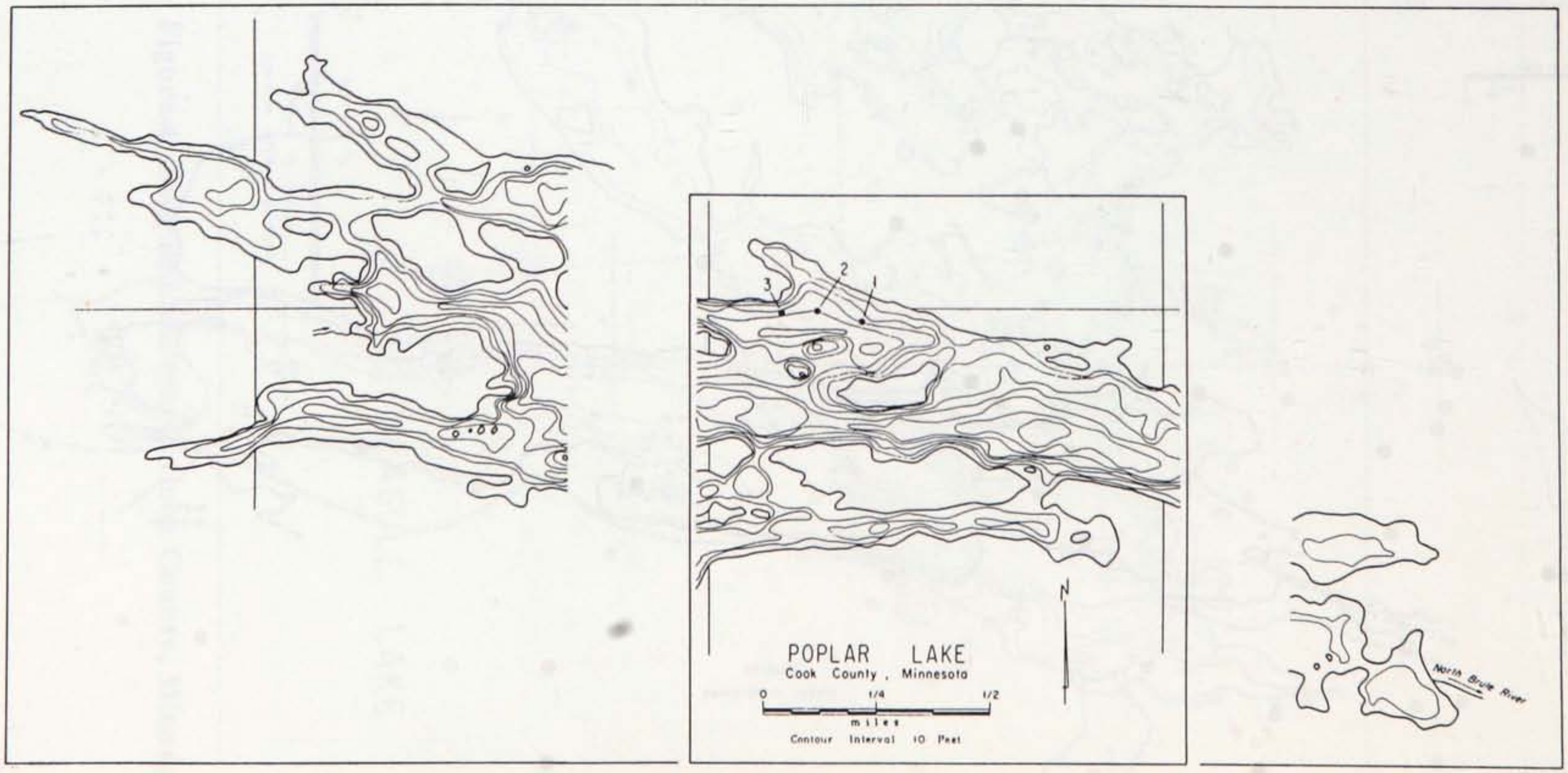


Figure 2. Poplar Lake, Cook County, Minnesota.

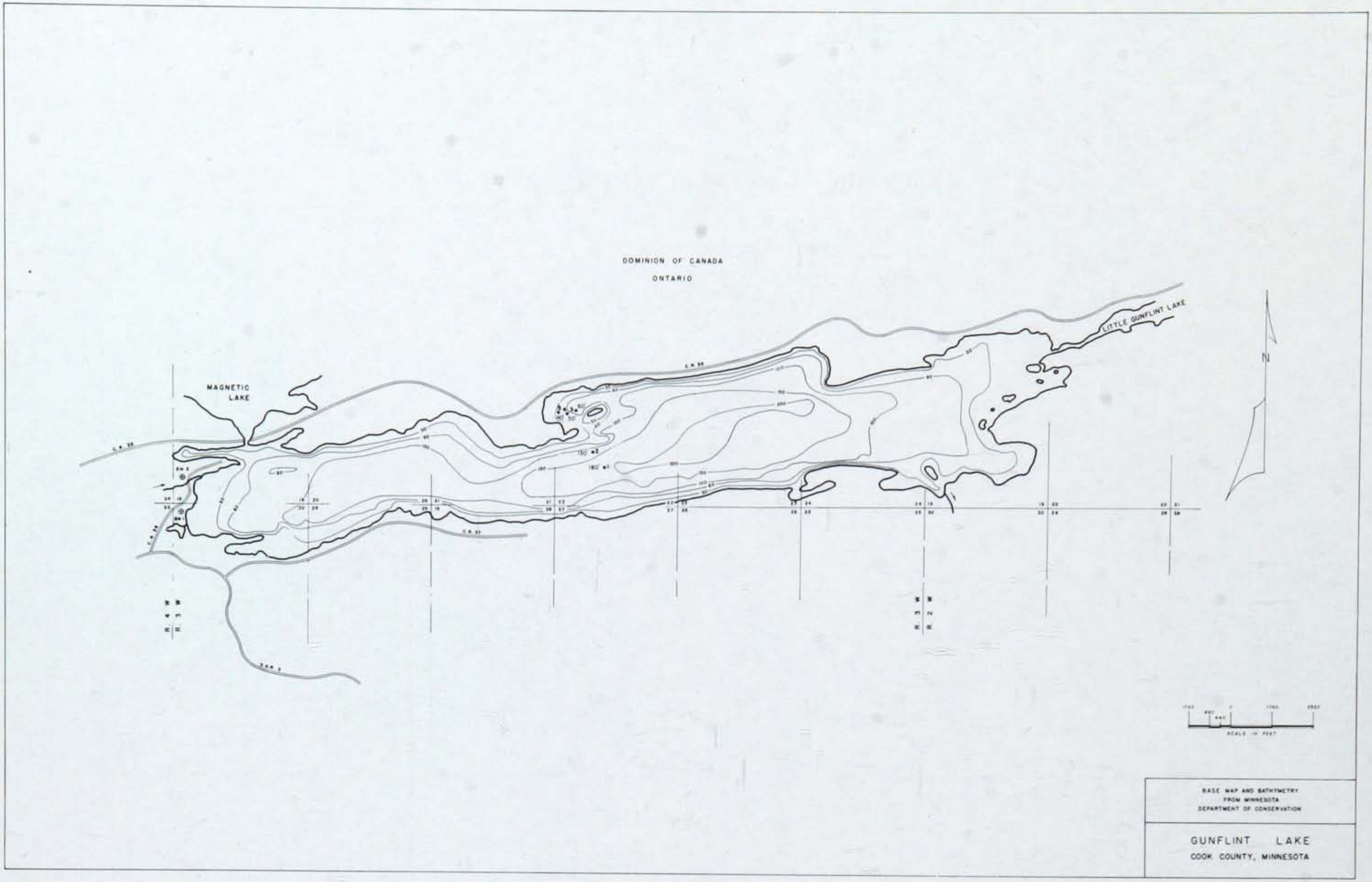


Figure 3. Gunflint Lake, Cook County, Minnesota.

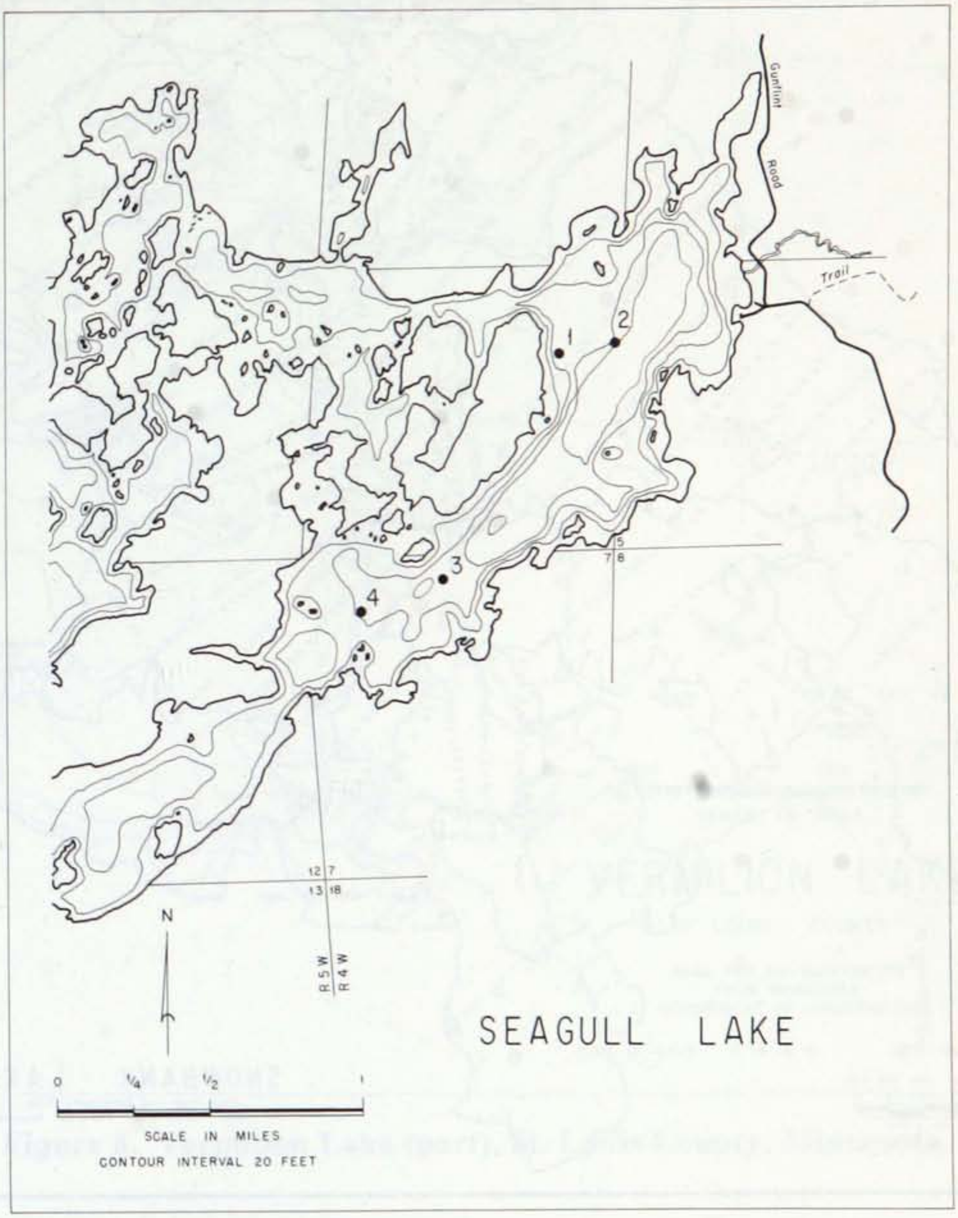


Figure 4. Seagull Lake (part), Cook County, Minnesota.

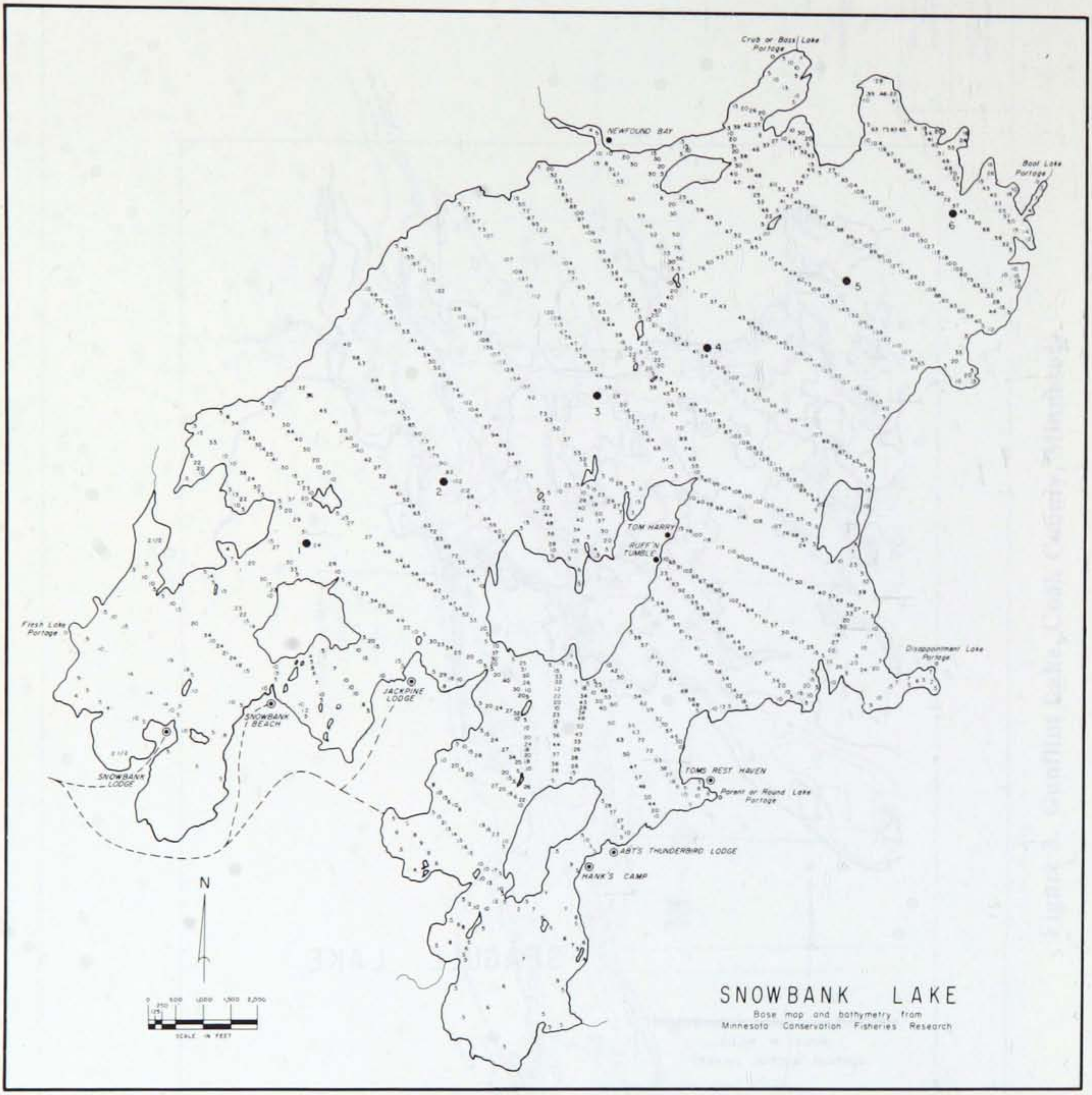


Figure 5. Snowbank Lake, Lake County, Minnesota.

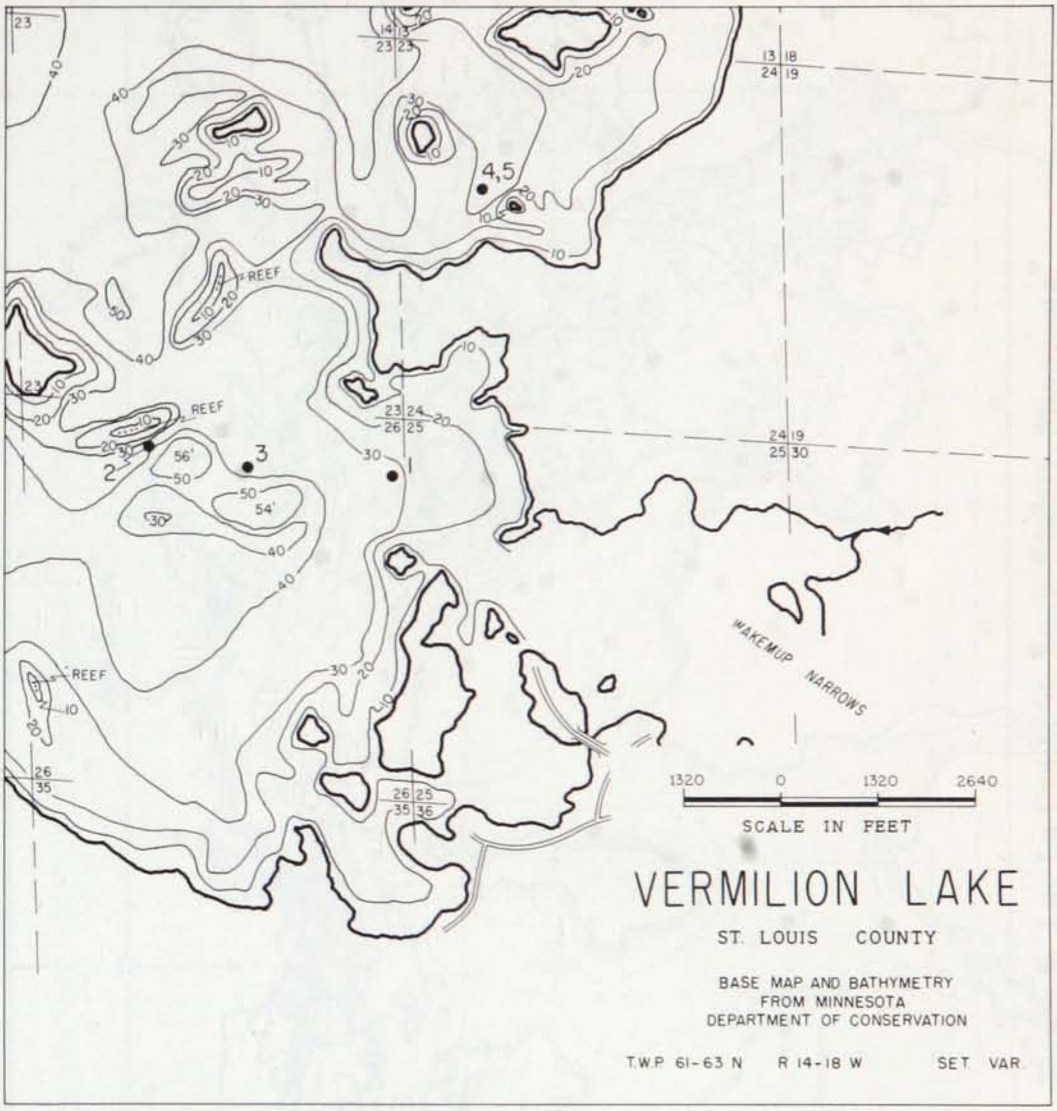


Figure 6. Vermilion Lake (part), St. Louis County, Minnesota.

Figure 7. Crane Lake, St. Louis County, Minnesota.

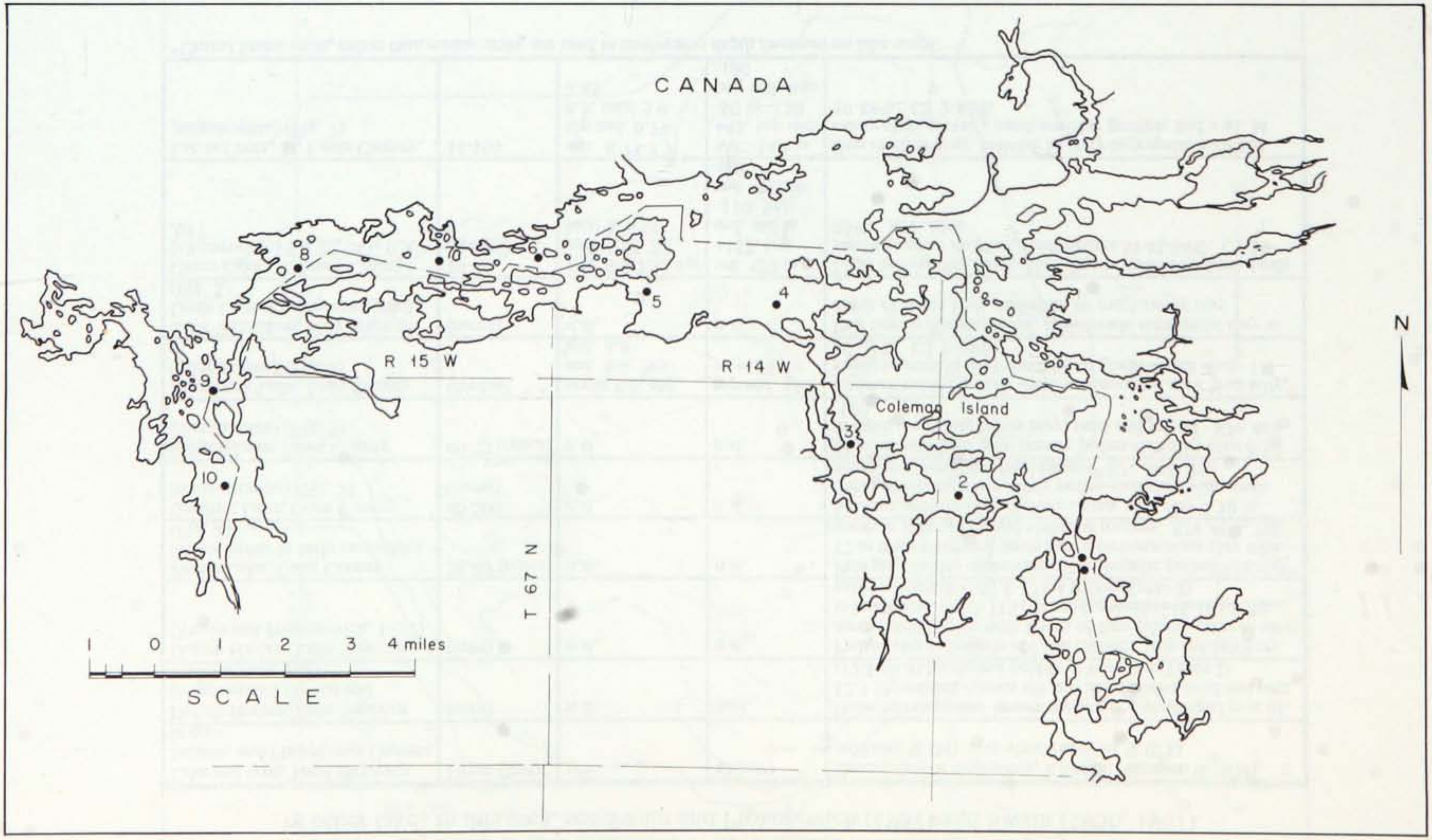


Figure 8. Lac La Croix, St. Louis County, Minnesota.

Table 2. Properties of lake sediments of northeastern Minnesota. For properties of other lakes in this area, see Swain and Prokopovich (1957) and Swain (1956, 1961).

