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Cu Distribution in the South Kawishiwi Intrusion of the Duluth Complex

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6/12/67

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INTRODUCTION

This paper presents data on the copper distribution in whole rock samples collected on two traverses in the Duluth gabbro complex. The purpose of determining the study was to investigate the possibility of using whole rock geochemistry as a prospecting tool.

The area selected for study lies in the South Kawishiwi intrusion of the Duluth gabbro, south of Ely, Minnesota. This area is being explored by several companies for copper-nickel deposits.

GENERAL GEOLOGY

The South Kawishiwi intrusion has not been adequately mapped at this time, but work by Phinney and Bonnichsen of the Minnesota Geological Survey indicates that it is a

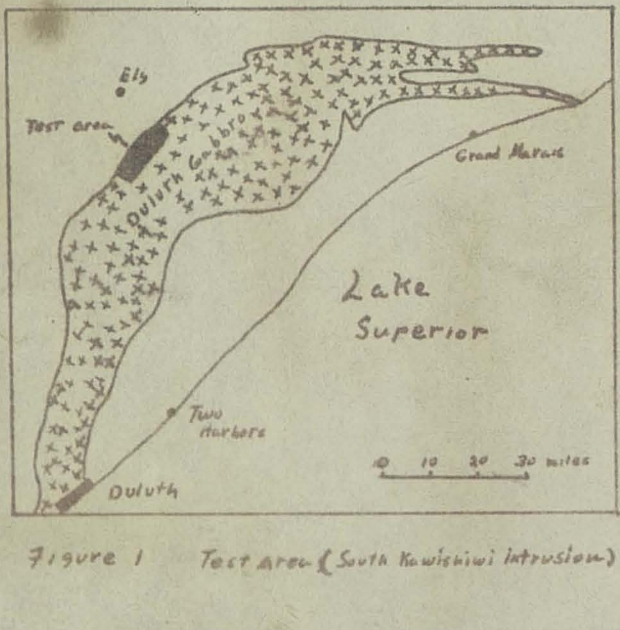

Figure 1 Test area (South Kawishiwi intrusion)

layered intrusion consisting of troctolites of varying composition with some anorthosites and anorthositic gabbro. Sulfide bearing areas are present in the contact zone on the western edge where the intrusion is in contact with older rock. The sulfides are thought to be due to magmatic segregation with later mobilization causing replacement textures in some areas. A dike-like structure at the northern end of the intrusion is thought to be the feeder dike through which the intrusion was emplace. Several inclusions of hornfels and iron formation within this dike have mineralization associated with them.

It is beyond the scope of this paper to give a full discussion of the South Kawishiwi intrusion. For more complete information the reader should consult the geologic map of the Gabbro Lake Quadrangle which may be obtained from the Minnesota Geological Survey.

SAMPLING PROCEDURE

Samples were taken from two areas within the intrusion.

The first area lies in the northern part of the Babbitt N. E. Quadrangle. Samples here were collected by myself and W. Bonnichsen who was mapping in the area for the Minnesota Geological Survey. The samples are scattered over several square miles and were not taken in a systematic fashion.

The second area is in the southern part of the Gabbro Lake Quadrangle. These samples were collected by W. C.

Phinney and lie along highway 1 which cuts across the strike of the intrusion.

Chip samples were taken of the freshest rock available at each site. An attempt was made to avoid sulfide bearing rocks as the presence of scattered visible sulfides would tend to give erratic results. Sample locations are shown in Plates 1 and 2.

TESTING PROCEDURE

Tests were run on the acid soluble content and on the total content of copper in each sample. Colorimetric methods employing 2,2' biquinoline as an indicator were used for both procedures.

Sample Preparation

A small portion of each sample was crushed in a hardened steel hand crusher. They were then transferred to a mortar and ground to fine sand size. Sieve tests were not made but it is estimated that approximately 80% passed 80 mesh and the largest particles were not more than 0.4 mm in size.

Acid Soluble Copper Procedure

A sample of approximately 200 mg is weighed out on a torsion balance and placed in a culture tube. One ml of 6 N HCl is added and the sample shaken for about 30 seconds. Ten ml of buffer solution, about 0.5 gm of hydroxylamine hydrochloride, and 2 ml of a 0.02% solution of 2,2′ biquinoline in isoamyl alcohol are added and the mixture shaken for 30 seconds. The color of the immiscible layer is then compared to standards of known copper content.

Total Copper Procedure

For running total copper content, a 200 mg sample is fused using $KHSO_4$ as a flux. The melt is cooled on the sides of the tube and digested with 3 ml of 6 N HCl in a hot water bath. After the melt is broken up the sample is diluted to 10 ml. A 1 ml aliquot is then tested using the same method as for acid soluble copper.