Lake and type, Total alkalinity, Sulfate, and Phosphorus Content in ppm	Depth (feet)*	pH	Eh(mv)	Description of Sediments, Kjeldahl Nitrogen % (KN), moisture % (M), clay-sized particles % (C1)
Duluth Harbor, Lake Superior (oligotrophic) (Swain and Prokopovich, 1957)	(core)	n.d.	n./d.	Holocene deposits: brown woody and pondweed peat (0-12.5 ft), reddish-brown silt and interbedded sand and peat (12.5-39.5) becoming pebbly at base (see Table 2)
Duluth Harbor, Lake Superior (Swain and Prokopovich, 1957)	(core)	n.d.	n.d.	Pleistocene sediments of Lake Duluth: pale reddish gray, sandy, pebbly clay with layers of fine salmon-colored sand in lower part (39.5-115 ft); sand, gravel (115-161.8 ft); gabbro bedrock (161.8-172.4 ft)(see Table 2)
Poplar Lake, Cook County (mesotrophic to early eutrophic) (Fig. 1)	38-40 (cores)	n.d.	n.d.	Pale gray-brown diatomaceous copropelic pollen-rich clay 12 in thick overlying more sandy carbonaceous clay with goethite spherulites and vivianite masses. KN .660-.720
Gunflint Lake, Cook County (obligotrophic) (Fig. 2)	60-200 (cores)	n.d.	n.d.	Medium gray-brown, diatomaceous, silty clay 5-10 in thick, overlying more sandy pollen-rich clay with small goethite spherulites; fecal pellets. KN .344-.412
Seagull Lake, Cook County (oligotrophic) (Fig. 3)	40-72 (cores)	n.d.	n.d.	Medium and light gray-brown, pollen-rich silty clay 8-12 in thick overlying sandy clay, sand and gravel. KN .468-.520
Snowbank Lake, Lake County (oligotrophic) (Fig. 4)	(dredge)	water 6.6, top sed. 6.6, bot. sed. 6.6	top sed. +90 to +138	Reddish brown gravel, sand, medium and dark gray silty, sandy sapropelic clay; nodules of goethite and wad. 1N 18-95%. C1 3-18%
Lake Vermilion, N.W. part, St. Louis County (early eutrophic) (Fig. 5)	(cores)	n.d.	n.d.	Pale brown diatomaceous, pollen-rich, copropelic clay to depth of about 10 in underlain by more sandy clay
Crane Lake, St. Louis County (oligotrophic) TA 22, SO_4 0.5, .037	10-73 (dredge)	wtr. 6.7-7.3, top sed. 6.85-7.1, total 6.5-7.0	wtr. -60 to +155, top sed. -60 to -110, bot. sed. -120 to +20	Light brown silty, peaty clay, fine to coarse feldspar sand; sandy goethite nodules, fecal pellets M 42-84%. C1 30-95%. KN .136.
Lac la Croix, St. Louis County, (oligotrophic) (Fig. 7)	14-105	wtr. 6.75-7.7, top sed. 6.79-8.5, total 5.9-8.85	wtr. -140 to +45, top sed. -50 to -120, bot. sed. 0 to -190	Pale reddish-gray, pelletal, slightly copropelic silty and sandy clay, gravelly sand; nodular goethite and wad. M 19-88%. C1 2-88%

*United States units, rather than metric units, are used to conform to depth contours on lake maps.

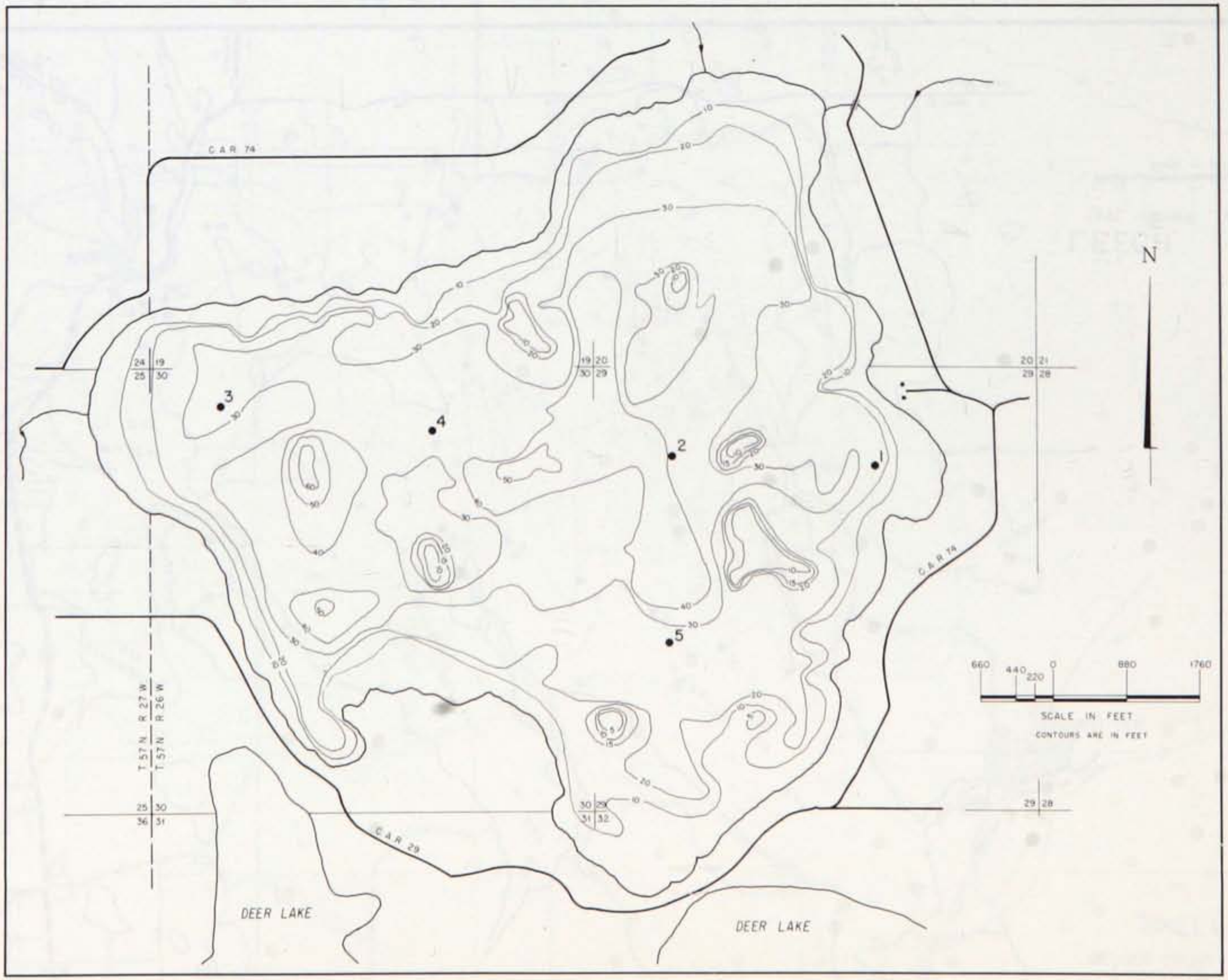


Figure 9. Moose Lake, Itasca County, Minnesota.

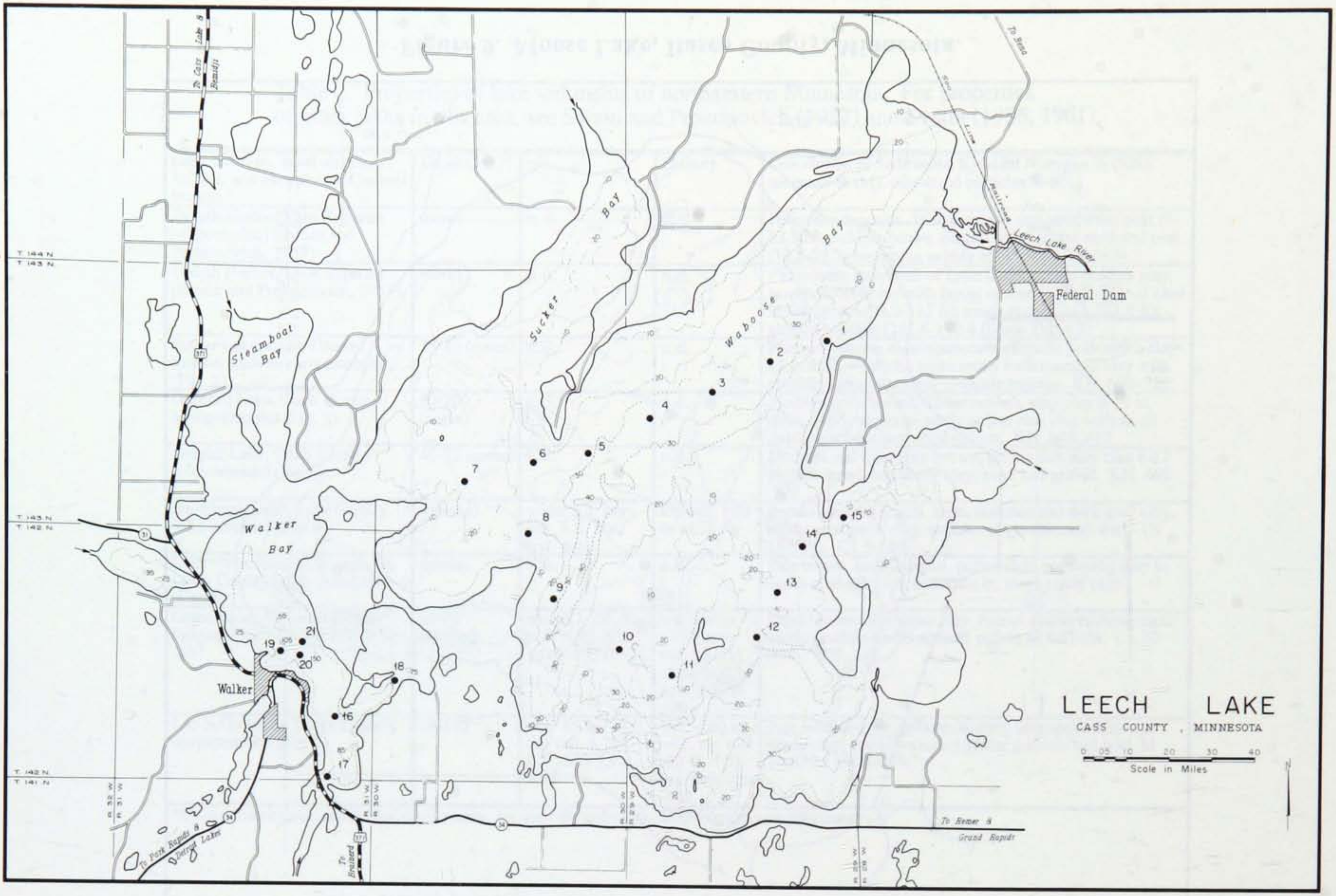


Figure 10. Leech Lake, Cass County, Minnesota.

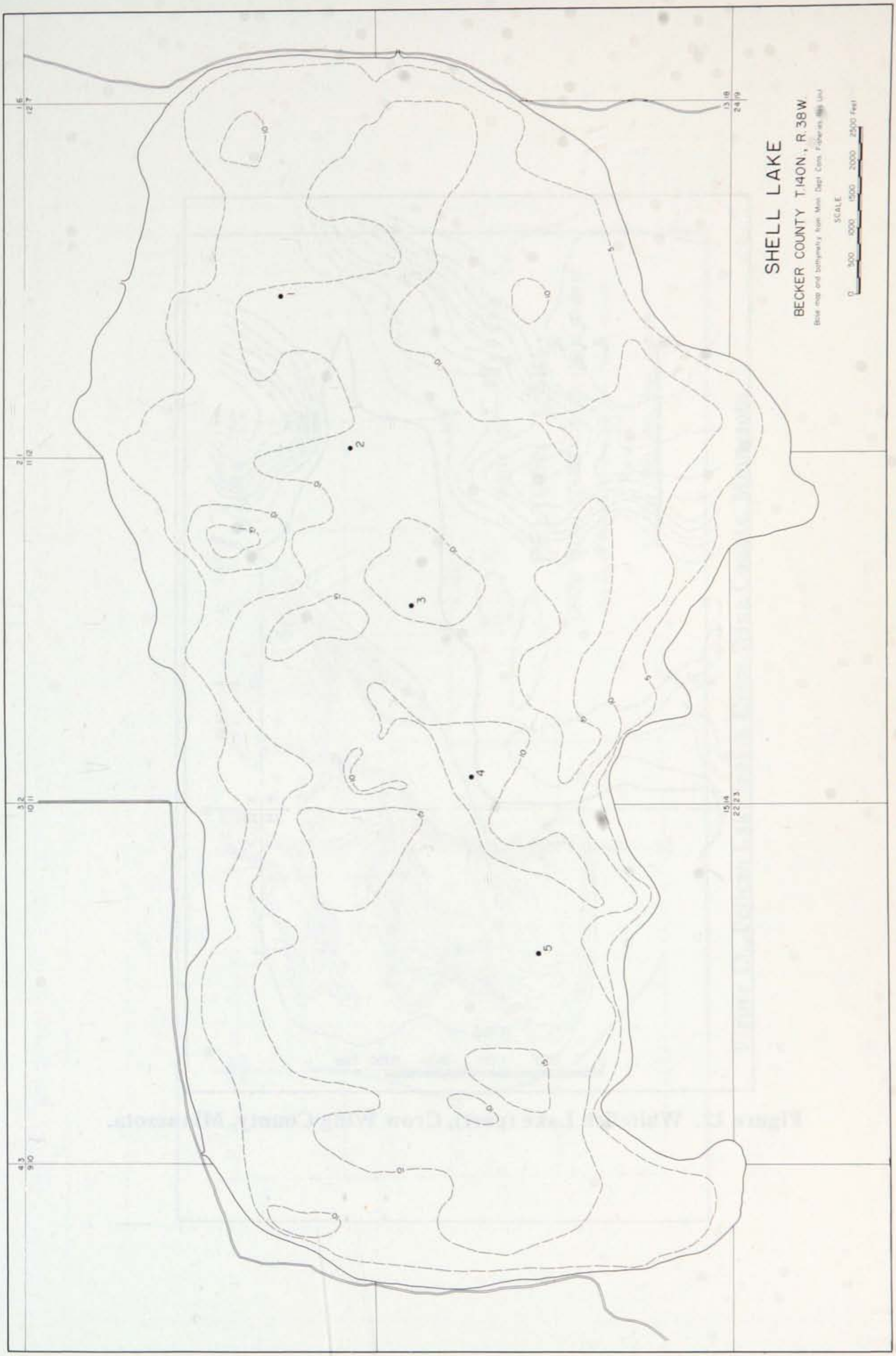


Figure 11. Shell Lake, Becker County, Minnesota.

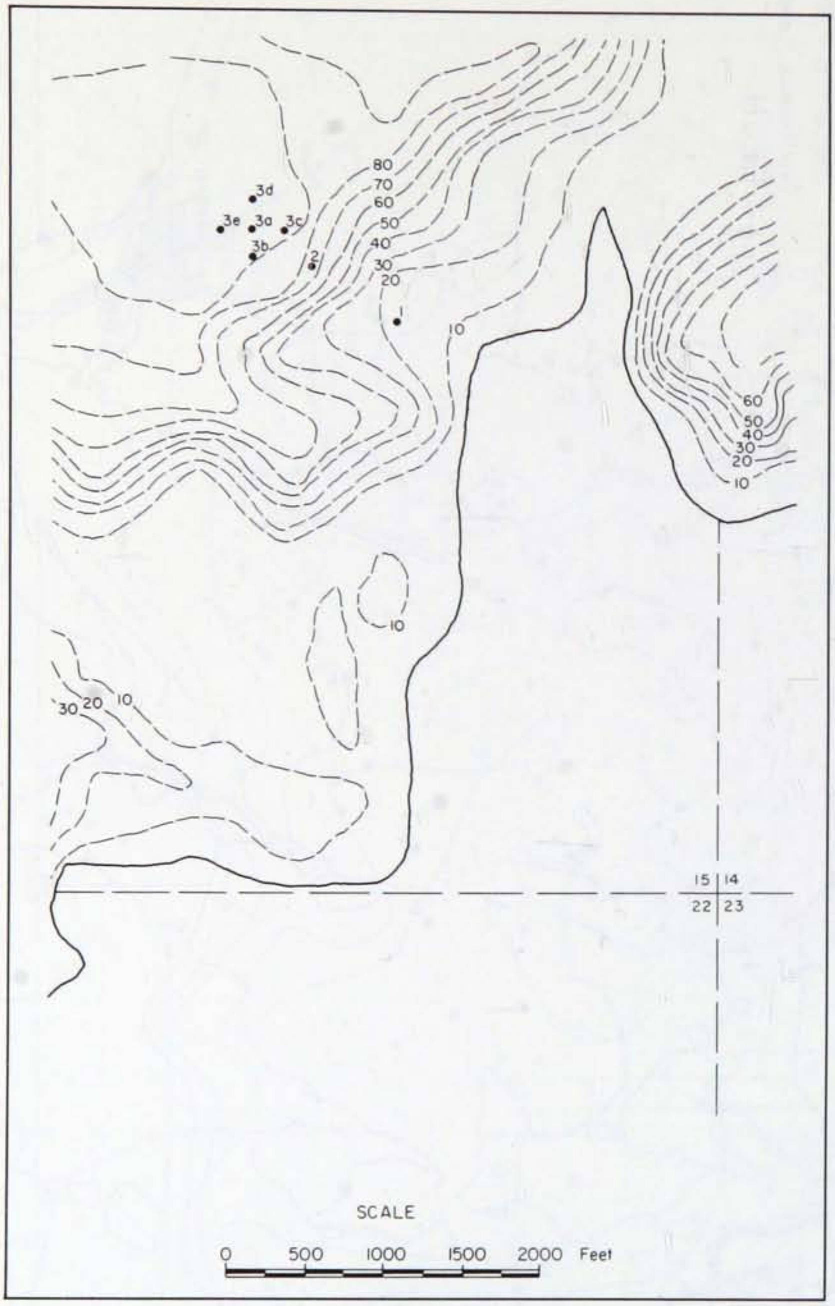


Figure 12. Whitefish Lake (part), Crow Wing County, Minnesota.

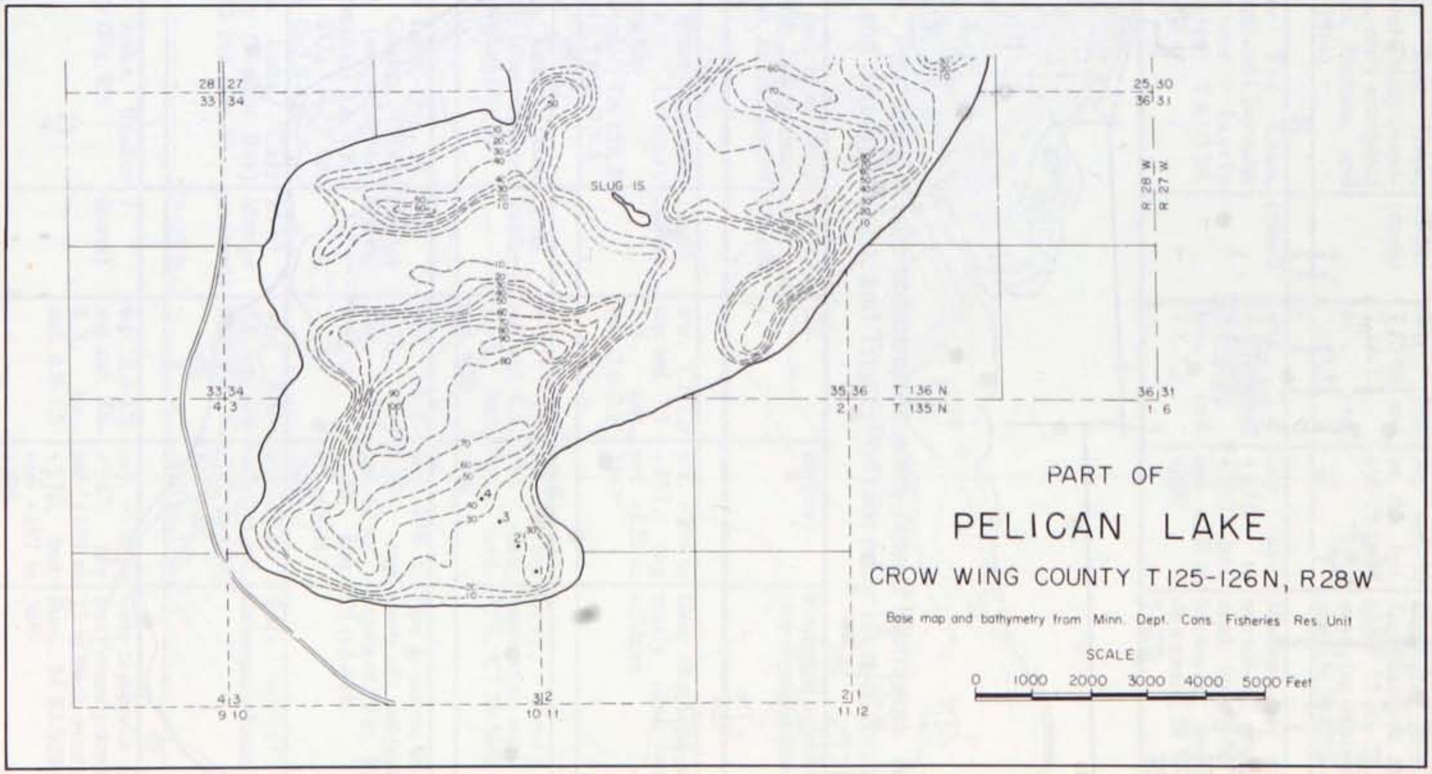


Figure 13. Pelican Lake (part), Crow Wing County, Minnesota.

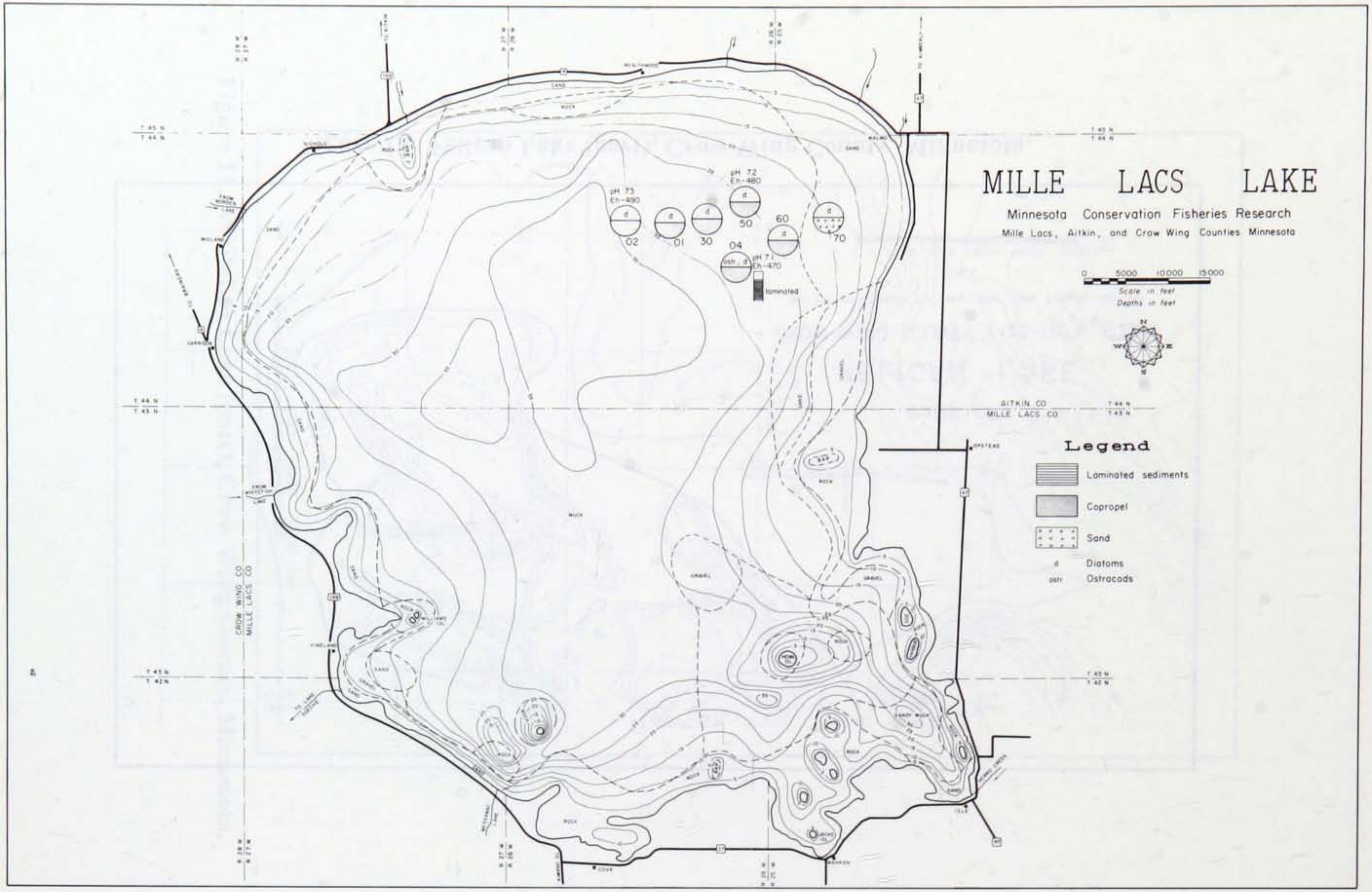


Figure 14. Mille Lacs Lake, Crow Wing, Aitkin, and Mille Lacs Counties, Minnesota.

Table 3. Properties of lake sediments in northwestern Minnesota.

Lake and type, total alkalinity, sulfate content in ppm	Depth (feet) of samples	pH	Eh (mv)	Properties, moisture % (M), clay-sized particles % (C1)
Upper Red Lake, Beltrami County (meso-trophic-early eutrophic) (Swain, Paulsen, and Ting, 1964)	13-14 (cores)	wtr. 7.5-7.65 top sed. 7.15-7.3, bot. sed. 7.4-7.55	top sed.-50 to -65, bot. sed.-25 to-65	Light-gray, fine, angular, diatomaceous copropelic sand, 15 to 20 in thick overlying sandy ostracodal marl. M 30-92%
Lower Red Lake, Beltrami and Clearwater Counties (early eutrophic) TA 139, $SO_4$3.04	(cores)	wtr. 7.4-7.55 top sed. 7.25-7.4, bot. sed. 7.1-7.2	top sed. +155 to +200, bot. sed. +203 to +209	Medium-gray molluscan, ostracodal, copropel, and marl, up to 30 in thick, becoming more marly downward, M 79-92%, C1 6-42%

Table 4. Properties of lake sediments in north-central Minnesota. See Swain (1961) and Swain, Paulsen, and Ting (1964) for other lakes in this area.

Lake and type, total alkalinity, phosphorus, nitrogen, sulfate oxygen in ppm	Depth (feet) of samples	pH	Eh (mv)	Properties, moisture % (M), clay-sized particles % (C1)
Lake Winnibigoshish, Itasca County (mesotrophic-alkalitrophic) TA 152, P .026, N 1.13, $O_2$7.7-8	1.5-45 (cores)	wtr. 7.2-7.5 top sed. 7.2-7.5, bot. sed. 7.0-7.1	wtr. +209 to +251, top sed. +122 to +167	Gray fine sand nearshore, marly sand and marl offshore
Moose Lake, Itasca County (mesotrophic-alkalitrophic) (Fig. 8)	26-49 (dredge)	wtr. 7.57, top sed. 6.8-7.05, bot. sed. 6.93	wtr. +95 top sed. -140, bot. sed. -130	Gray, sandy, silty copropelic marl. M 70-75%. C1 39-50%
Leech Lake, (Fig. 9), Cass County (Main Lake) (mesotrophic-alkalitrophic) TA 150-170, SO_4 5, P.06, N.118, $O_2$2.8-6.8	9-37 (dredge & core)	wtr. 6.7-7.95, top sed. 6.7-7.65	wtr. +39 to +195, top sed.-50 to -140, bot. sed. -50 to -200	Fine to coarse sand, marly sandy silt, and peaty marl to depths of 20 in. M 15-74%. C1 0.6-64%
Leech Lake, Cass County (Walker Bay) TA 152-162 (Fig. 9),	26-85 (dredge and core)	wtr. 7.35-7.4, top sed. 6.83-7.3	wtr. -30 to -45, top sed. -122 to-180, bot. sed. -100 to -118	Soft white slightly carbonaceous marl
Shell Lake, Becker County (Fig. 10)	7- (cores)	wtr. 8.4-8.9, top sed. 7.8-8.3, bot. sed. 6.9-7.5	wtr. +170 to +347, top sed. +149 to +170, bot. sed. +197 to +205	Gray copropelic silty *Chara* and *Potamogeton* marl up to 33 in thick overlying purer marl. M 82-92%. C1 24-36%

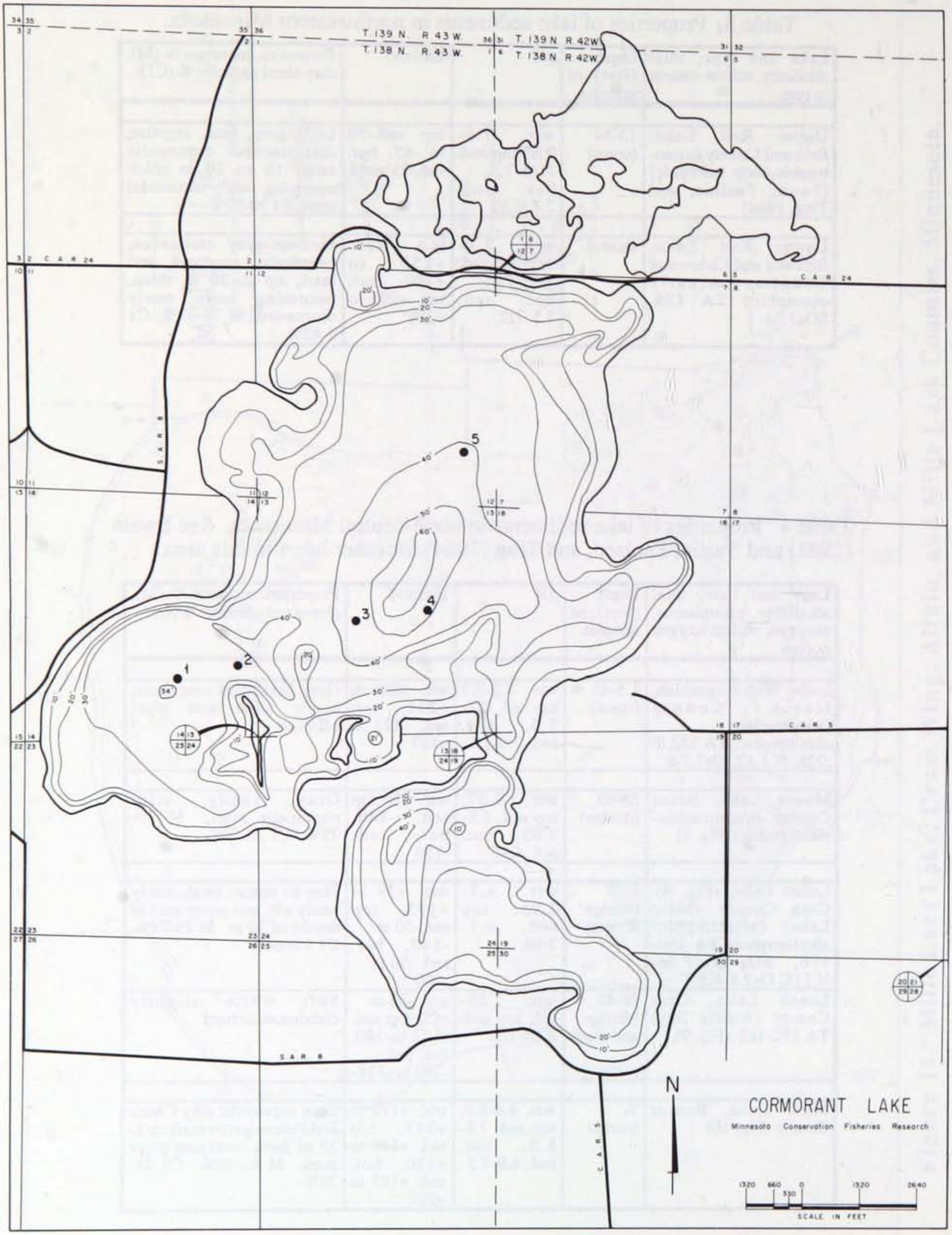


Figure 15. Cormorant Lake, Becker County, Minnesota.

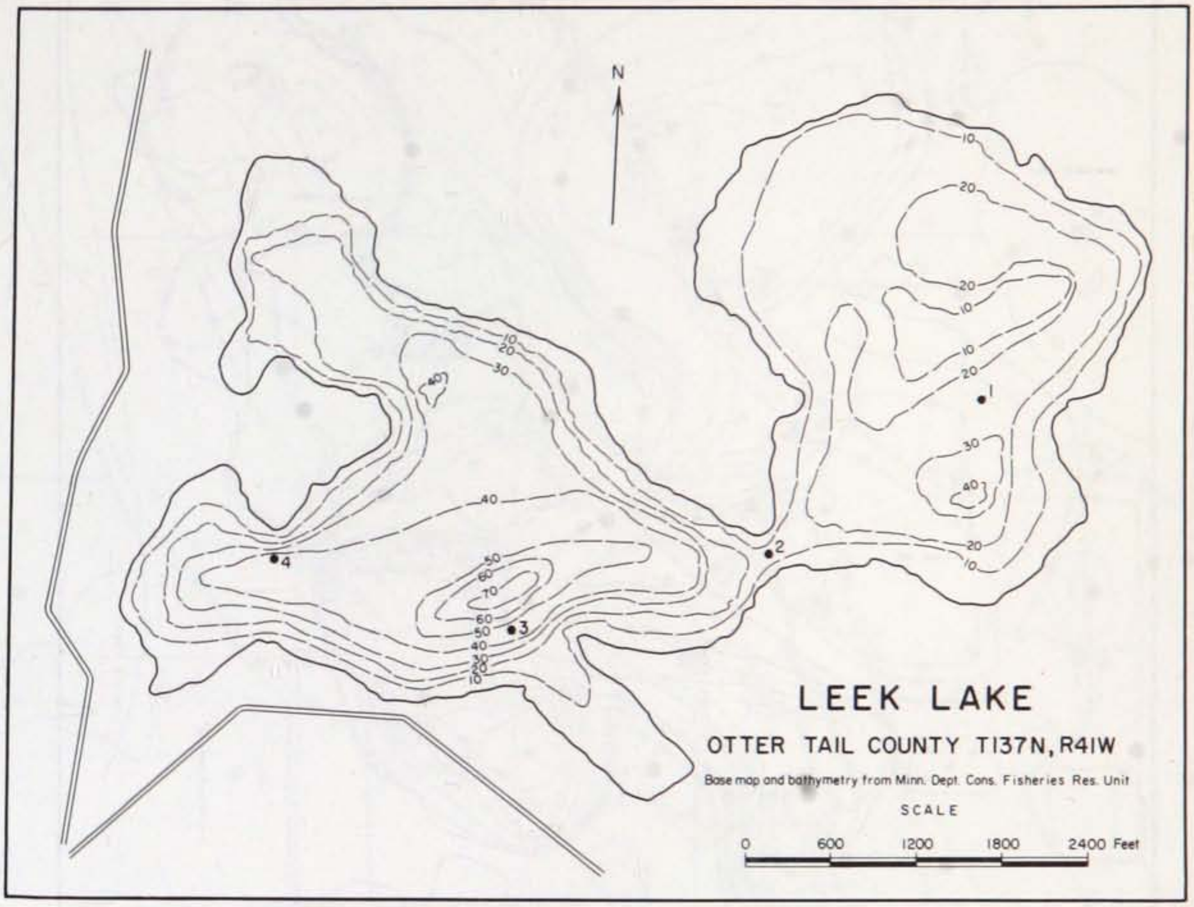


Figure 16. Leek Lake, Otter Tail County, Minnesota.

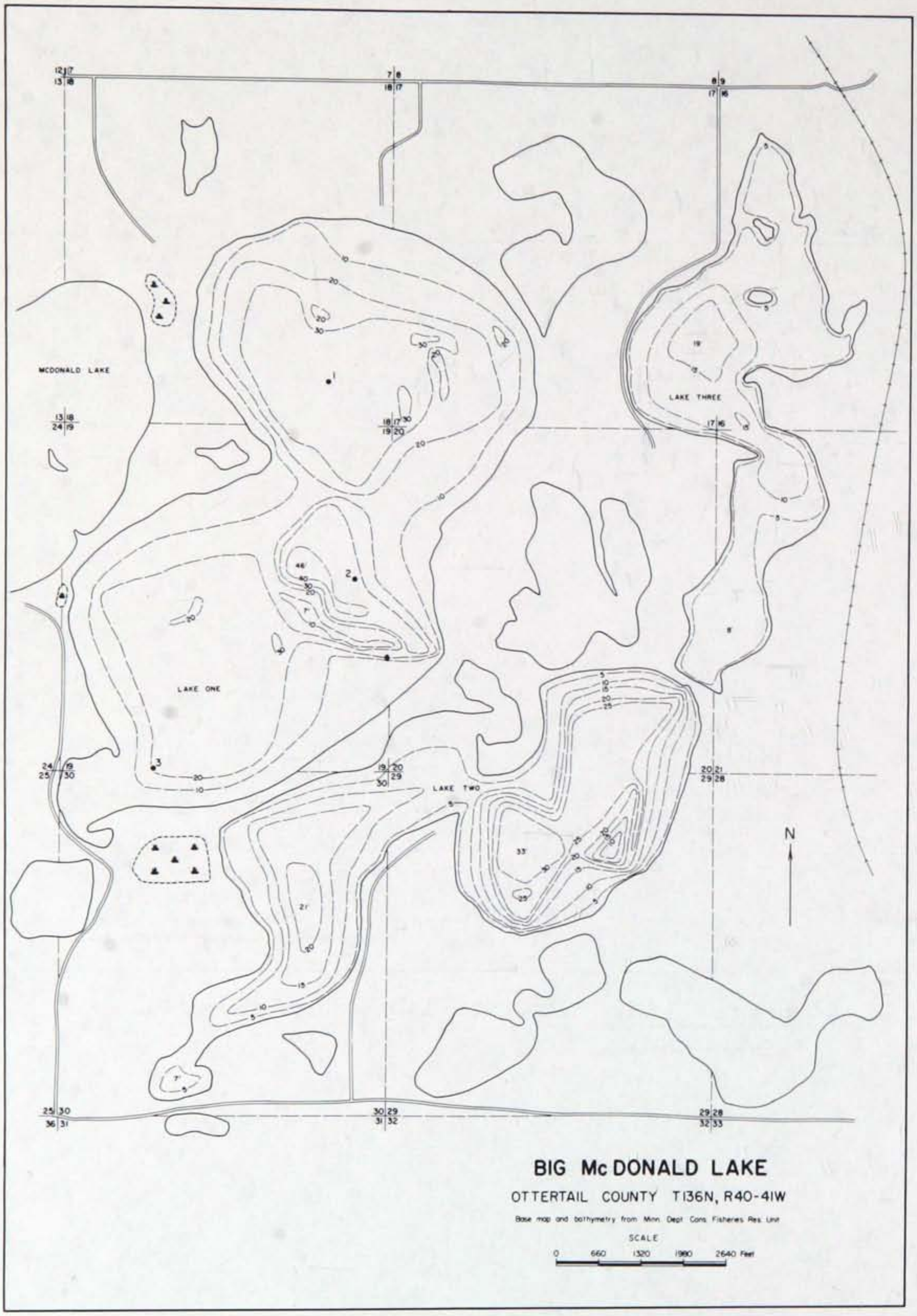


Figure 17. Big McDonald Lake, Otter Tail County, Minnesota.

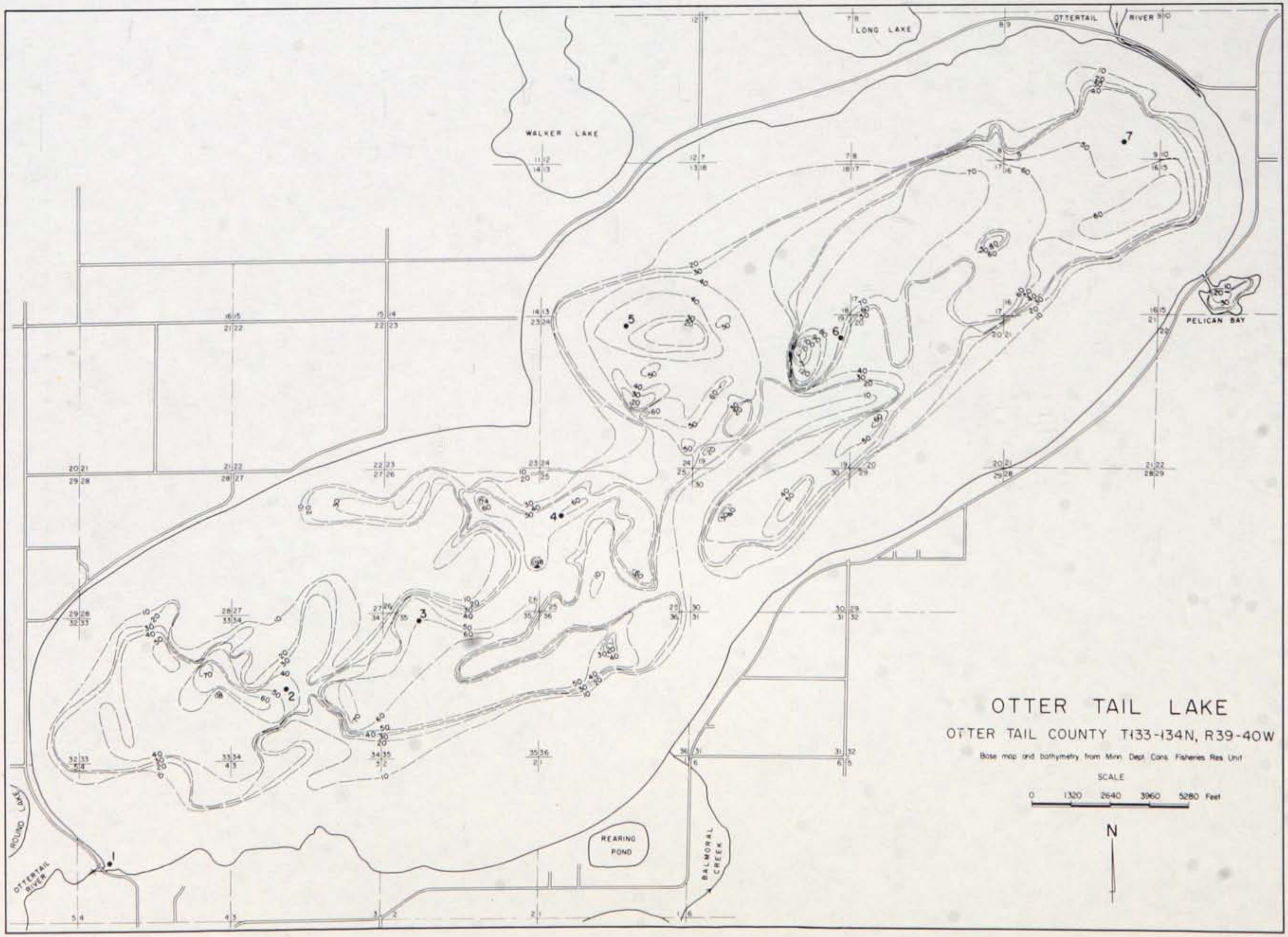


Figure 18. Otter Tail Lake, Otter Tail County, Minnesota.

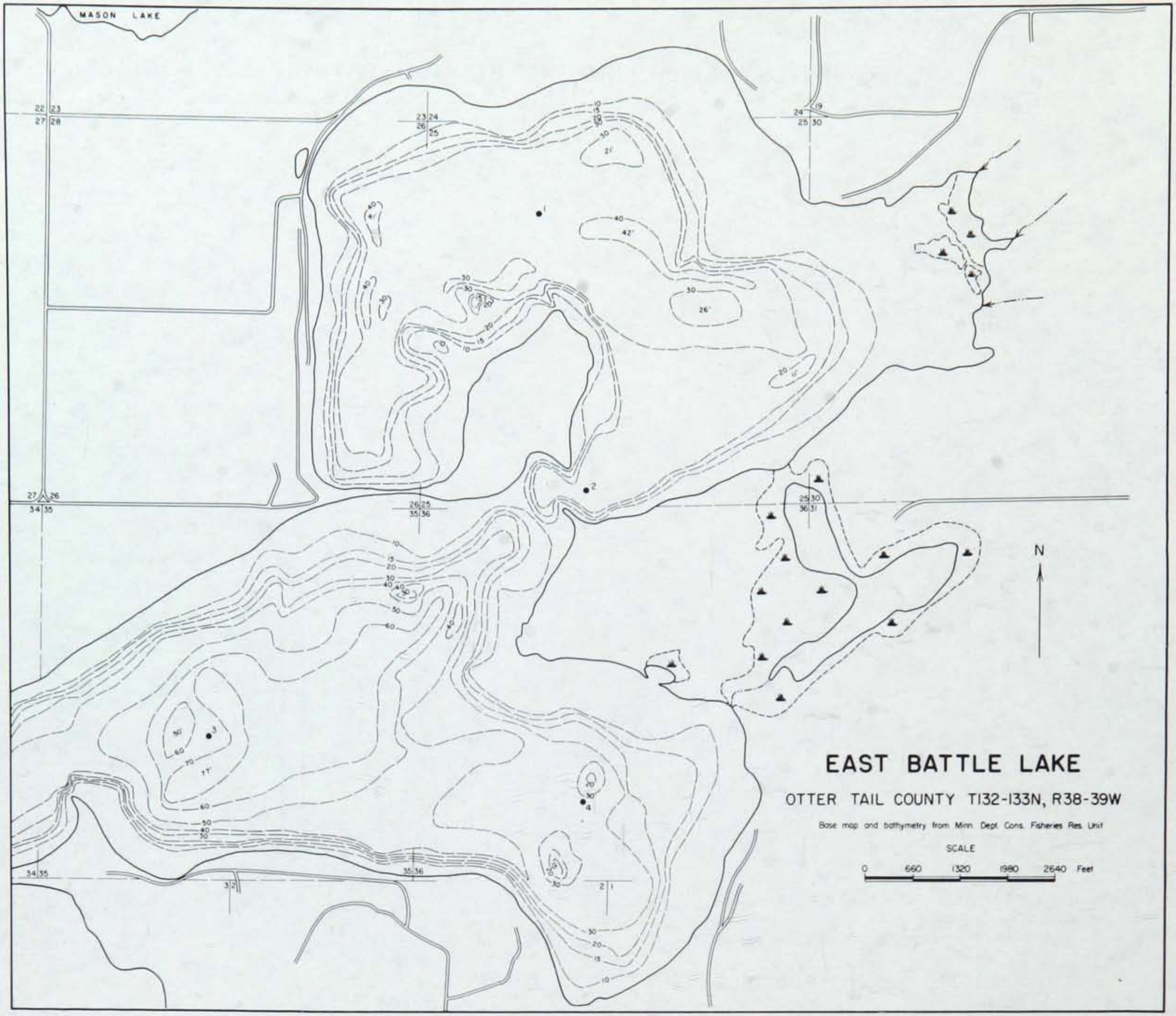


Figure 19. East Battle Lake, Otter Tail County, Minnesota.

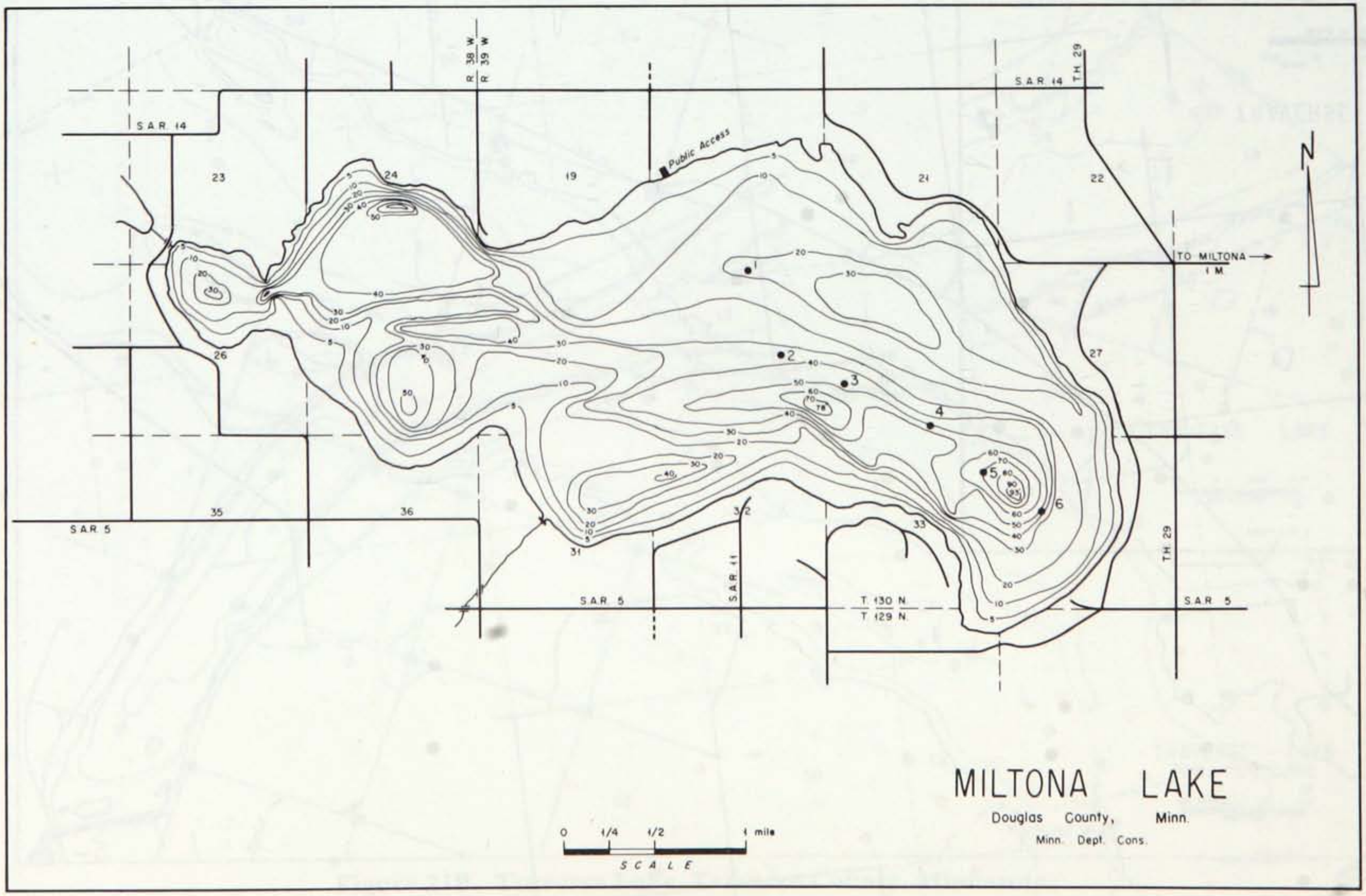


Figure 20. Lake Miltona, Douglas County, Minnesota.