Operator's charts for both procedures are included in the appendix. To simplify things the buffer solution used for both procedures was made up of sodium acetate and sodium tartrate. The published procedures used potassium sodium tartrate for the fusion method and sodium tartrate for the acid method. Hydroxylomine hydrochloride was used as the reducing agent but was not incorporated into the buffer solution because it has a tendency to become ineffective after a time.

RESULTS

Babbitt N.E. Quadrangle

In the Babbitt traverse it was found that both the acid soluble and the total copper content of the rocks follow a definite trend. It was also found that the copper content varied primarily with distance across the strike from the western contact. Although the samples had a large lateral spread along the strike, there was little variation in copper content parallel to the strike over a distance of up to two miles.

In Figures 2 and 3 the copper content in parts per million (ppm) is plotted against distance from a base line roughly parallel to and coincident with the western contact. Figure 2 shows acid soluble copper and Figure 3 shows total copper. It can be seen that the acid and total copper profiles show the same trends.

Gabbro Lake Quadrangle

In the Gabbro Lake traverse the acid soluble copper content of the samples is quite erratic. The sample interval in this traverse is greater than for the Babbitt traverse one and it was thought that this factor might be responsible for the lack of a definite trend. When the fusion tests were run, however, a relatively good trend showed up. It was found that the acid and total copper profiles do not show the parallelism that appeared in the previous traverse. Figure 4 shows the acid soluble profile and Figure 5 shows the total profile for the Gabbro Lake traverse.