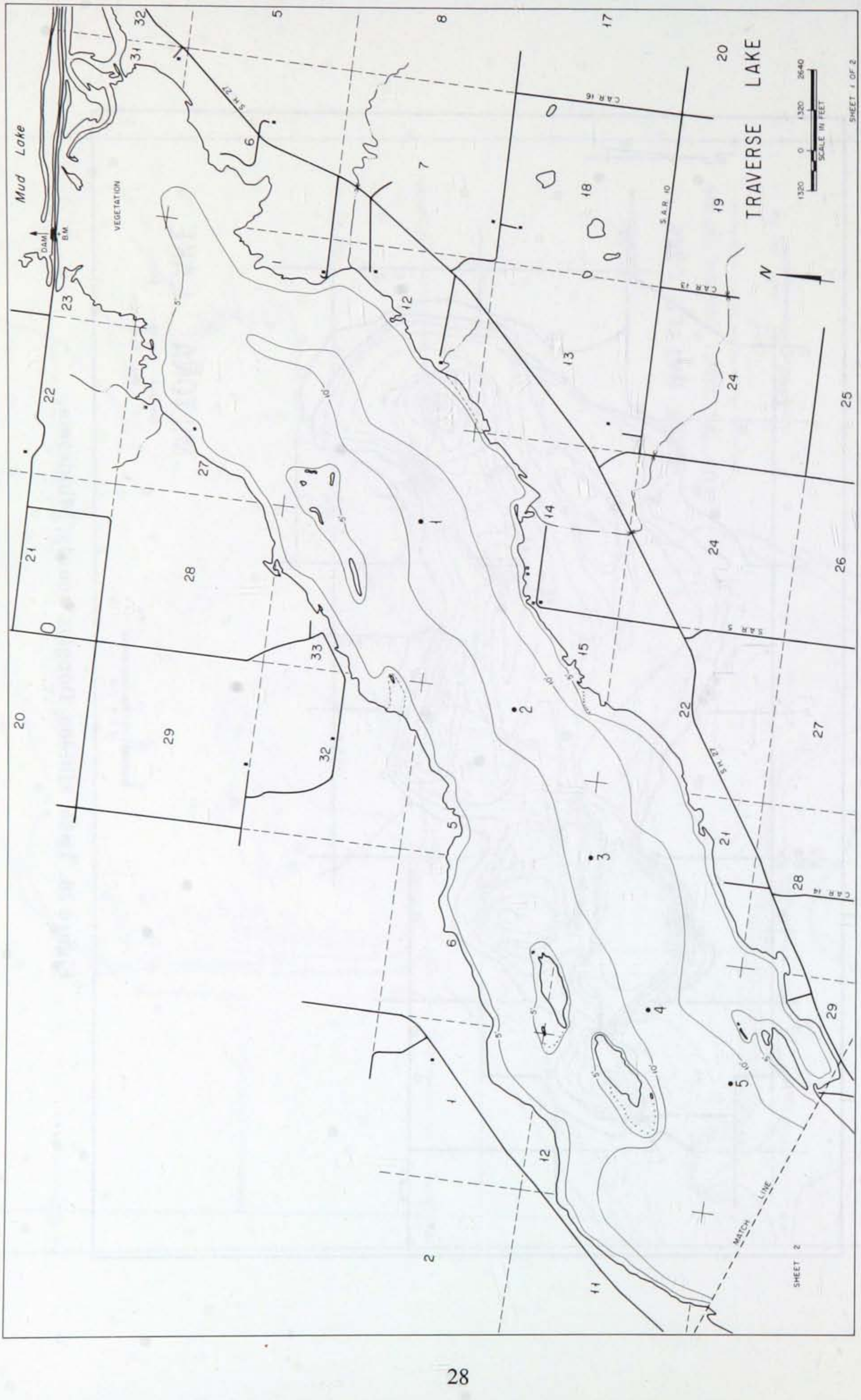


Figure 21A. Traverse Lake, Traverse County, Minnesota.

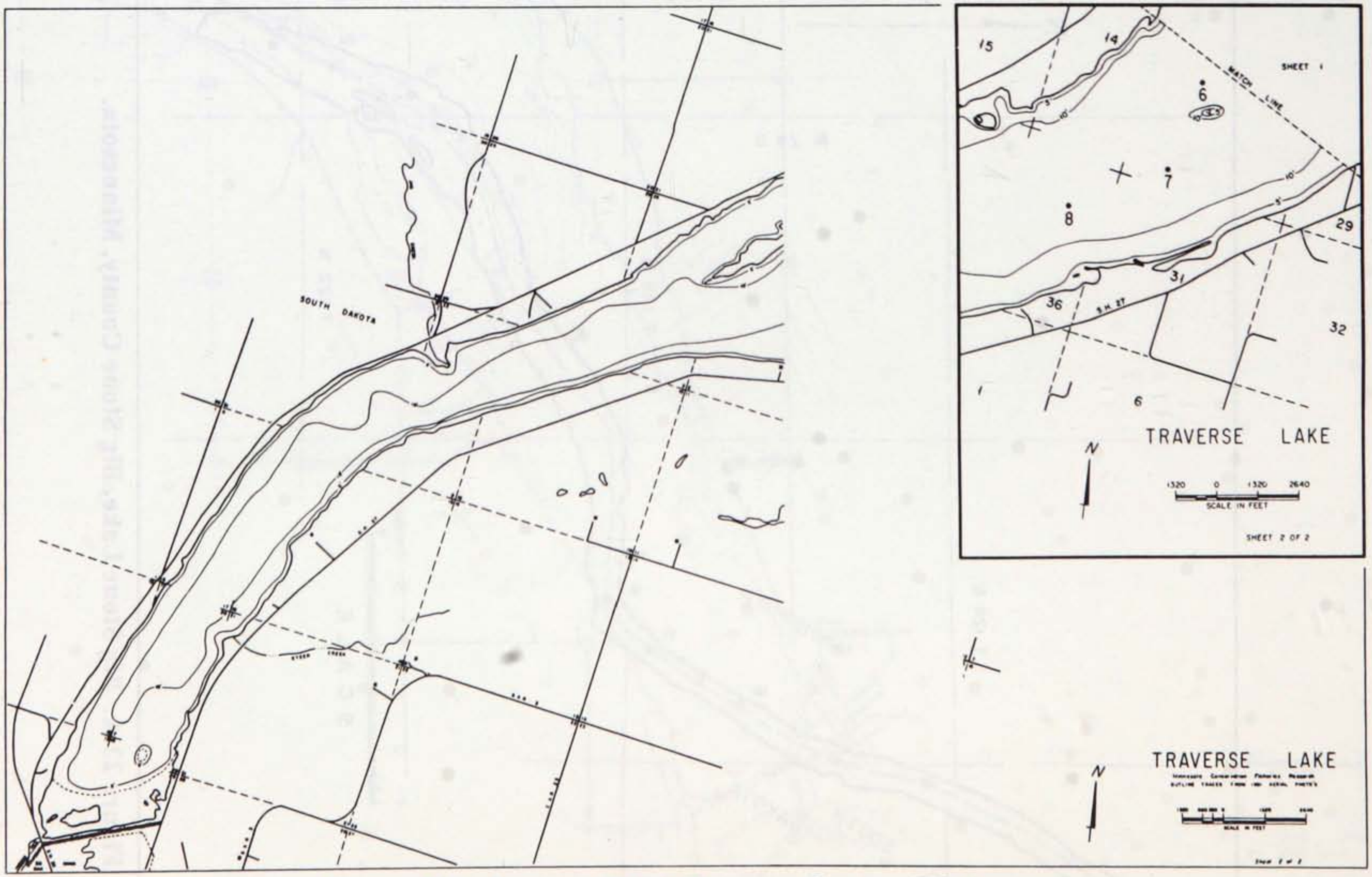


Figure 21B. Traverse Lake, Traverse County, Minnesota.

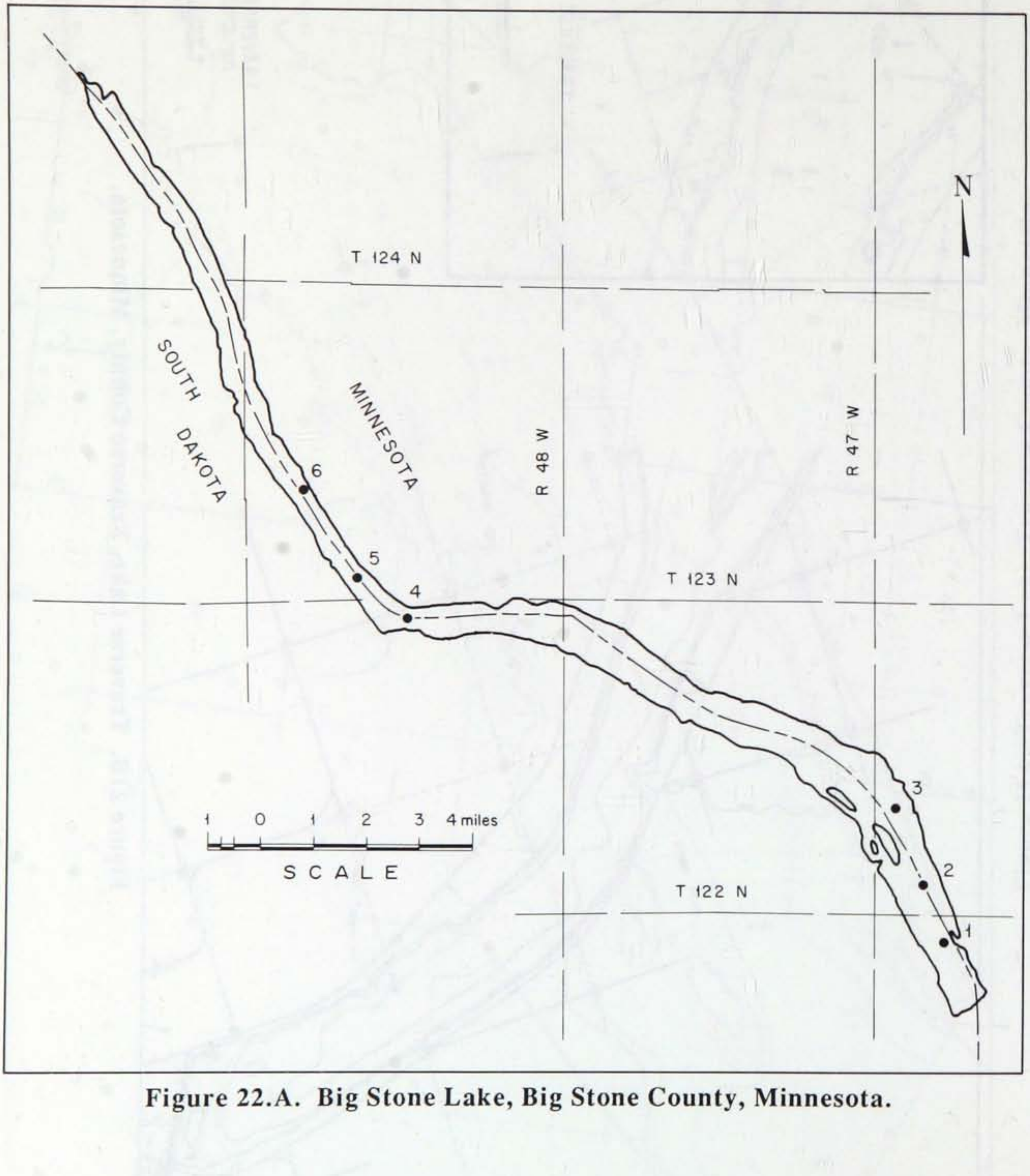


Figure 22.A. Big Stone Lake, Big Stone County, Minnesota.

Figure 22B. Big Stone Lake, Big Stone County, Minnesota.

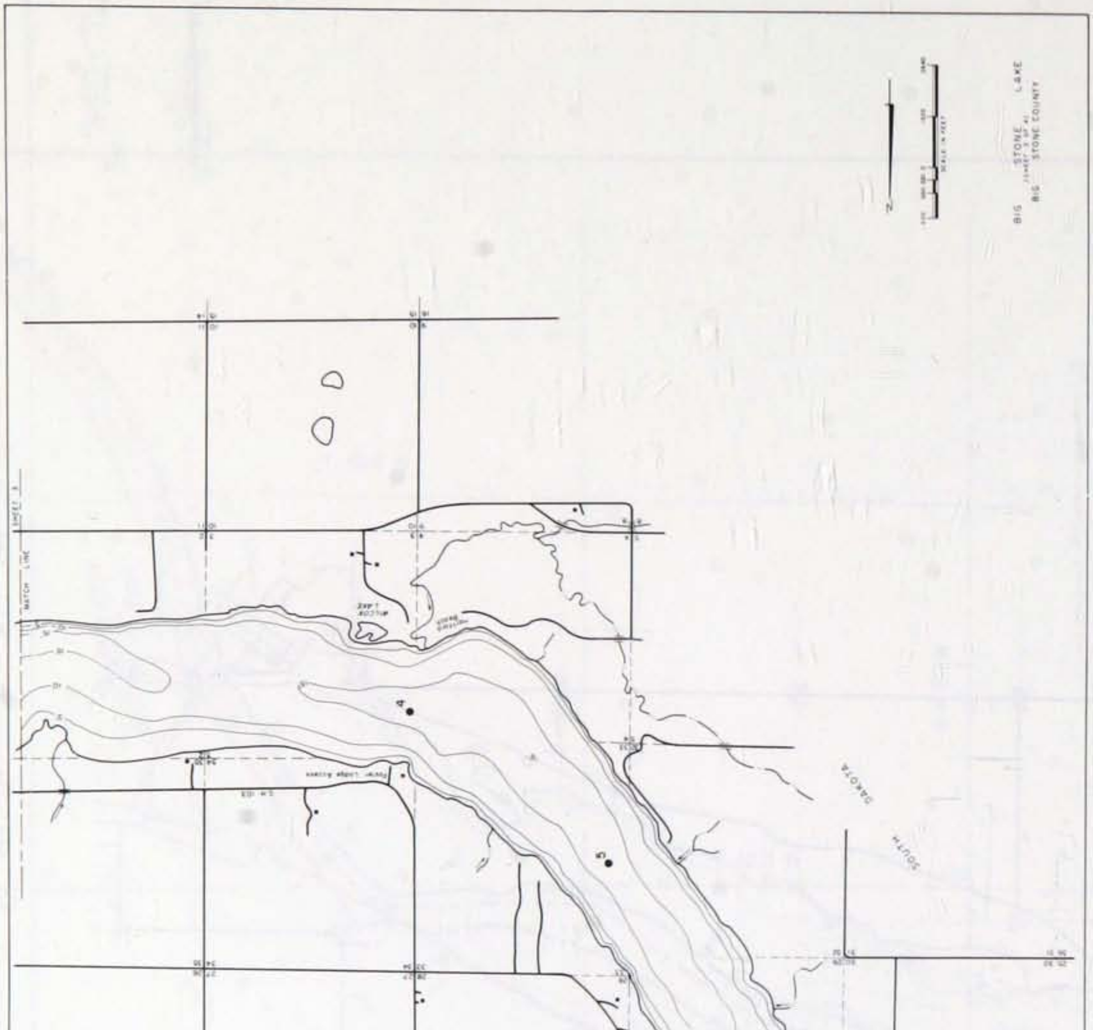


Figure 22C. Big Stone Lake, Big Stone County, Minnesota.

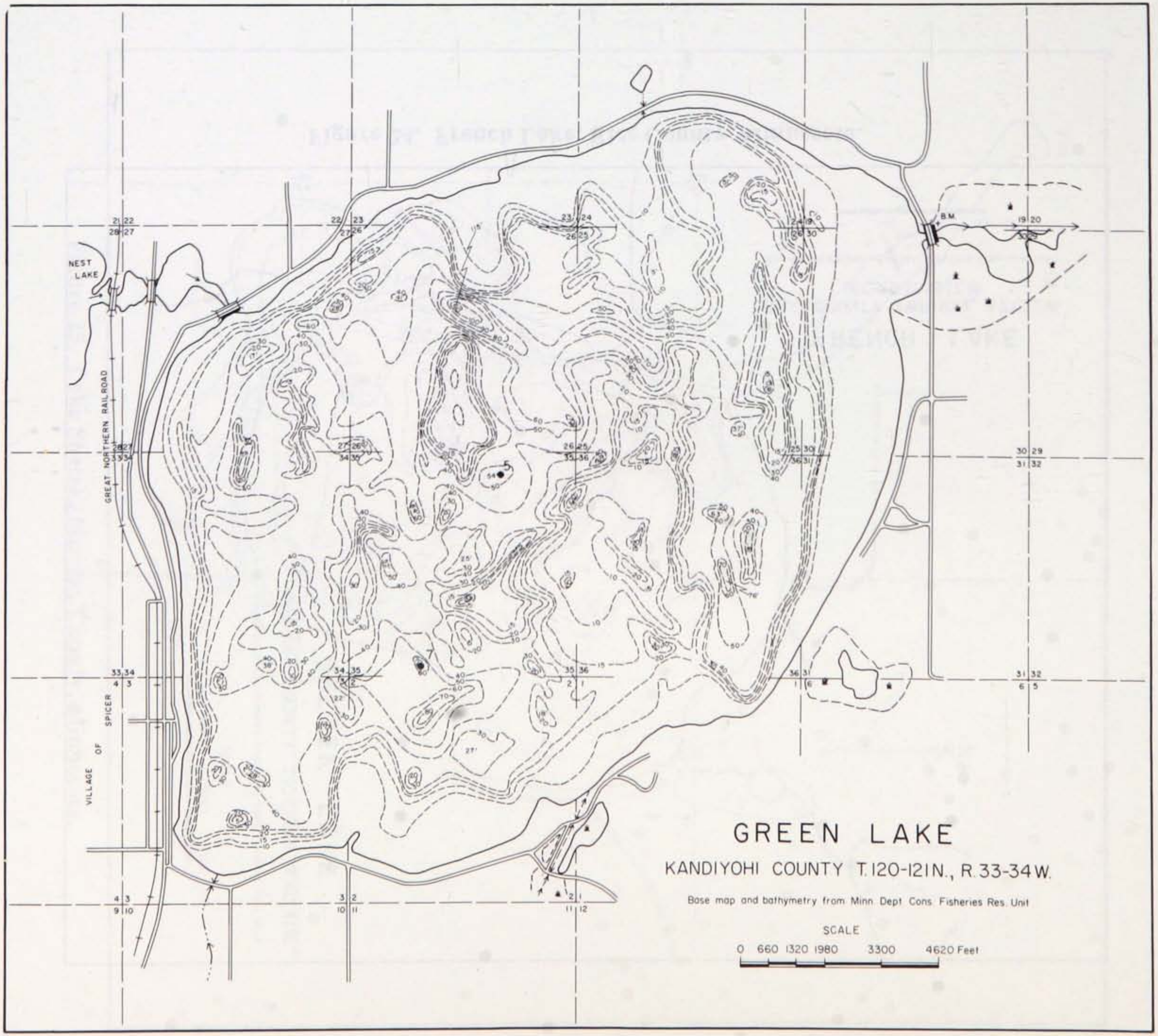


Figure 23. Green Lake, Kandiyohi County, Minnesota.

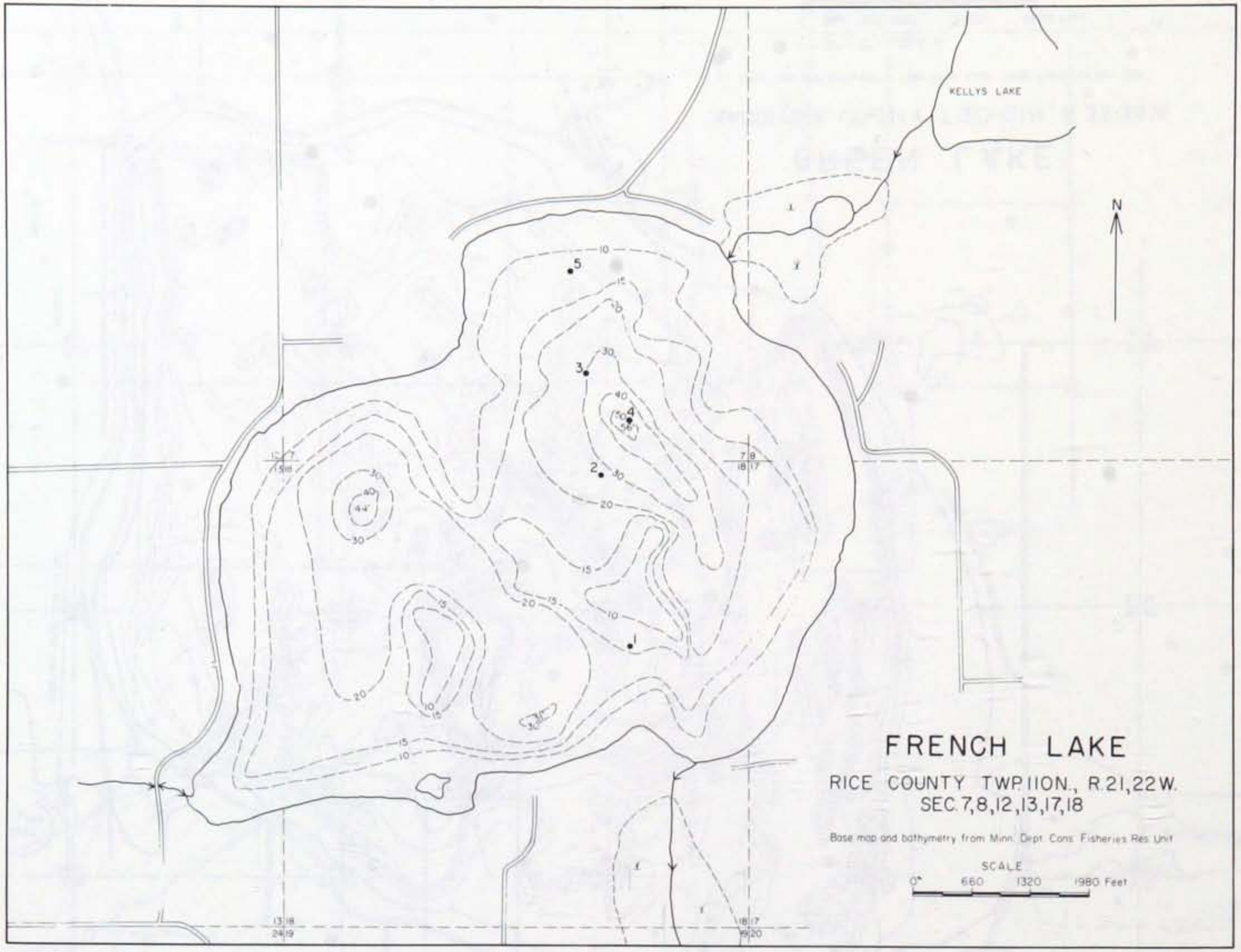


Figure 24. French Lake, Rice County, Minnesota.

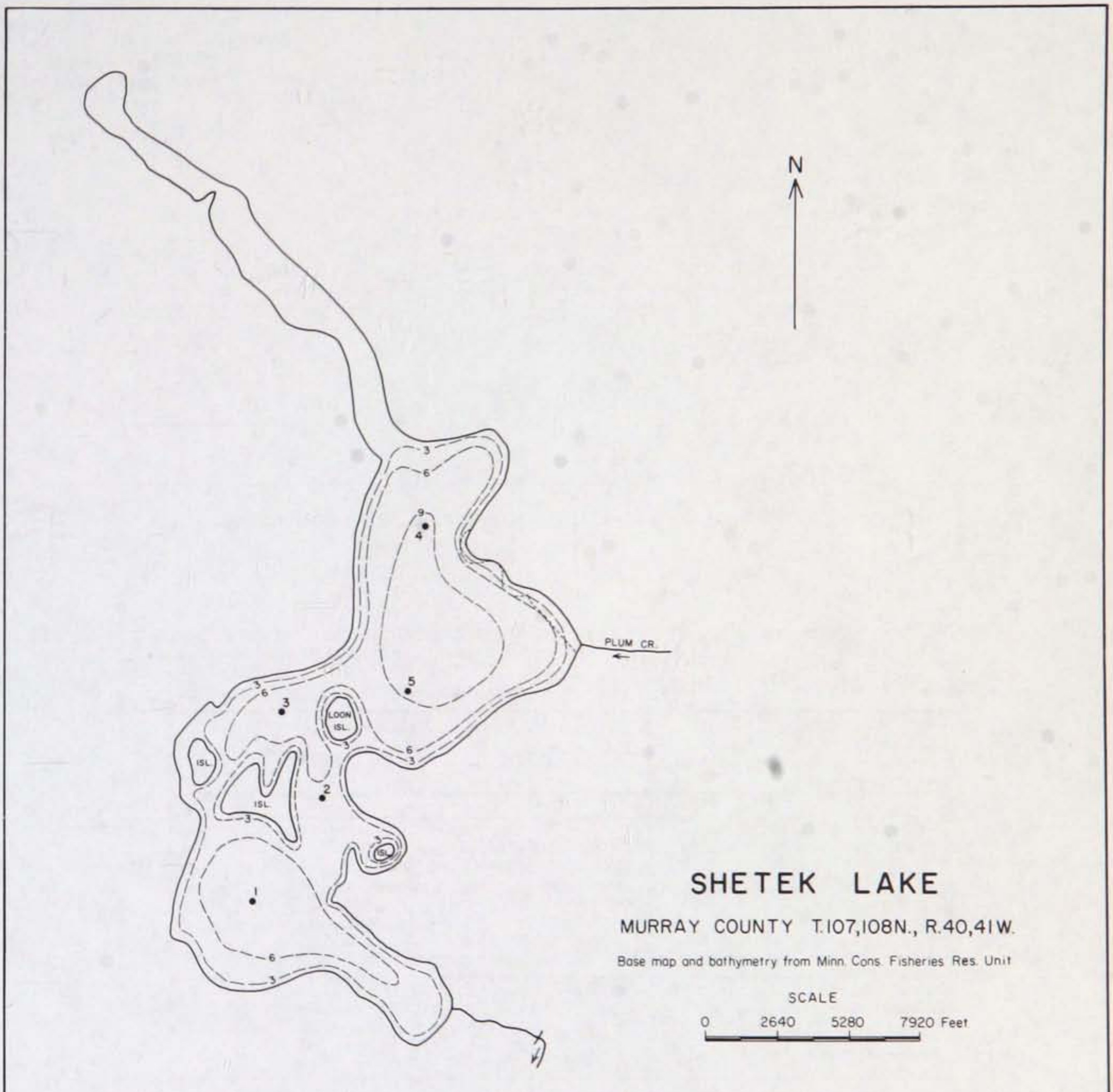


Figure 25. Lake Shetek, Murray County, Minnesota.

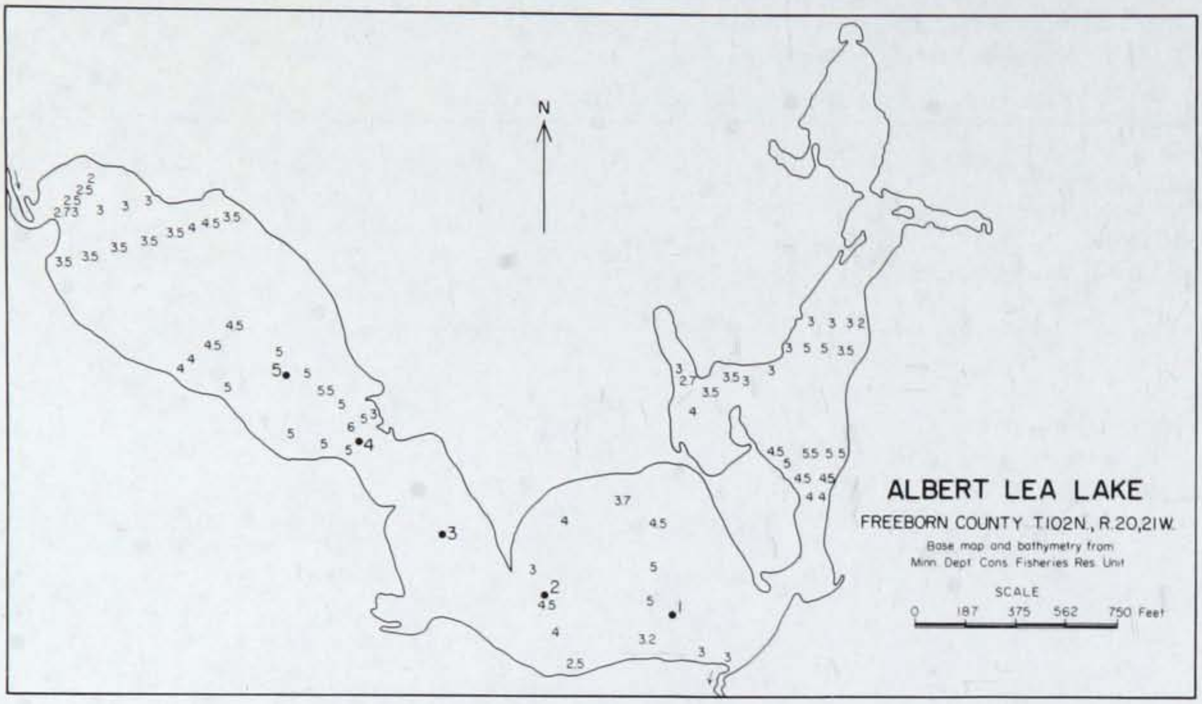


Figure 26. Albert Lea Lake, Freeborn County, Minnesota.

Table 5. Properties of lake sediments in east-central Minnesota. For other lakes in this area, see Swain and Pokopovich (1954); Swain (1956, 1961, 1967); Swain, Venteris, and ting (1964); Rogers (1962, 1965).

Lake and type, total alkalinity, sulfate, phosphorous, nitrogen, and oxygen in ppm	Depth (feet) of samples	pH	Eh	Properties
Whitefish Lake, Crow Wing County (eutrophic), TA 115, SO_4 4.0, P. 001, N 1.28, 0_2 4.7-9.1 (1955) (Fig. 1)	92 (cores)	wtr. 7.18-7.70, top sed. 6.35-7.10, bot. sed. 6.98-7.70	wtr. +191 to +281, top sed. +77 to +95, bot. sed. +74 to +119	Gray-brown copropelic diatomite, 12 in thick, overlying dark gray and brown sandy marly copropel, sapropel, sapropelic clay; goethite spherulites abundant; tough, tenacious.
Pelican Lake, Crow Wing County (eutropic) TA 101, SO_4 3.5, P 0.5, N. 79, O_2 0.2-7.8 (1955) (Fig. 12)	(cores)	wtr. 7.2-7.6, top sed. 7.35-7.5, bot. sed. 6.7-7.6	wtr. +209 to +377, top sed. +137 to +218, bot. sed. +137 to +221	Gray-brown silty diatomaceous copropel, tough and tenacious
Mille Lacs Lake, Crow Wing, Aitkin and Mille Lacs Counties (eutrophic) TA 125, SO_4 17.0, P .006, N 1.66, O_2 6.14-8.1 (1954) (Fig. 13)	21-29 (cores)	wtr. 6.9-7.2, sed. 7.1-7.2	wtr. -60 to -240 sed. -165 to -490	Gray diatomaceous silty and sandy copropel up to 20 in thick overlying more silty clayey and sandy sediments; vivianite masses, reddish sand at base in some cores; tough and tenacious.

Table 6. Properties of lake sediments in west-central and southwestern Minnesota. For descriptions of other lakes in this area, see Swain (1961) and Meader (1956).

Lake and type, total alkalinity, sulfate, phosphorous, nitrogen, and oxygen in ppm	Depth (feet) of samples	pH	Eh	Properties, Kjeldahl nitrogen (%), moisture (%), clay fraction (%)
Cormorant Lake, Becker County (eutrophic) (Fig. 14)	35-36 (cores)	wtr. 7.7-8.1 top. sed. 7.6-7.8, bot. sed. 6-8-7.3	wtr. +401 to +407	Gray copropelic marly silt, tough and tenacious, M 79-85, Cl 63-79
Leek Lake, Ottertail County (eutrophic) (Fig. 15)	18-66 (dredge and core)	wtr. 6.9-7.2, top. sed. 6.9-7.1, bot. sed. 6.8-7.8	m.d.	Gray sandy copropelic silt, marly silt and peaty sand, diatomaceous and cladoceran-rich M 50-83, C1 23-54
Big McDonald Lake, Ottertail County (eutrophic) TA 132-150, SO_4 8, O_2 4.8-9.6	4-70 (dredge and core)	wtr. 7.15-7.2, top sed. 7.13-7.25, bot. sed. 6.65-7.0	wtr. +380 to +437, top sed. +149 to +215	Littoral gravelly sand and profundal gray silty ostracodal copropelic marl, mollusks abundant, C1 8.5-58
East Battle Lake, Ottertail County (eutrophic) (Fig. 16) TA 180, O_2 0.2-8.0	20-75 (dredge and core)	wtr. 7.10-7.12, top sed. 7.15-7.2, bot. sed. 6.85-7	n.d.	Littoral pebbly molluscan sand and profundal gray silty copropelic diatomaceous marl, M 62-76, C1 49-62
Lake Miltona, Douglas County (eutrophic-alkalitrophic) (Fig. 17)	37-85 (cores)	wtr. 7.8-8.35, top sed. 7.6-7.9, bot. sed. 6.9-7.1	wtr. +437 to +461, top sed. +95 to +149, bot. sed. +145 to +189	Pale gray and tan sandy copropelic ostracodal marl up to 15 in thick overlying marly sand, M 68-86, C1 11-65
Ottertail Lake, Ottertail County (eutrophic) (Fig. 18)	21-70 (dredge and core)	top sed. 7.4-7.7, bot. sed. 7.4-7.65	top sed. +155 to +215, bot. sed. +185 to +251	Littoral gravel and sand containing many limestone pebbles; profundal gray silty copropelic ostracodal marl, M 77-90, C1 53-86
Lake Minnewaska, Pope County (eutrophic)	28 (cores)	n.d.		Pale gray silty finely sandy diatomaceous copropelic marl up to 20 in thick, overlying molluscan marly sand, KN .224-.440

Table 6. (Continued)

Traverse Lake, Traverse County (eutrophic) TA 235, SO_4 326, P .12, N .88, O_2 9.1 (Fig. 19)	9-10 (cores)	wtr. 7.8-8.3, top sed. 7.45-8.0, bot. sed. 7.2-7.7	wtr. +413 to +417, top sed. +137 to +185 bot. sed. +47 to +83	Gray sandy silty calcareous clay and clayey silt 24 in or more deep, M 45-74, C1 72-96
Big Stone Lake, Big Stone County (eutrophic)	9-14 (cores)	wtr. 7.5-7.7, top sed. 7.25-7.5, bot. sed. 6.85-7.1	wtr. +446 to +455, top sed. +41 to +113, bot. sed. +59 to +95	Gray sandy molluscan ostracodal diatomaceous silty marl and marly silt 15-20 in thick overlying more sandy silt with vivianite and fewer shells, M 59-81, C1 69-99
Green Lake, Kandiyohi County (alkalitrophic) (Fig. 20)	56-70 cores	n.d.	n.d.	Pale gray ostracodal marl 12-15 in thick overlying sandy and peaty marl and sand, KN .92-.26
Lake Shetek, Murray County (eutrophic) TA 172, SO4 316, P .269, N 5.45, O2 5-5.2 (Fig. 21)	5-9 (cores)	wtr. 8.1-8.15, top sed. 7.1-7.5, bot. sed. 7.05-7.2	wtr. +317 to +347, top sed. +62 to +116, bot. sed. +101 to +131	Gray copropelic calcareous sandy silt up to 2 ft thick becoming more sandy downward, M 57-78, C1 65-91
Turtle Lake, Martin County	3-6 (cores)	wtr. 8.3-8.35, top sed. 7.2-7.45, bot. sed. 6.9-6.9	wtr. +293 to +299, top sed. +89 to +113, bot. sed. +92 to +113	Dark gray carbonaceous copropelic sandy silt diatomaceous beds, finely cryst. pyrite, M 68-79, C1 79-90
Hall Lake, Martin County (eutrophic) P .15-1.5, N 2.3-12.9	(cores)	n.d.	n.d.	Gray calcareous sandy diatomaceous copropelic silt to depth of 40 ft
Albert Lea Lake, Freeborn County (eutrophic) P .15-1.5, N 2.3-12.9	(cores)	wtr. 9.6-9.65, top sed. 7.45-7.8, bot. sed. 6.65-7.05	wtr. +281 to +293, top sed. -4 to +38, bot. sed. +139 to +194	Light gray silty copropelic ostracodal marly silt and silty marl up to 22 in deep, becomes more silty upward, M 81-85, C1 48-91

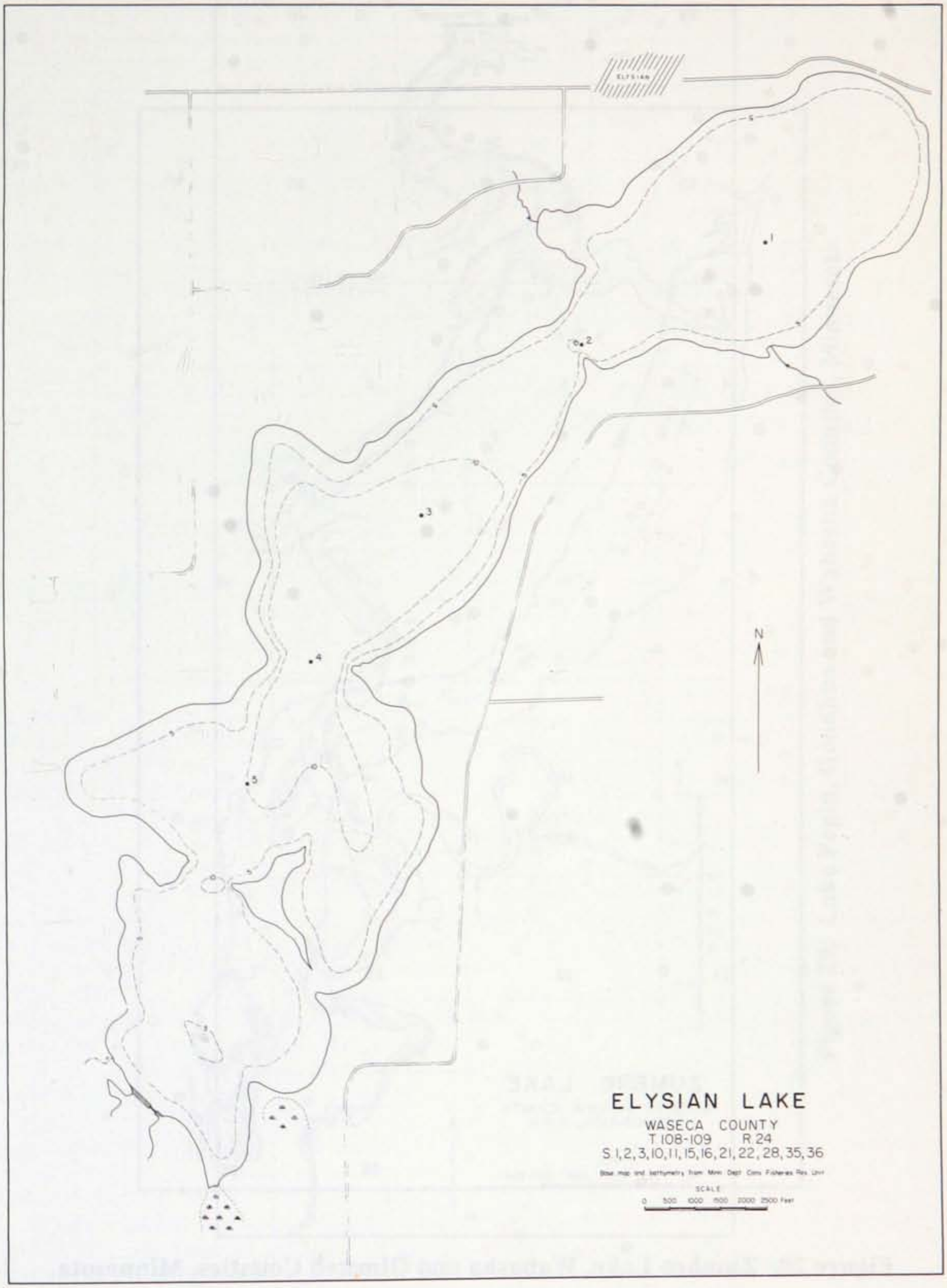


Figure 27. Elysian Lake, Waseca County, Minnesota.

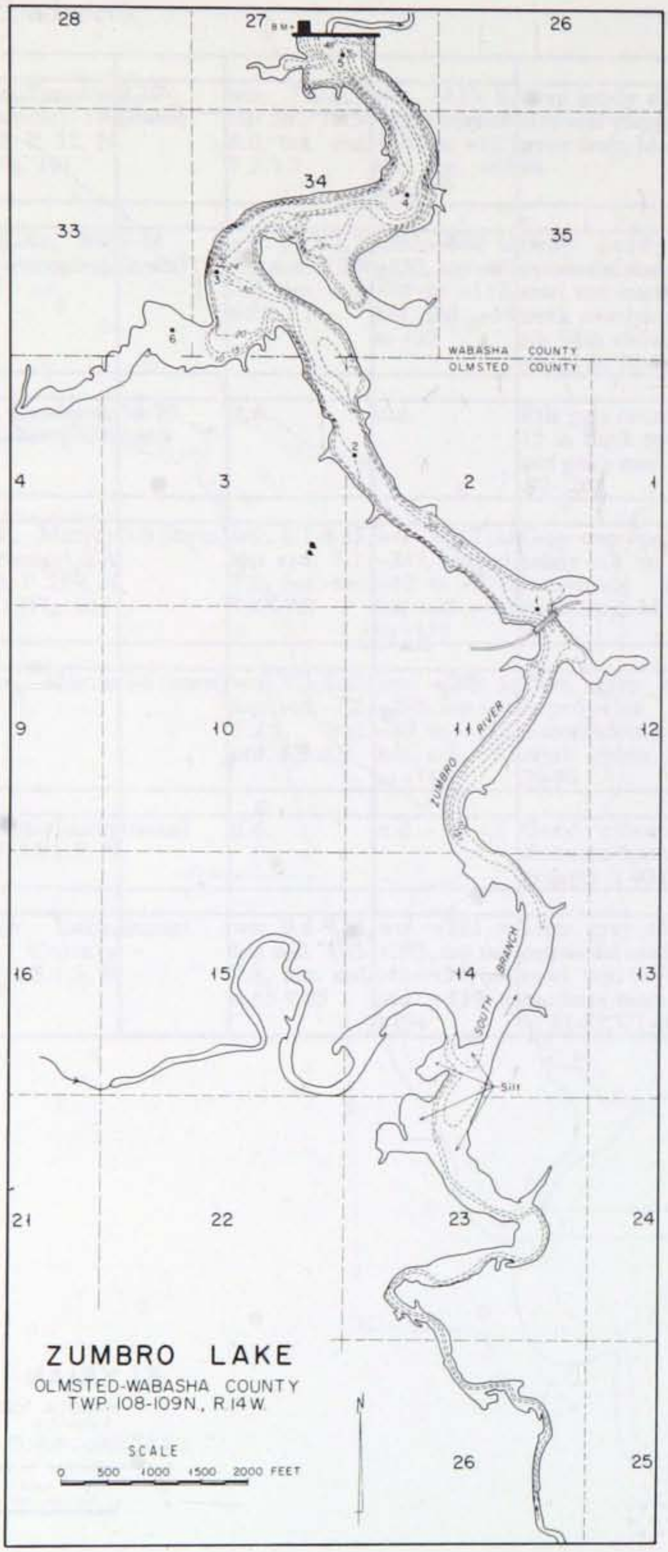


Figure 28. Zumbro Lake, Wabasha and Olmsted Counties, Minnesota.

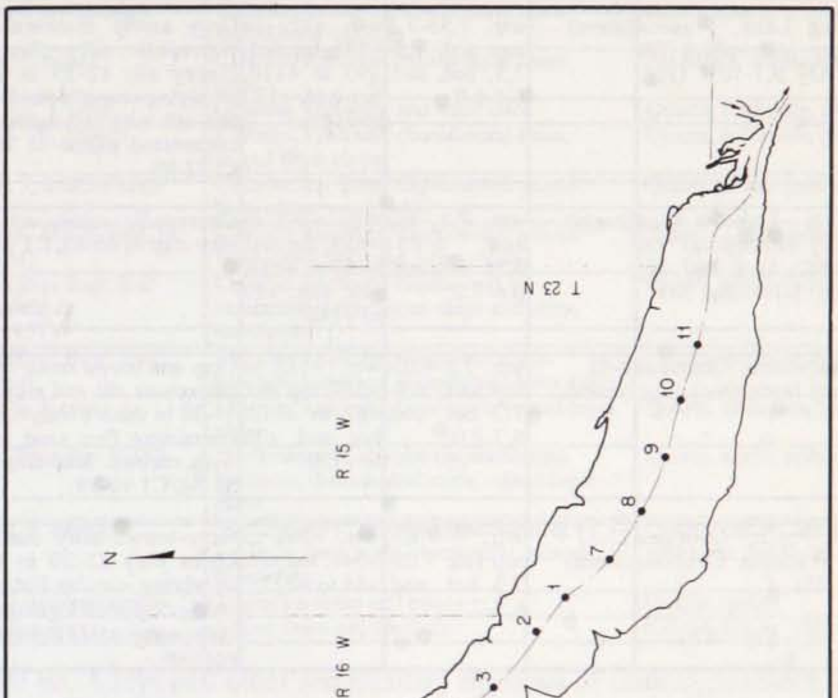


Figure 29. Lake Pepin, Goodhue and Wabasha Counties, Minnesota.

Table 7. Properties of lake sediments in southeastern Minnesota.

Lake and type, total alkalinity, sulfate, phosphorous, nitrogen, and oxygen in ppm	Depth (feet)	pH	Eh	Properties moisture (%), clay-sized particles (%)
Elysian Lake, Waseca County (eutrophic) TA 157, O_2 9.1-10.4 (Fig. 22)	(cores)	wtr. 7.55-7.8 top. sed. 7.2-7.5, bot. sed. 6.6-6.8	wtr. +221 to +245, top sed. +95 to +110, bot. sed. +137 to +149	Gray sandy diatomaceous copropelic silty clay and clayey silt 12-15 in thick overlying coarsely sandy clay and silt with fish bones and carbonized plants M 76-91, Cl 22-85
French Lake, Rice County (eutrophic) TA 110, SO_4 O, P .097, N_2 40, O_2 .1-7.6 (Fig. 23)	(cores)	wtr. 7.7, top sed. 6.85-7.25 bot. sed. 6.6-7.0	wtr. +341 to +359, top sed. +107 to +113, bot. sed. +77 to +142	Copropelic sandy silt and silty clay M 60-83, C1 90-99
Lake Zumbro, Olmstead County (eutrophic) (Fig. 25)	9-42 (cores)	wtr. 7.3-8.05, top sed. 6.9-7.2 bot. sed. 6.7-7.0	wtr. +323 to +347, top sed. +62 to +113, bot. sed. +77 to +110	Gray and brown sandy clayey calcareous silt and silty clay 15-20 in thick overlying silts containing fine sand layers with carbon. leaf frags. M 33-84, C1 96-99
Lake Pepin, Goodhue and Wabasha Counties (Fig. 25)	23-27 (cores)	wtr. 7-7.65, top sed. 7.05-7.3 bot. sed. 6.5-7.1	wtr. +341 to +348, top sed. +86 to +122,	Gray-brown silty diatomaceous clay 15-20 in thick overlying similar but more sandy clay with vivianite and manganese oxide masses and nodules

CLAY MINERALS

Analyses of clay mineral components of Minnesota lake sediments by X-ray diffraction were done by Peter Fleischer from samples supplied by the writer. Using the method of Warshaw and Roy (1961) to identify the clays and other components, samples were treated in the following ways prior to X-ray diffraction: (1) random-oriented samples, (2) water-oriented mount, (3) sample heated to 250° C, (4) sample heated to 500° C, and (5) sample glycolated.

Northeastern Minnesota. The X-ray analyses of clays and other minerals in several northeastern Minnesota lakes are given in Table 8. Normal chlorite, 7 Å layer minerals, represented by kaolinite and/or septechlorite, and 10 Å mica are the three principal layer silicates in lake sediments of this area. Mixed-layer silicates, dioctahedral and trioctahedral micas, and vermiculite are present in smaller amounts. These minerals, together with quartz, feldspars, and ferromagnesian minerals, represent the mineral composition of the glacial drift of the area, and to a lesser extent that of the Precambrian bedrock.

Northwestern Minnesota. The lakes of this area were not analyzed for clay minerals.

North-Central Minnesota. Sediments of two lakes, Cass and Walker Bay of Leech Lake, were analyzed for clay minerals (Table 8a). In both lakes, besides muscovite mica, only traces of 7 Å clay minerals were found.

East-Central Minnesota. Among the lakes analyzed for clay minerals in this area (Table 8b), kaolinite and chlorite are the most common clay constituents, but montmorillonite, both complexed and not complexed with organic matter, was noted. Some mixed-layer clays were found in Lakes Minnetonka and Mille Lacs. The absence of montmorillonite in the lake sediments of other areas in Minnesota and its presence in this area of high organic-productivity is noteworthy.

West-Central and Southwestern Minnesota. Clay minerals were absent or present only in small amounts in most of the lakes (Table 8b). 7 Å clays, septechlorite or kaolinite, or both, are the principal clay minerals noted in this area together with some dioctahedral micas and mixed-layer clays.

Southeastern Minnesota. Lake Pepin and Zumbro Lake were analyzed for clay minerals in this area (table 8b). Both lakes contain normal chlorite and kaolinite, together with dioctahedral mica and mixed-layer clays.

Table 8a. Clays and other minerals of lake sediments of northern and north-central Minnesota as determined by X-ray analyses by Peter Fleischer. Previously published references to lake in parentheses in first column.

Lake	Clay Minerals	Other Minerals
Burntside Lake, middle of core (Swain, 1956) Sta. 10	Chlorite, kaolinite, dioctahedral mica, mixed-layer clays,dioctahedral vermiculite	Quartz, feldspar, augite
Snowbank Lake, Sta. 4 dredge sample	Chlorite, kaolinite, dioctahedral mica, mixed-layer clays	Albite, quartz, augite
Crane Lake, Sta. 2, core	Chlorite, kaolinite, mixed-layer clays, mica	Feldspars, quartz, pyroxenes
Sea Gull Lake, Sta. 3, core	Chlorite, kaolinite, and trace mica	Quartz, feldspars, pyroxenes
Lac la Croix, Sta. 10, dredge samples	Chlorite, kaolinite, dioctahedral mica, mixed-layer clays	Quartz, feldspars, pyroxenes
Rainy Lake, Sta. 7, mid. of core (Swain, 1961)	Chlorite, kaolinite, dioctahedral mixed-layer clays, vermiculite	Quartz, albite, pyroxenes
Lake Kabetogama, Sta. 6, mid. of core (Swain, 1961)	Chlorite, kaolinite, dioctahedral mixed-layer clays and mica, vermiculite	Quartz, albite, pyroxenes
Lake Superior, Silver Bay, Sta. 0-2, top core (Swain & Propkopovich, 1957)	Chlorite, kaolinite, diocta- and tri-octahedral mixed-layer clays and mica, vermiculite	Quartz, albite, orthoclase
Lake Superior, Silver Bay, Sta. 0-2, mid. of core	Chlorite, kaolinite, dioctahedral and trioctahedral mica, some mixed-layer clays	Quartz, feldspars, pyroxenes
Gunflint Lake, Sta 2, core	Chlorite, kaolinite, trace mica, mixed-layer clays	Quartz, feldspars, pyroxenes
Lake Superior, Silver Bay Sta. 0-2, bot. of core	"Sedimentary" chlorite (septechlorite) kaolinite, dioctahedral mica, mixed-layer clays	Quartz, albite, orthoclase, augite
Moose Lake, Sta. 3, dredge sample	"Sedimentary" chlorite (septechlorite) kaolinite,trace mica, vermiculite, mixed-layer clays	Quartz, calcite, feldspars, pyroxene, dolomite
Cass Lake, Sta. 1 dredge sample	Traces kaolinite and mica	Calcite, quartz
Leech Lake, Walker Bay	Traces mica and kaolinite	Calcite, quartz, albite, dolomite

Table 8b. Clays and other sedimentary minerals of central, southern, and southwestern Minnesota.

Lake	Clay Minerals	Other Minerals
Mille Lacs Lake, Sta. 4, core sample	Trace kaolinite and mixed-layer clays	Quartz, feldspars, pyroxenes
Clear Lake, Sta. 8, middle of core (Swain, 1961)	Traces mica, kaolinite, and chlorite	Calcite, quartz
Blue Lake, Sta. 4, middle of core (Swain, 1961)	Organic-complexed montmorillonite and/or dioctahedral vermiculite, mica, kaolinite, chlorite?	Calcite, quartz, albite
Prior Lake, Sta. 9, middle of core (Swain, 1956)	Chlorite, kaolinite, mica, mixed-layer clays	Quartz, feldspars, dolomite
Cedar Lake, Sta. 2, middle of core (Swain, 1956)	Trace kaolinite, mica, or mixed-layer clays	Calcite, quartz
Green Lake, Sta. 5, bottom of core	Traces mica and kaolinite	Calcite, quartz, dolomite, feldspars, gypsum
Ottertail Lake, Sta. 4, dredge	Traces mica and kaolinite	Calcite, quartz, feldspars
Lake Miltona, Sta. 2, bottom of core	Trace kaolinite, but essentially no clay minerals	Calcite, quartz, dolomite, feldspars
Cormorant Lake, Sta. 2, bottom of core	Chlorite?, kaolinite?, mixed-layer clays and mica	Quartz, dolomite, calcite, feldspars
Lake Shetek, Sta. 2, bottom of core	Chlorite, kaolinite, dioctahedral mica and mixed-layer clays	Quartz, feldspars, calcite, dolomite, aragonite
Albert Lea Lake, Sta. 2, bottom of core	No detectable amount	Calcite, quartz
Lake Traverse, Sta. 2, bottom of core	Chlorite?, kaolinite?, dioctahedral mica and mixed-layer clays	quartz, calcite, dolomite, feldspars, aragonite, pyrite?
Zumbro Lake, Sta. 3, bottom of core	Chlorite, kaolinite, dioctahedral mica, and mixed-layer clays, vermiculite	Quartz, felspar, calcite, gypsum
Lake Pepin, Sta. 1, bottom of core	Chlorite, kaolinite, dioctahedral mica, and mixed-layer clays	Quartz, feldspar, dolomite?
Lake Pepin, Sta. 2, bottom of core	Chlorite, kaolinite, dioctahedral mica, mixed-layer clays	Quartz, dolomite, feldspar

FOSSILS

The preserved organic remains in Minnesota lake sediments cover a great variety of both plants and animals, and include diatoms, other algae, pond weeds and other larger plants, thecamoeboid and tintinnoid protozoans, sponge spicules, gastropods, bivalves (pelecypods), insect parts, cladocerans, and ostracodes. The writer will summarize below the distribution only of the Ostracoda, with which he is most familiar (Fig. 36), and will refer in general terms to the other fossil residues.

CARBOHYDRATES

Only a limited amount of work has been done on the carbohydrates of lake sediments in Minnesota (Rogers, 1965; Swain, 1967).

Methods of study. Total carbohydrate content of sediment samples is determined by a phenol-sulfuric acid colorimetric method (Rogers, 1965). Free monosaccharides are extracted from the sediments with boiling water and analyzed by chromatographic methods (Rogers, 1965). Monosaccharides occurring in polymeric form in the sediments are extracted with sulfuric acid and the individual sugars analyzed by chromatographic and enzymatic methods (Rogers, 1965; Swain, 1967; Swain and others, 1967a). Examination of the polysaccharides in Minnesota lake sediments has been made only in Cedar Creek Bog, east-central Minnesota.

Northeastern Minnesota. The bottom sediments of several northeastern Minnesota lakes were analyzed for total carbohydrates (Table 9). The relatively high carbohydrate content in the sediments of Poplar Lake and Kabetogama Lake is due to the highly organic copropelic nature of the profoundal sediments, compared to the generally low but well-preserved organic content of the other lake sediments studied in this area. The values for Gunflint Lake are high because the samples were obtained from a part of the lake basin that apparently acts as a sump for the settled organic matter, much of which is preserved.

Northwestern Minnesota. In this area carbohydrates have been studied only in Lake of the Woods and in Red Lake Bog. The qualitative analysis of monosaccharides and oligosaccharides in a sediment sample in Lake of the Woods is given in Table 13. It is possible that effluent from the paper mill at International Falls contributed some of the sugars, although an attempt was made to avoid such contamination by selecting samples far out in the lake with no visible effluent particles.

Moderately rich total carbohydrates were obtained from a core in Red Lake Bog (Fig. 34). Higher values were found in sedge peat than in underlying woody peat.

North-Central Minnesota. The carbohydrate content of Cass Lake and Leech Lake (Table 9) is moderate, reflecting the early eutrophic nature of the lakes and fair preservation of the settled organic matter.

East-Central Minnesota. The total carbohydrate content of sediments of several lakes and bogs in east-central Minnesota is given in Tables 10-12. The four bogs, Rossburg Bog, Aitkin County (Swain, 1967); Kirchner Marsh, Dakota County (Swain, 1965); Cedar Creek Bog (Swain and Prokopovich, 1954); and Bethany Bog, Anoka County, were not described in the above discussion of lake sediments. A brief summary of the stratigraphy of Bethany Bog is given in Table 12; that of the other bogs was given previously. The total carbohydrates of the sediments of Blue and Clear Lakes are higher than those of northern Minnesota lakes because of the more advanced stage of trophication in these lakes and generally higher content of carbohydrate-rich plants.

In the bog sediments there is a definite relationship between stratigraphy and total carbohydrate content (Swain, 1970). The stratigraphic sequence in the bogs in turn reflects the trophic history of the area (Swain, 1967). The carbohydrate content of Kirchner Marsh "gyttja" (copropel) is much lower than that in other lake sediments in eastern Minnesota (Swain, 1970), due perhaps both to the high protein nature of the sediments and to their high degree of humification.

Analyses of individual sugars in this area have been obtained of Blue Lake, Clear Lake, and Rossburg Bog sediments and of the living plants associated with them (Rogers, 1965; Swain, 1970). The results are discussed in the publications cited. The principal findings were that the plant sugars and sediment sugars are different, and that there is indication of appreciable modification of the sediment sugars by microorganisms during sedimentation and diagenesis.

Polysaccharide contents based on enzymatic analyses of Cedar Creek Bog peat were found by F.T. Ting (unpublished report) to decrease rapidly with depth. Starch residues were found only in the upper 10-12 in of the peat in which roots of living plants occur. Cellulose residues were confined to the upper 5 ft and decreased rapidly below 10 in.

West-Central and Southwestern Minnesota. The total carbohydrates of the upper part of the sediments of East Battle Lake, Leek Lake, and Big McDonald Lake in western Minnesota and of the complete sequence of lake sediments of Hall Lake, southwestern Minnesota, are given in Table 9 and in Swain (1970). The total carbohydrates of the upper sediments of these lakes are comparable in amount to those of the eutrophic lakes of central Minnesota, and indicate that the amount of source material and manner of its preservation have been similar to that in the central lakes.

The individual sugars were analyzed by M.A. Rogers for the Hall Lake sediments (Swain, 1970). A definite increase in total carbohydrates as well as in individual sugars at around 20 ft depth shows that a period of increased productivity or preservation, or both, occurred several thousand years ago in this area.

Southeastern Minnesota. Carbohydrate analyses have not yet been made on lake sediments in southeastern Minnesota.

Table 9. Carbohydrate contents of lake sediments in northeasten, north-central, and west-central Minnesota (analyses by D. Deischl).

Lake and core number; 3 ft cores	Total carbohydrate mg/g on dry weight basis		
	Top	Middle	Bottom
Seagull Lake, Sta. 1	8.7	12.1	7.9
Poplar Lake, Sta. 1	26.7	36.6	26.3
Gunflint Lake, Sta. 1	26.6	21.3	n.d
Burntside Lake, Sta. 1	16.8	7.0	11.2
Kabetogama Lake, Sta. 5	17.2	24.2	11.5
Rainy Lake, Sta. 3	15.3	9.8	27.7
Leech Lake, Sta. 3	25.2	61.2	40.3
Crane Lake, Sta. 2	31.5	36.0	27.7
East Battle Lake, Sta. 3	31.2	35.7	28.1
Cass Lake, Sta. 1	31.9	19.9	27.0
Big McDonald Lake, Sta. 3	12.8	27.8	22.5
Leek Lake, Sta. 1	30.0	24.3	15.4

Table 10. Carbohydrate contents of lake sediments in east-central Minnesota compared to carbohydrate conetents of sediments from Coos Bay, Oregon (analyses by M.A. Rogers).

Lake	Sediment	Total carbohydrate mg/g on dry weight basis
Blue Lake	Sapropel	58.6
Blue Lake	Copropel with *Elodea*	105.0
Clear Lake	Copropel and marl	16.0
Clear Lake	Copropel and marl	40.0
Clear Lake	Copropel and sand with *Najas*	36.7
Clear Lake	Marl and copropel	48.3
Clear Lake	Copropel	19.1
Clear Lake	Copropel and sapropel	21.2
Coos Bay	Mudflat sand, Mica bay	0.0
Coos Bay	Clay and sand, outer bay	3.4
Coos Bay	Mudflat sand, Mica bay	1.0

Table 11. Carbohyrate contents of Rossbury Bog peat; values are in mg/g of carbohydrates expressed as glucose equivalent, on a dry weight but not ash-free basis. Dotted line represents base of *Sphagnum* peat at each station; dashed line represents base of copropelic peat at each station.

Sta. 1 depth (ft.)	mg/g	Sta. 2 depth (ft.)	mg/g	Sta. 4 depth (ft.)	mg/g	Sta. 7 depth (ft.)	mg/g	Sta. 10 depth (ft.)	mg/g
0-2	83.4	0-0.5	106.5	0-0.5	87.7	0-0.5	175.7	0-0.5	163.5
5-8	46.8	0.5-0.7	86.1	0.5-0.7	131.8	0.5-0.7	175.0	0.5-0.7	250.7
8-10	58.1	0.7-1.0	124.3	0.7-1.0	113.5	0.7-1.0	185.9	07.-1.0	233.9
10-12	101.5	2--4	111.7	1-2	100.2	1-2	161.0	2-4	56.9
....	....	4-5	93.2	2-3	148.8	2-3	173.2	4-6	40.2
12-15	68.0	5-6	87.7	3-4	88.6	3-4	85.1	6-8	48.7
15-18	20.4	6-8	114.3	4-5	52.5	4-5	81.9	8-10	50.3
--------	-------	8-10	82.3	5-6	57.3	5-6	90.5	10-12	49.4
18-20	0.23	10-12	135.4	6.7	128.9	6-7	122.6	....	....
		....	....	7-8	36.3	7-8	97.9	12-15	14.9
		12-14	58.0	8-9	30.7	8-9	117.7	15-18	19.4
		14-16	35.6	9-10	65.6	9-10	59.0	18-20	8.5
		16-18	38.1						
		18-20	66.3						
		20-22	8.0						
		---------	--------						
		22	0.08						

Table 12. Carbohydrate contents of Bethany Bog peat, 1 mile south of Coopers Corners, Anoka County, Minnesota (analyses by M. Malinowsky).

Depth	Type of peat	Total carbohydrates mg/g dry weight
Surface Sample A	*Sphagnum* moss	702.4
Surface Sample B	*Sphagnum* moss	524.0
0-0.5 ft	*Sphagnum* peat and moss	394.8
0.5-1 ft	*Sphagnum* peat and moss	582.2
2-3 ft	*Sphagnum* peat	251.1
3-4 ft	*Sphagnum* peat	257.6
4-5 ft	*Sphagnum* peat	219.2

Table 13. Carbohydrate contents of lake sediments in northwestern and east-central Minnesota (analyses by A. Blumentals and F.M. Swain); separations of sulfuric acid extracts of lake sediments were made by paper chromatography in BuOH:HOAC:H_2O (5:1:4); samples of cooking starch, humic acid prepartion, and peat from Dismal Swamp, Virginia, were run for comparison. An "X" indicates detected but not quantified.

Table 13. Carbohydrate components of lake sediments in northwestern and east-central Minnesota (analyses by A. Blumentals and F.M. Swain); separations of sulfuric acid extracts of lake sediments were made by paper chromatography in BuOH:HOAC:H_2O (5:1:4); samples of cooking starch, humic acid preparation, and peat from Dismal Swamp, Virginia, were run for comparative purposes.

Sugar components	# of spls. in which found	Aver Rf*	Cedar Cr. Bog, MN**	Dismal Swamp, VA	Rush Lake, MN	Cooking starch	Humic Acid	Lake of the Woods, MN
Raffinose in starch	1	.04				X		
Raffinose?	28	.064	35-36 ft	6-7 ft	X			X
Lactose in starch	1	.093				X		
Lactose?	6	.133	35-36 ft					X
Galactose in starch	1	.155				X		
Glucuronic acid?	3	.125	35-36 ft					X
Fructose?	4	.298	2-3 ft					
Rhamnose?	7	.376	32-33 ft					X
Arabinose	27	.283		6-7 ft	X			X
Glucose	33	.239	38-39 ft			X	X	X
Component of humic acid	50	.474	38-39 ft	6-7 ft	X	X	X	X

* On paper chromatograms.

** Greatest depth at which found.

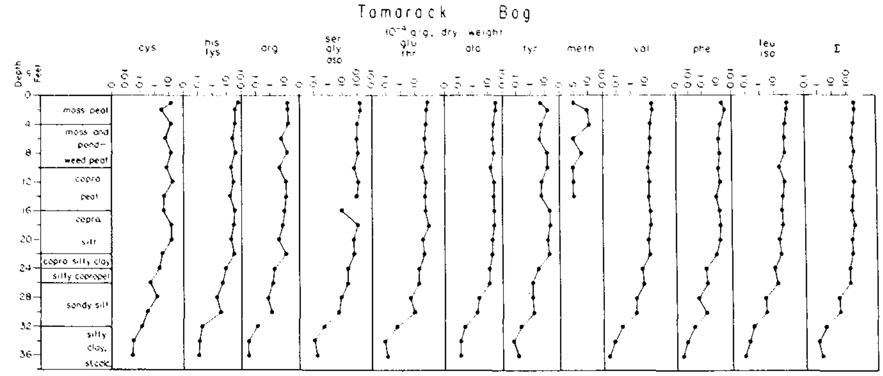


Figure 30. Amino Acids of Tamarack Bog Sediments.

PROTEIN AMINO ACIDS

Though considerably more study has been made of the amino acid content of Minnesota lake sediments than of carbohydrate content, coverage of lakes in the state is still very small.

Methods of study. The analysis of Minnesota lake sediments for protein amino acids has been done by acid hydrolysis and chromatography as described in earlier papers (Swain, 1961, 1967; Swain, Venteris, and Ting, 1964). Most of the earlier work emphasized paper chromatography for separation of the amino acids in acid hydrolyzates, but in recent years an automatic amino acid analyzer has been used.

Separation of free amino acids, extracted with water from the sediments, has been carried out only to a limited extent.

Northeastern Minnesota. The bottom sediments in lakes of this area contain a surprising variety and amount of amino acids (Table 14), considering the relatively low organic-productivity of the lakes in general. In particular, the sediments of Snowbank Lake and Gunflint Lake, the waters of which are low in dissolved solids, have high amino acids content. This points to good preservation conditions and a low degree of humification of the settled organic matter, as well as to probable contributions from interstitial organisms. Chironomid larval remains were observed in several of the core samples from Gunflint Lake, and fecal pellets are common in the bottom sediments.

Northwestern Minnesota. The amino acid contents of sediments from Upper Red Lake and Lower Red Lake (Table 15) and from Lake of the Woods (Swain, 1961) generally are lower than those of the northeastern Minnesota lakes. The reason for this difference, despite their lower organic-productivity, is thought by the writer to be the better preservation conditions in the northeastern lakes. The difference in the contribution by interstitial organisms in the two sets of lakes cannot be evaluated at present, but should be investigated further.

North-Central Minnesota. In this area, only Kabekona Lake sediments have been analyzed for amino acids (Swain, 1961). In these marls the amino acids are very low in amount (.02 parts per 10,000 of the wet sediments - moisture content 74.6%) and only glycine and alanine, together with traces of glutamic acid and threonine, were found. Thus, while the total productivity of this lake is probably higher than that of northeastern Minnesota lakes, the preservation conditions of the organic matter in the sediments are poorer. Whether this is the result of negative redox conditions and resulting anaerobic bacterial action in the Kabekona marls cannot be properly assessed at present.

East-Central Minnesota. The amino acids in lake sediments of this area have been analyzed for a number of lakes and bogs (Swain, Blumentals, and Millers, 1959; Swain, 1961, 1965; Swain, Venteris, and Ting, 1964). Additional sets of analyses for Mille Lacs Lake and Tamarack Bog, Aitkin County (Fig. 30) are shown in Tables 16 and 17. There is a general correspondence of the amount and variety of amino acid residues to state of trophication and stratigraphy, and to some details of bog history, in the amino acid residues from these deposits. In Tamarack Bog, moss peat and methionine extend to 14 ft.

Representative auto-analyzer chromatograms of amino acids from Rossburg Bog and Kirchner Marsh were given by Swain (1970).

West-Central and Southwestern Minnesota. The amino acid contents of acid hydrolyzates of sediments of Big Kandiyohi Lake were analyzed qualitatively by Meader (1956). He found a mixture of the amino acids commonly found in sediments, predominantly leucine, alanine, glutamic acid, and aspartic acid, with lesser amounts of cystine, glycine, lysine, arginine, methionine, and valine.

Southeastern Minnesota. The lake sediments of this area have not been analyzed for amino acids.

Table 14. Amino acid residues from sediments of northeastern Minnesota lakes (10^{-4} g/g sample).

Lake, station, position in core, wt. of dry sample; 3 ft cores	cys	lys	his+ arg	ser+ gly + asp	glu +thr	ala	tyr	met +val	phe	leu+ iso	Sum
Gunflint Lake No. 3											
Top, 5.5 g	2	10	12	20	9	9	7	9	2	4	84
Mid. 9.4 g	5	4	21	18	11	8	5	7	3	8	90
Bot. 9.8 g	4	8	12	9	7	5	3	2	2	4	56
Crane Lake No. 1											
Top, 6.9 g	8	4	7	4	5	3	1	2	2	4	38
Mid. 10.6	1	2	8	5	4	3	1	1	1	1	27
Bot. 13.4 g	1	1	5	3	3	2	1	2	1	3	22
Snowbank Lake No. 2											
Top, 2.5 g	12	10	44	53	33	19	9	13	11	9	213
Mid. 2.3 g	9	16	35	45	21	20	22	18	16	19	221
Bot. 2.1 g	14	16	57	54	32	19	31	28	24	24	299
Poplar Lake No. 2											
Top, 5.0 g	8	8	9	19	17	7	2	6	3	13	92
Mid. 5.8 g	6	7	9	16	16	12	3	10	5	17	101
Bot. 6.5 g	4	8	7	14	13	10	3	8	3	9	79
Burntside Lake No. 8											
Top, 6.15 g	5	5	18	14	17	10	2	15	1	7	94
Mid. 12.4	5	4	13	10	13	5	1	8	8	5	72
Bot. 11.2 g	8	4	18	9	16	7	1	12	1	5	81
Burntside Lake No. 10											
Top, 7.4 g	5	3	9	12	17	10	3	12	2	10	83
Mid. 12.5	1	tr	1	1	2	1	tr	3	1	1	11+
Bot. 12.5g	1	1	3	1	1	tr	tr	2	tr	1	10+
Sea Gull Lake No. 1											
Top, 6.7 g	19	5	4	1	24	9	1	12	1	10	86
Mid. 11.9	11	5	27	4	12	5	2	4	1	3	74
Bot. 11.7 g	10	2	21	3	10	5	3	3	1	1	59
Lake Kabetogama No. 5											
Top, 6.9 g	12	3	10	6	9	6	1	8	1	5	61
Mid. 14.7	1	2	1	1	1	2	tr	1	tr	1	10+
Vermilion Lake No. 2											
Top, 8.7 g	9	22	26	52	39	19	5	15	5	17	209
Bot. 10.2 g	15	15	15	34	28	14	4	15	5	15	160
Rainy Lake No. 6											
Top	tr	tr	2	tr	1	tr	tr	tr	tr	tr	3+
Lac la Croix No. 5											
	1	4	7	14	7	5	1	2	tr	5	46+

Table 15a. Amino acids in core samples from Upper Red Lake, Minnesota (paper chromatographic analyses by G.V. Pakalns).

Core number, amino acids	Quantities in 10^{-4} g/g wet weight; 3 ft cores		
	top	middle	bottom
<u>Core No. 6</u>			
Cystine	tr	tr	tr
Lysine	1	1	tr
His + arg	1	tr	tr
Ser + gly + asp	2	tr	1
Glu + thr	2	1	1
Alanine	2	3	1
Tyrosine	1	tr	tr
Valine	tr	tr	2
Phenylalanine	tr	tr	1
Leucine and isoleucine	1	tr	1
Totals	10+	6+	7+
<u>Core No. 9</u>			
Cystine	6	2	—
Lysine	1	1	tr
His + arg	1	—	—
Ser + gly + asp	3	3	2
Glu + thr	2	2	1
Alanine	3	4	2
Tyrosine	1	1	tr
Valine	1	1	3
Phenylalanine	tr	tr	tr
Leucine and isoleucine	2	1	1
Totals	20+	15+	9+
<u>Core No. 13</u>			
Cystine	—	2	tr
Lysine	1	1	1
His + arg	—	1	—
Ser + gly + asp	4	3	3
Glu + thr	3	2	2
Alanine	5	4	2
Tyrosine	tr	tr	2
Valine	1	tr	1
Phenylalanine	tr	tr	tr
Leucine and isoleucine	2	1	1
Totals	16+	14+	12+

Table 15b. Amino acids in core samples from Lower Red Lake, Minnesota.

Core number, amino acids	Quantities in 10^{-4} g/g wet weight; 3 ft cores		
	top	middle	bottom
Core No. 2			
Cystine	1	tr	—
Lysine	1	15	1
His + arg	3	5	2
Asp +ser+gly	2	3	4
Glu + thr	2	3	3
Alanine	2	1	8
Tyrosine	1	1	1
Valine	tr	tr	1
Phenylalanine	tr	tr	tr
Leucine and isoleucine	2	2	2
Totals	14+	30+	22+
Core No. 4			
Cystine	—	tr	—
Lysine	tr	1	tr
His + arg	5	—	—
Asp+ser+gly	2	2	1
Glu + thr	3	1	tr
Alanine	8	3	tr
Tyrosine	1	1	—
Valine	1	—	tr
Phenylalanine	tr	tr	—
Leucine and isoleucine	3	2	tr
Totals	23+	10+	1+
Core No. 7			
Cystine	tr		2
Lysine	1		2
His + arg	tr		4
Asp+ser+gly	1		3
Glu + thr	3		3
Alanine	2		2
Tyrosine	1		1
Valine	tr		1
Phenylalanine	tr		tr
Leucine and isoleucine	2		4
Totals	9+		22+

Table 16. Amino acids in core samples from Mille Lacs, Minnesota (paper chromatographic analyses by G.V. Pakalns).

Amino acids	Quantities in 10^{-4} g/g wet weight; 3 ft cores	
	Sample 1 (top)	Sample 4 (bot)
Cystine	0	0
Lysine	tr	tr
His + arg	2	1
Asp +ser+gly	2	3
Glu + thr	1	1
Alanine	6	6
Tyrosine	1	8
Valine	1	tr
Phenylalanine	tr	tr
Leucine and isoleucine	2	2
Totals	15+	21+

Table 17. Amino acid residues of peats of Tamarack Bog; values are in 10^{-4} g/g of dry peat (analyses by G.V. Pakalns).

Depth (feet)	cys	his+lys	arg	asp+ser +gly	glu+thr	ala	tyr	met	val	phe	leu+ isol	Sum
0-1	11.9	69.7	14.9	119.2	32.2	54.8	6.8	4.8	37.3	31.3	83.0	465.9
1-2	4.2	59.5	16.7	131.8	77.9	50.0	16.2	9.5	42.4	59.4	83.8	551.4
2-4	13.9	53.6	19.1	99.8	74.6	37.5	7.9	10.1	31.7	20.8	69.9	438.9
4-6	6.9	35.7	6.9	94.8	66.5	37.0	6.0	4.5	32.0	12.2	60.5	363.0
6-8	13.6	56.1	16.2	102.3	70.1	40.1	15.7	7.2	23.7	15.8	67.4	428.7
8-10	8.3	22.1	6.6	77.1	47.2	21.9	15.8	4.7	16.2	12.7	35.9	268.5
10-12	16.7	41.7	13.2	113.5	76.3	43.1	7.2	4.7	24.9	16.3	63.2	420.8
12-14	6.3	20.2	11.5	97.7	66.3	40.3	7.5	5.0	19.6	9.5	57.1	341.0
14-16	6.3	46.2	9.4	8.6	71.4	43.3	27.9	0	33.9	16.3	45.2	308.5
16-18	14.2	45.5	8.5	105.0	91.7	43.9	34.8	0	39.0	19.2	48.7	450.5
18-20	16.4	24.3	5.8	69.9	55.0	30.8	19.3	0	18.8	11.1	26.9	278.3
20-22	5.6	44.4	11.1	77.4	61.5	33.2	22.9	0	24.6	9.8	35.4	325.9
22-24	2.9	9.3	2.3	27.0	25.0	14.1	5.7	0	7.8	1.3	9.6	105.0
24-26	0.8	6.3	1.8	28.0	24.9	14.9	1.5	0	8.2	2.5	16.1	105.0
26-28	1.1	3.3	0.9	9.3	6.7	3.9	1.1	0	3.0	0.6	2.3	32.2
28-30	0.6	5.7	1.3	7.8	10.0	3.2	2.0	0	2.9	1.3	3.3	38.1
30-32	0.2	0.3	0.2	0.8	0.8	0.4	0.3	0	0.3	0.4	0.5	4.2
32-34	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0	0.1	0.1	0.1	1.1
34-36	0.1	0.1*f*	0.1	0.2	0.2	0.2	0.1	0	ftable 14 tr	0.1	0.1	1.2+

HYDROCARBONS

The hydrocarbons and other lipoid substances of Minnesota lakes show a relationship between amount and kind of source material and the trophication stages of the lakes (Swain and Prokopovich, 1954, 1957; Swain, 1956).

Methods of study. The hydrocarbons of lake sediments and of some associated living plants were extracted with a mixture of benzene + methanol (80:20) or in some cases with benzene + methanol + acetone (70:15:15). Use of acetone was limited because of the possibility of its undergoing aldol condensation in the presence of either acidic or alkaline solutions to diacetone alcohol and perhaps to mesityl oxide. After removal of sulfur, the extract was dried and separated by absorption chromatography, as described previously (Swain, 1956). The resulting three fractions were taken to represent saturated hydrocarbons, aromatic hydrocarbons, and asphaltics.

The saturated hydrocarbon fractions of some samples were separated into a normal alkane fraction and a branched alkane (plus other residues) fraction by treatment with 5 Å molecular sieve, which absorbs the normal alkanes. These were recovered by dissolving the sieve in 30% hydrofluoric acid. The resulting fractions were separated on a gas chromatographic column (Varian-Aerograph Model 204) equipped with flame ionization detectors. Partial characterization of the fractions was made by comparison with known standards. Mass spectral analyses have been made of some samples, but this area is greatly in need of further study.

Gas chromatographic-mass spectral analyses of the marsh gases in several bogs, marshes, and lakes have been done (Swain, 1975; Swain, Johnson, and Pitman, 1977; Swain, 1986).

Northeastern Minnesota. Hydrocarbon analyses of Burntside Lake and Silver Bay, Lake Superior, sediments were reported previously (Swain, 1956; Swain and Prokopovich, 1957). Chromatographic analyses of hydrocarbons of sediment samples from Lake Kabetogama and Rainy Lake are given in Table 18. The main finding was that although the hydrocarbons and total lipoids form a relatively small proportion of the lake sediment sample, around 200-400 ppm, the hydrocarbons form a greater part of the extracts than in central and western Minnesota lakes. This is due to the greater proportion of pigments and other extractable materials in the more eutrophic lakes of central and western Minnesota. No gas chromatographic analyses have been made of sediment lipoids in this area.

Northwestern Minnesota. The lake sediments of this area have not been analyzed for hydrocarbons.

North-central Minnesota. The lake sediments of this area have not been analyzed for hydrocarbons.

East-central Minnesota. Analyses for hydrocarbons and other lipoid substances were made in sediments of several lakes and bogs in this part of Minnesota (Swain and Prokopovich, 1954; Swain, 1956, 1967). The amounts of hydrocarbons and asphaltics obtained from the eutrophic sediments of the lakes and from the peats of Cedar Creek and Rossburg Bogs are directly related to their state of trophic development. The occurrence of 2-naphthol in the moss peats of Rossburg Bog (Swain, 1967) is thought by the writer to be due to the activity of growth-accelerating enzymes or auxins.

The general distribution of hydrocarbons and their relation to stratigraphy in Rossburg Bog is shown by infrared absorption spectra of ether extracts of the sediments (Swain, 1967). Low-temperature distillation products of the copropel sediment in Rossburg Bog were mainly toluene, which probably was derived during distillation from carotenes in the copropel (Swain, 1967). Low-temperature distillation of the overlying moss peat in Rossburg Bog yielded principally hydrated phenol, which may have formed from sphagnol or another acidic peat constituent.

A 14-g sample of Cedar Creek moss peat was distilled on the oil bath at 175° C for three hours. The distillate was a pale brownish to greenish-brown, light-gravity liquid with a strong odor of pyroligneous acid. When scanned in ultraviolet light, the distillate showed a prominent absorption maximum at 268 mμ, suggesting that one of its components is a hydrated phenol.

Several species of aquatic plants from Blue Lake and Clear Lake were analyzed for hydrocarbons (Table 19). Aromatic hydrocarbon fractions exceeded the saturated hydrocarbons in most of the plants, and were present in similar or lesser amounts than the asphaltic fractions. Polar compounds represented mainly by chlorinoid and carotenoid pigments generally, but not entirely, far exceeded the hydrocarbons in amount. Gas chromatograms of the total alkanes as well as of the normal (retained on 5 Å mol. sieve) and branched alkanes (not retained on 5 Å sieve) showed a variety of compounds between C15 and C32. Examples of the gas chromatograms were given by Swain (1970).

West-Central and Southwestern Minnesota. Hydrocarbon analyses of sediments from Big Kandiyohi Lake were made by Meader (1956) (Table 23). The relatively high content of aromatic hydrocarbons, which differs from that in most of the other Minnesota lake samples studied, has not been satisfactorily explained.

The other lake sediments of this area have not been analyzed for hydrocarbons.

Southeastern Minnesota. The lake sediments of this area have not been analyzed for hydrocarbons.

PIGMENTS

The chlorophyll-derived pigments of sediments and plants of several Minnesota lakes were studied previously (Paulsen, 1962; Swain, Paulsen, and Ting, 1964; Swain, 1967). The carotenoid pigments have been only slightly studied in Minnesota lake sediments (op. cit.). Examination of several lake sediment samples for flavinoid, or yellow-fluorescing pigments, was made earlier (Swain and Venteris, 1964). Some additional analyses are reported here.

Methods of study. Chlorophyll, pheophytin, and other chlorinoid pigments were extracted with 90% acetone from the wet sediment under conditions described previously, and the extracts were analyzed by absorption spectrophotometry (Swain, Venteris, and Ting, 1964). The few carotenoid pigment studies were performed on the same types of extracts as for chlorinoids, and the extracts were dried and separated by paper chromatography in petroleum ether; the developed chromatogram was then cut into pieces, the colored bands dissolved in carbon disulfide, and the solutions scanned in an absorption spectrophotometer for detection of carotenes.

Flavinoid pigments were detected as yellow-fluorescing spots in hydrochloric acid hydrolyzates being analyzed by paper chromatography for amino acids. The fluorescent spots were cut out of the developed but unstained chromatograms, dissolved in n-heptane, and scanned in an absorption spectrophotometer for riboflavin and associated pigments. Representative absorption spectra of the lake pigments were given by Swain, Paulsen, and Ting (1964) and by Swain (1970).

Northeastern Minnesota. The chlorinoid and carotenoid pigment contents of several lakes in this area differ widely (Table 21) as a result of varying degrees of productivity of the lakes. Although all the lakes are either oligotrophic or very early eutrophic in development, the pigment contents vary by two orders of magnitude. In the less productive lakes, carotenoids are about equal to chlorophyll-derived pheophytin, but in the higher-productivity lakes, carotenes exceed pheophytin.

Northwestern Minnesota. The pheophytin content of the upper part of the sediments of Upper

Red Lake were analyzed by Paulsen (1962) and by Swain, Paulsen, and Ting (1964). A rapid decrease in pheophytin from the surface downward is probably due to its use as food by interstitial organisms, because the sediment is uniform in nature and organic content and is not in an oxidized state. Though not measured quantitatively, carotenoid pigments appear to exceed chlorophyll derivatives except in the upper few centimeters of the sediment.

The chlorophyll-derived pigment of Red Lake Bog (Fig. 31) shows an increase in dark decomposed peats 6.5-8.2 ft below the surface as compared to lower and higher levels (Fig. 31). The reason for this increase is unknown, but may reflect an interval of increased wetness. No open water stage is known to have occurred in the bog.

The other lake sediments in this area have not been analyzed for pigments.

North-Central Minnesota. The pigment contents of sediments of Lake Itasca and Long Lake were studied by Paulsen (1962) and by Swain, Paulsen, and Ting (1964). Lake Itasca is characterized by an increase in pigment contents of the surface sediments from shallow to deep water as related to total organic content, and by a decrease of pigments downward in the sediments probably due to their use as food by interstitial organisms. Long Lake generally has lower pigments throughout the sediments than Lake Itasca, probably because of its generally lower organic-productivity.

The carotene content of Lake Itasca sediments is similar to or lower than the pheophytin content, whereas in Long Lake carotenes seem to exceed pheophytin considerably.

The other lake sediments of north-central Minnesota have not been analyzed for pigments.

East-Central Minnesota. In this area, the sediments of Blue Lake and Rossburg Bog have been studied for chlorinoid pigments (Paulsen, 1962; Swain, Paulsen, and Ting, 1964; Swain, 1967). The flavinoid pigments of Cedar Creek Bog and of isolated sediment samples of other area lakes were also studied (Swain and Venteris, 1964; Swain, Paulsen, and Ting, 1964).

The pheophytin content of calcareous Blue Lake sediments is closely related to the productivity history in the lake and shows an early stage of eutrophication followed by a period of lesser productivity that preceded the present eutrophic cycle. The distribution of pheophytin seems to show the trophic history of the lake better than does the total organic matter of the sediments.

The contents of riboflavin and riboflavin phosphate of the marl sediments of Cedar Creek Bog are mainly low to absent, but are sufficiently high to be detected in some of the copropelic and peaty deposits of this and other lakes in east-central Minnesota. There is a relationship of the flavinoid pigments, not only to total organic matter, but to the activity of interstitial organisms in these lake sediments.

West-Central, Southwestern, and Southeastern Minnesota. The lake sediments in these areas have not been analyzed for pigments.

Northeastern Minnesota Lake Sedimentation Mercury. The mercury content of short cores of sediments of Crane Lake and Lake Kabetogama, northeastern Minnesota, were studied by Meger (1983, 1986). Data were available to permit a pre-1880 (pre-cultural) and post-1880 evaluation of mercury levels. These were based on Cesium-137 profiles in cores of the sediments. Cs-137 peak was assumed to represent the year 1963. Extrapolation of the Cs-137 peak depths in the sediments yielded sedimentation rates ranging from 0.19 ± 0.06 cm/year in Crane Lake to 0.23 ± 0.04 cm/year in Lake Kabetogama.

Meger found background levels of 0.03 to 0.06 micrograms per gram dry weight of mercury in copropelic sediments at the two lakes. Post-1880 levels of mercury increased by as much as twofold over the pre-1880 values. Meger decided that atmospheric loading was the most likely source of these values.

Table 18. Chromatographic analyses of hydrocarbons from lake sediments in northeastern Minnesota. For further data on cores see Swain, 1961 (analyses by I. Porietis).

Lake, station, position in core, sediment type	Wt. of spl. (g)	Wt. ext (g)	Sat. HC (g)	Arom. HC (g)	Asphaltics (g)	Polar Cpds. (g)
Lake Kabetogama, Sta. 5, top of core, copropel	20	3.2455	.0058	.0065	.0076	3.2256
Lake Kabetogama, Sta. 5, mid. of core, clay	20	0.0254		not chromatographed		
Lake Kabetogama, Sta. 5, bot. of core, sand	20	0.0068		not chromatographed		
Rainy Lake, Sta. 7, top of core, clay	10	0.1817	.0039	.0018	.0095	.1665
Rainy Lake, Sta. 7, mid. of core, clay	10	0.0076	.0028	.0032	.0700?	none
Rainy Lake, Sta. 7, bot. of core, clay	10	0.0084	.0029	.0035	.0020?	none

Table 19a. Chromatographic separation of lipid substances of lake plants from Blue Lake, Minnesota (analyses by F.M. Swain and D.A. Peterson).

Species and date of collection	Extract, % of sample	Heptane fraction %	Benzene fraction %	Pyridine fraction %	Polar cpds. %
Myriophyllum exalbescens, 10-21-60	0.463	0.003	0.074	0.078	0.308
Ceratophyllum demersum, 10-21-60	0.499	0.007	0.072	0.033	0.387
Elodea canadensis, 10-21-60	0.339	0.052	0.032	0.086	0.216
Green algae, 12-29-60	0.350	0.008	0.019	0.006	0.217
Ceratophyllum demersum, 12-29-60	0.689	0.008	0.024	0.257	0.400
Green algae, 12-29-60	0.362	0.005	0.023	0.078	0.256
Elodea canadensis, 12-29-60	0.337	0.004	0.021	0.126	0.186

Table 19b. Chromatographic separation of lipid substances of lake plants from Clear Lake, Minnesota (analyses by D. Peterson).

Species and date of collection	Extract, % of sample	Heptane fraction %	Benzene fraction %	Pyridine fraction %	Polar cpds. %
Myriophyllum exalbescens, 10-21-60	0.756	0.068	0.063	0.196	0.429
Najas quadalupensis, 10-21-60	0.434	0.008	0.026	0.081	0.319
Potamogeton illinoiensis, 10-21-60	0.882	0.008	0.050	0.423	0.401
Typha latifolia, 10-21-60	1.505	0.012	0.313	0.399	0.776
Chara sp., 12-29-60	0.553	0.006	0.081	0.121	0.345

Table 20. Chromatographic analyses of lipoid substances from Big Kandiyohi Lake, Minnesota (Meader, 1956).

Fraction:	Top 6 in Silty Copropel	Bottom 6 in Copropel	Description
Core No. 3: 31 in long; 14.5 ft deep			
Total lipoids			
weight extract (gm.)	0.1951	0.17	Top: Black tarry wax.
% total sample	0.81	0.53	Bottom: Black to dark brown tarry wax; creosote odor.
Heptane fraction			Top: Colorless to slightly yellow clear wax.
weight fraction (S-free)	0.0013	0.0074	Bottom: Clear solid wax containing cloudy granular sulfur particles; weak white fluorescence.
% sample	0.005	0.02	
% lipoids	0.67	4.35	
% non-polar lipoids	2.02	14.42	
% hydrocarbons	17.33	36.27	
Benzene fraction			Top: Milky, discoid to subspherical sulfur globules in clear wax; weak yellowish fluorescence.
weight of fraction (S-free)	0.0062	0.013	Bottom: Greenish-brown to black wax.
% sample	0.03	0.04	
% lipoids	3.18	7.65	
% non-polar lipoids	9.64	24.34	
% hydrocarbons	82.67	63.73	
Pyridine-methanol fraction			Top: Black tarry wax.
weight fraction (gm.)	0.0568	0.0309	Bottom: Black tarry wax.
% sample	0.24	0.1	
% lipoids	29.11	18.18	
% non-polar lipoids	88.34	68.23	
Core No. 9: 18.5 in long; 15.5 ft deep			
Total lipoids	.265	0.2468	Top: Black, tarry wax; creosote odor.
weight of extract (gm.)	0.90	1.13	Bottom: Brownish-black tar.
% total sample			

Table 21. Chlorinoid and carotenoid pigment contents of 1-m sediment cores in northeastern Minnesota lakes, dry weight basis.

Lake, station, and position in core	Organic matter %	Pheophytin ppm	Carotenes ppm
Rainy lake, Sta 6			
Top	7.3	7.1	7.0
Middle	5.7	3.3	3.5
Bottom	6.1	7.0	3.5
Kabetogama Lake, Sta 5			
Top	10.9	76.0	171.0
Middle	5.6	9.1	11.3
Bottom	6.7	3.1	5.7
Burntside Lake, Sta. 10			
Top	12.6	60.4	163.9
Middle	10.7	10.1	13.6
Bottom	8.5	21.4	10.7
Vermilion Lake, Sta. 3			
Top	34.3	228.6	880.5
Middle	34.4	251.4	457.4
Bottom	33.4	226.9	339.8
Sea Gull Lake, Sta. 1			
Top	19.3	27.5	92.1
Middle	28.9	24.3	134.3
Bottom	14.9	18.3	87.5
Poplar Lake, Sta. 2			
Top	29.7	90.0	271.4
Middle	20.5	88.5	237.9
Bottom	23.6	119.3	389.0
Gunflint Lake, Sta. 8			
Top	22.6	29.6	44.6
Middle	24.5	42.4	44.1
Bottom	23.6	19.9	55.3

Table 22. Ratios of amino acids in Kirchner Marsh sediments.

Type Sediment	Depth (feet)	val/gly	thr/gly	val/ala	phe/arg	tyr/gly
Peaty Copropel	17.0-17.08	1.00	.64	1.08	.61	.62
	17.3-17.4	.87 1.07	.51 .47	1.10 1.20	.76 .65	.49 .39
	17.44-17.7	1.09	.56	.92	1.15	.54
	17.95-18.03	1.02	.63	1.03	.85	.77
	19.3-19.37	1.10	.67	.95	.76	1.17
	19.5-19.6	.92	.59	.88	.83	.61
	19.8-19.9	1.26	.64	.94	.80	.95
Copropel	40.74-40.8	.72	.72	.86	.38	1.03
	40.9-40.98	.74	.78	.79	.82	1.15
	41.06-41.14	.76	.74	.83	.87	1.19
Clay	43.8-43.9	.79	.67	.92	1.14	.49
	44.0-44.09	.79	.71	.95	.69	1.19
	44.17-44.25	.77	.72	.86	.66	1.09

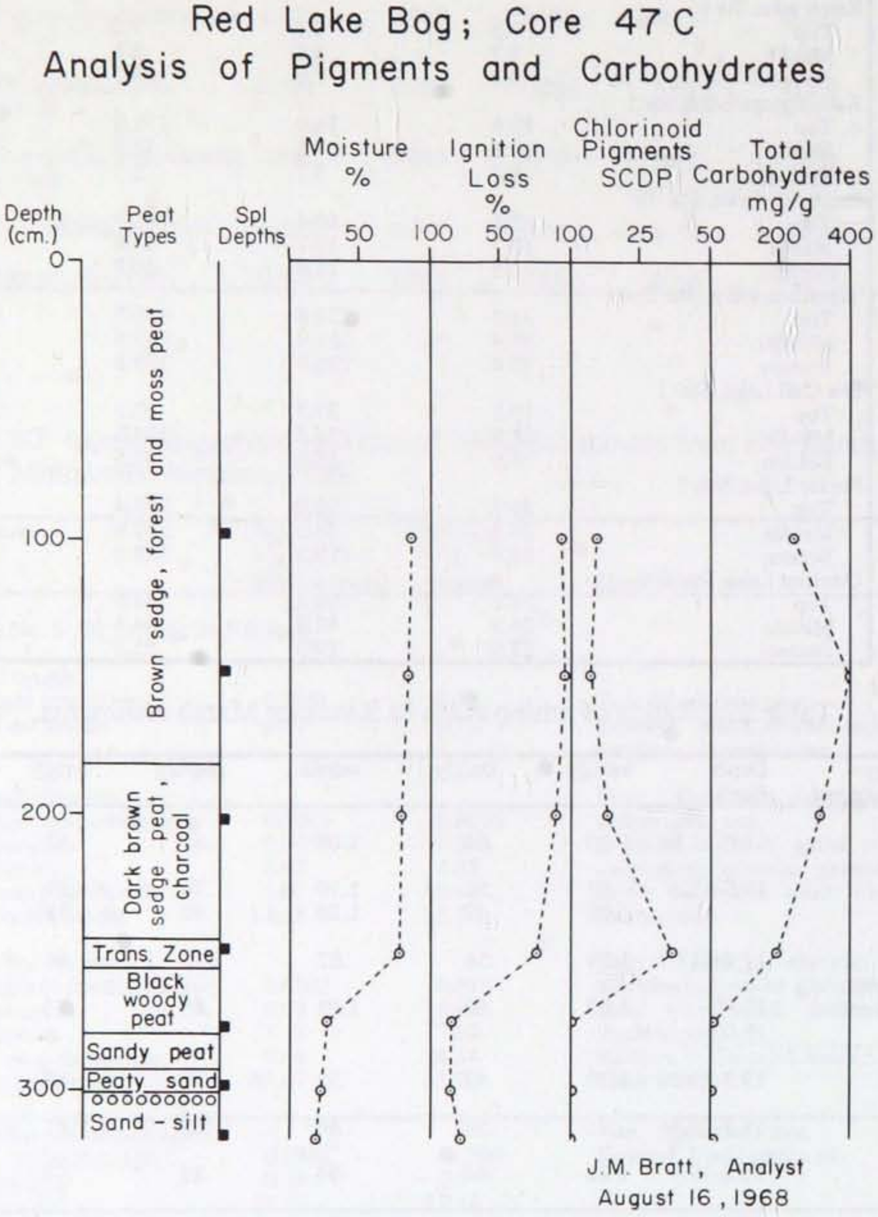


Figure 31. Moisture content, ignition loss, chlorinoid pigments, and total carbohydrates of a core from Red Lake Bog.

DISCUSSION

Classification of bottom sediments of lakes. A classification of lake sediments given by Swain (1956) is used in this report.

A. Organic detritus
  1. Peat; phytogenic, coarse (caustopsephite), fine (caustopsammite and caustopelite)
  2. Copropel; phytogenic and zoogenic, the latter commonly including chitinous arthropod exoskeletons (copropelite)
  3. Sapropel; black mainly phytogenic, involving bacterial decay by both aerobes and anaerobes, but in an essentially anaerobic environment (sapropelite)

B. Biogenic and authigenic mineral substance
  1. Marl (limestone, dolomite) may be subdivided on basis of
     a) texture (calcirudite, calcarenite, calcilutite)
     b) composition (algal, *Potamogeton*, etc.)
     c) fabric (oölite, chalk)
  2. Diatomite (diatomite)
  3. Agglutinated Protista; sarcodinids - *Difflugia*, *Centropyxis*, etc.; ciliates-tintinnids
  4. Others; ferric oxides and carbonates (ironstones), sodium chloride halite (rock salt), calcium sulfate (anhydrite, gypsum)

C. Terrigenous substance
  1. Gravel, sand, silt, and clay (rudite, arenite, lutite)

Lake sediment facies. Fig. 34, which shows principal lake sediment facies in Minnesota, and a map showing regional limnologic control factors (Swain, 1956) show several relationships. The lake sediment Facies I, principally allogenic clays in northeastern Minnesota, has (1) Precambrian igneous and metamorphic bedrock with no cover or a thin cover of glacial drift; (2) glacial drift of gray Des Moines type; (3) rather high annual runoff of 6-10 in, which causes rapid exchange of lake waters; (4) an excess of precipitation over evaporation, which further enhances the rapid exchange of lake waters; (5) low to moderate total alkalinity, generally less than 50 ppm; and (6) low values of sulfate ion, chloride ion, total phosphorus, and total nitrogen in the lake waters, all of which indicate oligotrophic to early eutrophic lake waters. Locally, more advanced eutrophication is developed in some of the smaller lakes with low exchange rates of the water.

Lake sediment Facies II, mixed allogenic clastics and authigenic copropel and marl in northwestern Minnesota, has (1) thick glacial drift and Pleistocene lake beds; (2) moderate annual runoff (though when combined with a low evaporation-rate, the exchange rate of lake waters is still likely to be relatively high); (3) moderate total alkalinity, about 100 ppm, which probably would be higher except for the high exchange rate of lake waters; (4) low values of sulfate and chloride; and (5) moderate values of total phophorus and nitrogen, in line with the mesotrophic to early eutrophic nature of the lakes in this area.

Lake sediment Facies III, mainly authigenic marl with lesser amounts of copropel and allogenic clastics, has (1) a terrane of thick gray calcareous Des Moines-type drift; (2) moderate runoff and either no or slight excess of evaporation of precipitation; (3) moderate alkalinity, indicating that marl is being precipitated about as fast as it is introduced; (4) low sulfur and chloride content; and (5) moderate total phosphorus and nitrogen, which combined with the other features, show that these lakes are in an alkalitrophic-mesotrophic to early eutrophic stage.

Facies IV, authigenic copropel with more or less marl and allogenic fine clastics, has (1) generally heavy but locally thin drift cover; (2) Mankato- and Des Moines-type mixed calcareous gray drift, and red, Superior-type iron-rich drift; (3) moderate annual runoff, but (4) evaporation in slight excess of precipitation over much of the area, resulting in a summer hydroponic effect that in turn enhances algae growth in the lake and contributes to the copropel-rich sediments of these lakes; (5) moderate total alkalinity, but (6) sulfate ion, chloride ion, and total phosphorus and nitrogen generally higher than in the preceding facies and characteristic of temporary-hardness eutrophic and dystrophic or hypereutrophic lakes.

Lake sediment Facies V, allogenic silt and authigenic marl, has (1) Cretaceous sulfate-rich gypsiferous shales underlying glacial drift or reworked into the drift; (2) gray mixed-calcareous Mankato-Des Moines-type drift and leached pre-Wisconsin drift; (3) relatively low runoff and high evaporation with resulting low exchange-rate of lake waters, except perhaps the elongate riverlike lakes of the western border; (4) high total alkalinity, high sulfate, high chlorides, high from the Cretaceous as well as the high evaporation rate.

These properties, all of which produce a hydroponic effect on aquatic vegetation in summer, are characteristic of permanent-hardness eutrophic and dystrophic or hypereutrophic lakes.

Lake sediment Facies VI, allogenic fine clastics and more or less copropel, has (1) Paleozoic carbonate and clastic rocks with thick to thin drift cover; (2) predominantly pre-Wisconsin drift, considerably leached of soluble material; (3) moderate to high annual runoff but with appreciable summer evaporation and hydroponic summer effect, particularly where coupled with (4) moderate to high total alkalinity, sulfate ion, and chloride ion, and total phosphorus and nitrogen. The lakes in this facies are in eutrophic-argillotrophic stages of development and have both temporary and permanent hardness characteristics.

A generalized Limnogenetic Rule applies to the vertical succession of lake sediments in Facies I-V, in which Facies I conditions at the base of the lake sediment sequence are followed in turn by Facies II, III, IV, and perhaps V conditions, depending on the present-day stage of development.

Clay minerals. The clay minerals of Facies I (Fig. 33) are represented mainly by 14 Å chlorite and 7 Å kaolinite, with lesser amounts of 10 Å illite, mica, and mixed layer clays. The chlorite probably came from the metamorphic Precambrian rocks of the area, whereas the kaolinite and illite came from the glacial drift. Facies II sediments were not studied for clay minerals.

The lake sediments of Facies III are low in clay minerals, with only small amounts of kaolinite and mixed-layer clay. The glacial drift of the area apparently supplied these clay minerals. There is some evidence for sedimentary chlorite in both Facies I and III.

Facies IV sediments are more heterogeneous in their clay mineral assemblages than those of the other Minnesota areas, perhaps because of the variable drift and bedrock types of this district. Montmorillonite, both organic-complexed and noncomplexed, is present in the lake sediments of this area. The source of the montmorillonite is not known but may be authigenic.

Facies V sediments are relatively low in clay minerals; most of the clay-sized sediments are feldspar and perhaps quartz. Mica and mixed-layer 10 Å clays and 7 Å clays, kaolinite, and septechlorite, are present in small amounts. The Cretaceous shales of the area may be a source of these clays; if so, may not have contributed much.

The clay minerals of Facies VI include chlorite, kaolinite, and mixed-layer clays. These presumably have been derived from Superior, Des Moines, and Mankato drifts that represent a wide variety of Precambrian and Paleozoic bedrock sources.

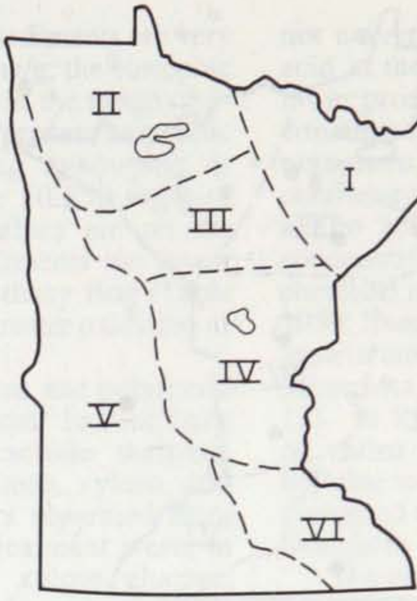
Fossils. Ostracoda are absent or almost so (Fig. 34) in the profundal lake sediments of northeastern Minnesota (Facies I), probably because of lack of food supplies, low carbonate-content, and lack of suitable substrate of the clayey bottoms of the oligotrophic lakes. The littoral environments of these lakes have not been studied in detail for ostracodes, but the writer did not find them in the lakes studied. The *Cyclocypris*? sp. collected by Samuel Eddy in Silver Bay, Lake Superior, is a poorly calcified form. Other fossil remains in northeastern Minnesota lake sediments are predominantly evergreen pollen, *Difflugia* spp., *Centropyxis* spp., and diatoms of the Fragilaridae and Melosiridae. Other diatoms, insect parts, cladocerans, egg cases, and (in littoral sediments) unionid clams and sponge spicules are also present locally.

In the mesotrophic-early eutrophic lakes of northwestern Minnesota (Facies II) ostracodes are common to abundant and are dominated by *Candona*. *C. ohioensis* occurs more in the bottom parts of some cores than higher up, where *Limnocythere* spp. are more common. Melosiroid diatoms, along with other types, are abundant, and thecamoeboids and some mollusks are common.

The north-central Minnesota lake sediments (Facies III) have a large variety of ostracodes, also dominated by *Candona*. *C. ohioensis* is abundant, along with *C. simpsoni*, *C. nyensis*, *C.* cf. *candida*, and *Darwinula stevensoni*. *Ilyocypris* sp. and others also appear. *Valvata tricarinata*, *Pisidium* sp., *Viviparus* sp., and other mollusks are common littoral forms. The diatoms, cladocerans, and others are diverse in these lakes.

In contrast to those of the preceding and following areas (Facies III and V), the ostracodes of Facies IV are much scarcer in *Candona*, especially in *C. ohioensis* and in *Limnocythere*. *Cypridopsis vidua* is common. Melosiroid diatoms are much less common in this than in the preceding facies. Other diatoms, as well as cladocerans, are abundant, but mollusks are generally less abundant in these richly organic sediments.

The ostracodes of Facies V sediments are again dominated by *Candona ohioensis* and other *Candona*, particularly *C. lactea*, which had not been especially noted in the previous facies. Many other



I Mainly clay, sand, and gravel (wih generally low organic content and locally high surficial organic content).
II A mixture of clay, sand, copropel, and marl.
III Mainly marl and copropel, with lesser amounts of silt and sand.
IV Mainly copropel and marl.
V Mainly silt and marl, with copropel and sand locally important.
VI Mainly clay silt and sand.

Figure 32. Principal lake sediment facies in Minnesota.

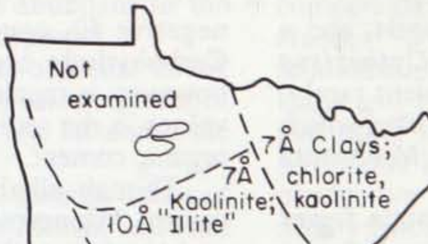
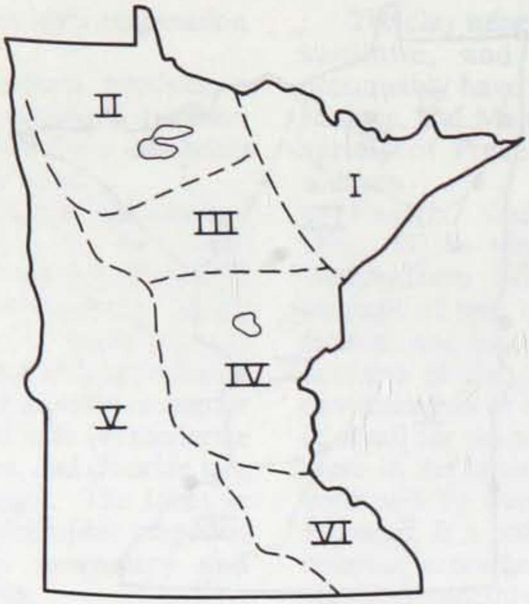


Figure 33. Principal clay mineral facies in Minnesota lake sediments.



I Few or no Ostracoda.
II *Candona ohioensis* and *Limnocythere* (common).
III *C. ohioensis, C.* spp., *Darwinula, Ilyocypris* (abundant).
IV *C. ohioensis, Limnocythere, Cypridopsis vidua* (common).
V *C. ohioensis, C. lactea, Cytherissa* (abundant).
VI Few Ostracoda, *Candona* spp. and others (common to rare).

Figure 34. Ostracoda biofacies in profundal Minnesota lake sediments.

ostracodes, cladocerans, clams and snails, and a great variety of diatoms occur here. *Cytherissa lacustris*, a cold-water species, is present rarely. *Potamocypris* sp. occurs in Albert Lea Lake, which is transitional with the southeastern Minnesota lakes.

Facies VI profundal sediments contain fewer Ostracoda than the preceding areas. Several species of *Candona* and a few others occur, but *C. ohioensis*, *C. lactea*, *Limnocythere* and others common in central and western Minnesota are not found. Littoral samples of lakes of this facies have not been studied for fossil content.

Carbohydrates. The total carbohydrate content of the Minnesota lake sediments reflects not only the state of trophication in the lake but also the redox conditions in the accumulating sediments. The deeper lakes with well-developed hypolimnion are likely to contain around 0.25 mg/g of carbohydrates if the lake is early-eutrophic and if negative Eh conditions occur in the sediments. Carbohydrate content of the oligotrophic lakes, however, is much lower, owing to the positive Eh values in the sediments as well as to their smaller organic content.

Though alkalitrophic and eutrophic lakes of central Minnesota are somewhat higher in total carbohydrates than the oligotrophic lakes, the difference is not outstanding. Both positive and negative Eh values are represented and the conditions for preservation are variable. The fact that the total carbohydrate content of Minnesota lake sediments varies by only a few factors rather than by orders of magnitude, as compared to Minnesota peats, indicates that preservation conditions for carbohydrates in the lacustrine environment are generally not good.

The consistency of the pattern of carbohydrate-preservation in older lake sediments is shown for Rossburg Bog in Table 11. The oligotrophic, precopropelic, silty, and calcareous sediments are very low in total carbohydrates, < .1 mg/g; the eutrophic copropels contain carbohydrates in the range of 8-68 mg/g, values comparable to present eutrophic Minnesota lakes; the overlying dystrophic or hypereutrophic moss peats have 50-250 mg/g of total carbohydrates. These values are on the average higher than in lake sediments but lower than values for moss peats in Bethany Bog (Table 12), apparently due to relatively greater oxidation of Rossburg peats.

Rogers (1965) found both free and polymeric sugars in Minnesota lake sediments. In Blue Lake sediments, the free sugars include maltose, sucrose, lactose, glucose, galactose, xylose, and mannose. The combined sugars separated from Blue Lake sediments by acid treatment were, in order of decreasing abundance: xylose, glucose, arabinose, galactose, mannose, rhamnose, ribose, and glucuronic acid. The carbohydrate components of aquatic plants and algae growing in Blue Lake were, in decreasing order: glucose, galactose, xylose, and arabinose. Evidence is that these plants are not the only source of carbohydrates in the associated sediments, but that microbiological effects and ilyotrophic (mud-eating) and other interstitial organisms contribute to, and alter, the carbohydrates in the accumulating sediment.

In Rossburg Bog, Aitkin County (Swain, 1967), the carbohydrate components show a gross relationship to stratigraphy: ribose is characteristic of the copropelic peat of the deposit and may owe its origin to animal degradation products. Glucose, arabinose, and xylose are more abundant in the moss peat than in the underlying copropel.

The carbohydrate components of Cedar Creek Bog peat (Table 13) indicate the possible presence of the oligosaccharides raffinose and lactose at the base of the peat accumulation.

The individual as well as total carbohydrates of Blue Lake, Clear Lake, Kirchner Marsh, and Hall Lake sediments (Swain, 1970) show *increases* at depth, thought to result from earlier periods of trophication. Whether these increases represent periods of warming and of drying or wetting cannot be ascertained at present.

Amino acids. Sedimentary hydrolyzable amino acids parallel carbohydrates in variety and distribution. Lakes in northeastern Minnesota offer favorable conditions for the accumulation and preservation of the amino acid residues of whatever organic matter is available, hence the rather surprising amount and variety of amino acids in these sediments (Table 14). The characteristic, but not universal downward *decrease* of each amino acid in these lake sediments is apparently due to lower productivity of the lake in prior times and/or consumption of amino acids by interstitial organisms. Lake sediments of central Minnesota commonly show a downward *increase* in individual amino acids, which may indicate a downward concentration either by interstitial organisms or by chemical means (Swain, Blumentals, and Millers, 1959; Swain, 1961). About 15-17 of the common protein amino acids are commonly separable from Minnesota lake sediments and peats (Tables 15 and 17). In Rossburg Bog peats (Swain, 1967) ratios of valine to alanine, tyrosine to alanine, and arginine to alanine differ in the upper moss peat as compared to the underlying copropelic peat and are thought to be due to source differences.

The ratios in Kirchner Marsh copropel and clay of valine, threonine, and tyrosine to glycine, to which they may degrade (Vallentyne, 1964), are shown in Table 22. The ratio val/gly is noticeably higher in the peaty copropel than in the underlying sediments, whereas this is not the case with thr/gly and tyr/gly ratios. The val/gly ratio variations may indicate a degradation of valine to glycine, but in view of the other results a difference in source material may be a cause of the observed change with depth. The ratio of arginine to proline, one of its degradation products, also suggests that this type of degradation may have occurred in Kirchner Marsh.

Hydrocarbons and related substances. Much more modern work needs to be done on these compounds in Minnesota lake sediments. Previous studies (Swain, 1956, 1967) have shown a relationship between the state of eutrophication of lakes and the kind and amounts of hydrocarbons and other lipoid substances in the accumulating sediments both in space and in time. The more productive the lake, the more asphaltic and other nonhydrocarbon benzene-extractable materials occur in the sediments. Phenolic compounds are prominent low-temperature distillation lipoid substances in some of the mossy peats of Minnesota, while the copropelic sediments yield toluene, perhaps from residual carotenoid pigments, on low-temperature distillation (Swain, 1967).

Naphthols can be extracted from some mossy peats of Minnesota. These may have been formed through the activity of growth-accelerating auxin compounds in the accumulating peat (Swain, 1967).

Meader (1956) found relatively high content of aromatic hydrocarbons in a high-sulfate lake with sapropelic sediments in west-central Minnesota (Lake Kandiyohi). It is not known whether this is the result of special source material or of diagenetic changes in the organic matter.

When the saturated hydrocarbon chromatographic fractions of Minnesota lake sediments and aquatic plants are treated with 5 Å molecular sieves to separate the normal alkanes, a variety of these are found by gas chromatographic analysis. They include the homologous series n-$C_{20}H_{44}$ through n-$C_{31}H_{64}$.

The branched-chain aliphatic compounds include those having the general range from C_{15} to C_{32}. Among these compounds are the isoprenoids farnesane $C_{15}H_{32}$, pristane $C_{19}H_{40}$, and phytane $C_{20}H_{42}$. Mass spectral analysis has also verified one of the compounds as a C_{21} isoprenoid hydrocarbon.

The total and branched alkanes of the plant samples studied show a predominance of odd- over even-numbered carbon compounds. This is less so in the lake sediments, where in several instances no preference was noted.

In the few samples studied, the normal alkanes, alone of the sediments, showed little or no preference for odd-numbered carbon compounds.

Pigments. Three principal classes of organic pigments have been separated from Minnesota lake sediments and peats (Swain, 1961; Swain and Venteris, 1964; Swain, Paulsen, and Ting, 1964; Swain, 1967): (1) chlorophyll, pheophytin, and other chlorinoid or tetrapyrrole pigments; (2) ∝ – and β - carotenes, other carotenes, and xanthophylls or tetraterpene pigments; and (3) riboflavin and other yellow-fluorescing compounds and possible flavones or benzopyran pigments.

Both chlorinoid and carotenoid pigments are highly variable in amount in the oligotrophic and early eutrophic lake sediments studied, probably because of the location of accumulations of evergreen pollen, diatoms, and other algal source material. As the lakes become more productive, carotenes seem to predominate over pheophytin and other chlorins.

Pheophytin and β - carotene are common constituents of the older lake sediments of Minnesota and typically show a relationship to the trophic development of the deposit. Carotene is evidently more sensitive than pheophytin to later eutrophic and dystrophic stages of the lakes and bogs, as it is nearly absent in some peats while residual pheophytin remains are common. This seems to be related to primary source differences rather than to preservation stability in the sediments.

Flavinoid pigments have been little studied in Minnesota lakes and bogs. These substances, as well as associated compounds of probable heterocyclic nature, are apparently formed in the shallow sediments by microorganisms and by interstitial organisms of various kinds. They seem to be present in amounts up to 50 ppm or more in some copropelic and peaty sediments (Swain and Venteris, 1964) and decrease with depth due to instability.

Other organic substances. Such other organic substances as organic acids, alcohols, heterocyclic compounds, etc. have been studied only cursorily in Minnesota lake sediments. Water extracts of Minnesota peats show abundant C=O stretching absorption in infrared analyses, which are probably mostly the carboxyl groups of organic acids. The indoles and other heterocyclic compounds seem to decrease more rapidly with depth than do the flavinoids. The presence of heteroaromatic compounds in visible-ultraviolet and infrared spectra of Minnesota lake sediment extracts has been noted (Swain and Venteris, 1964; Swain, 1965, 1967) but not investigated further.

In conclusion, the writer has indicated some of the more important stratigraphic, mineralogic, and organic geochemical properties of selected lake sediments in Minnesota and their interrelationships. Clearly, only a small amount of detailed work has been done and much analytical investigation needs to be carried out to obtain answers to the many remaining problems.

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