Figure 2
Babbitt N.E. Quadrangle
Acid Soluble Copper

Babbitt N.E. Quadrangle

Figure 2

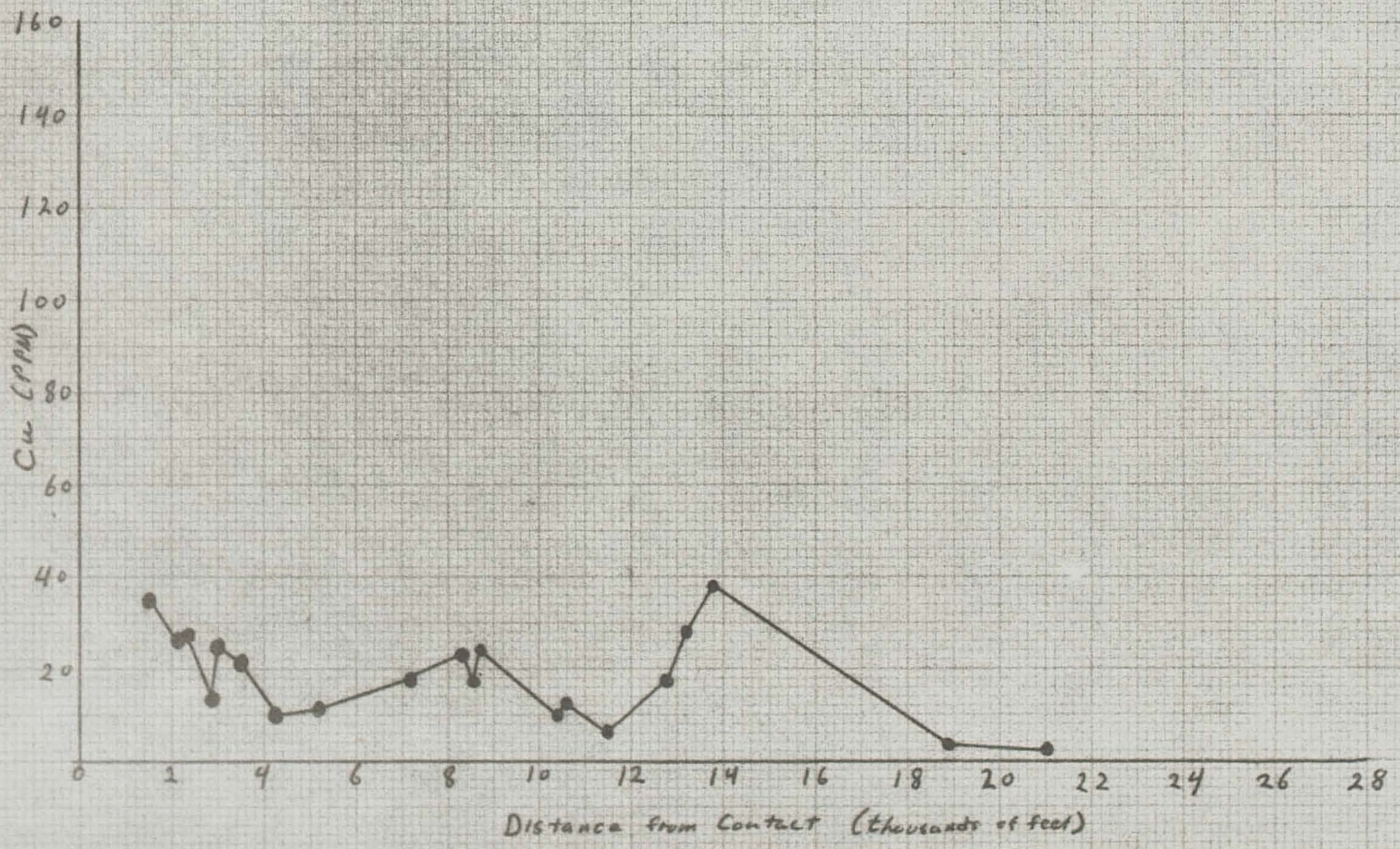

Fig 2

Figure 3
BabbiTT N.E. Quadrangle
Total Copper

BabbiTT NE Quadrangle

Figure 3

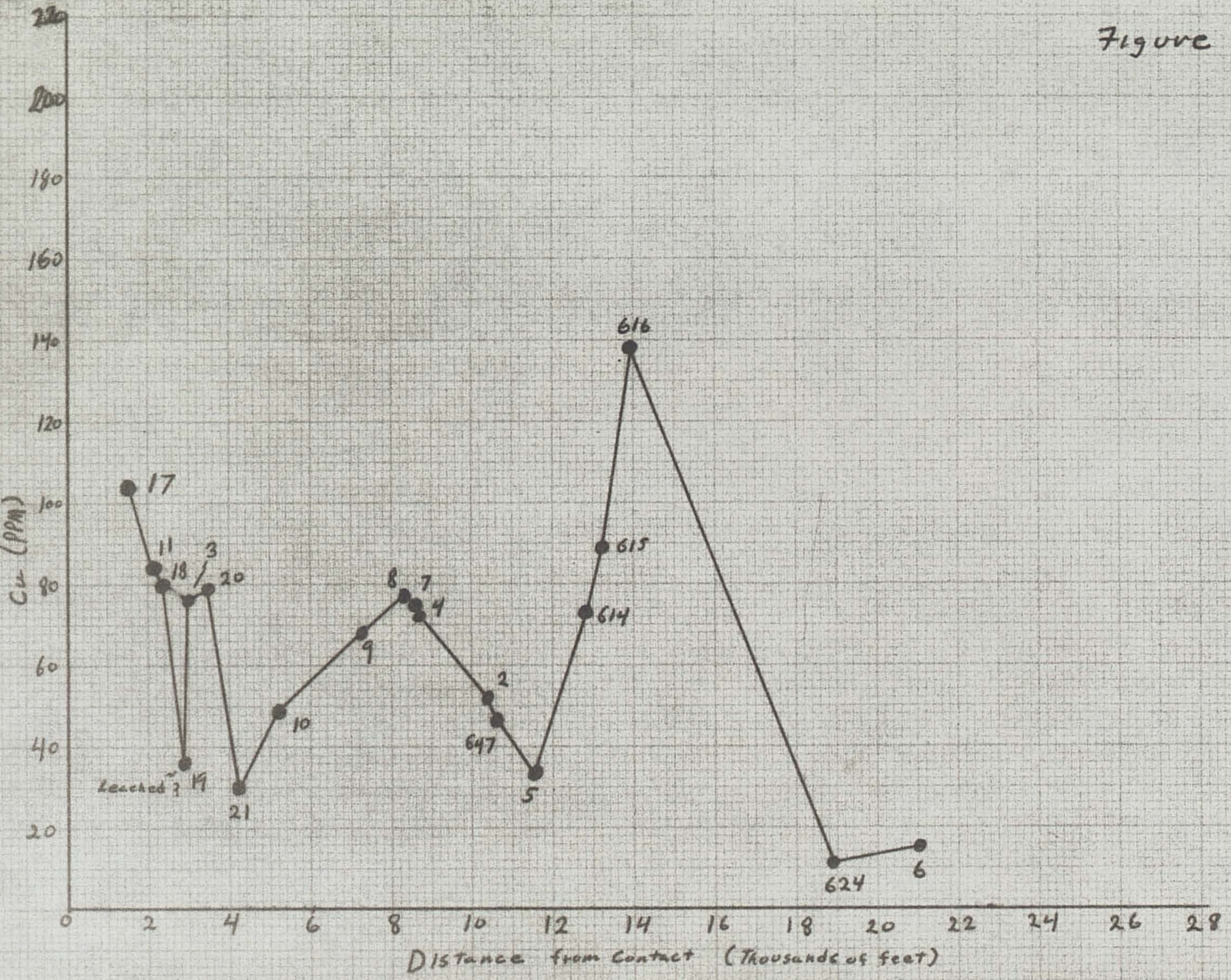

Fig 3

Figure 4
Gabbro Lake Quadrang
Acid Soluble Copper

Gabbro Lake Quadrangle

Figure 4

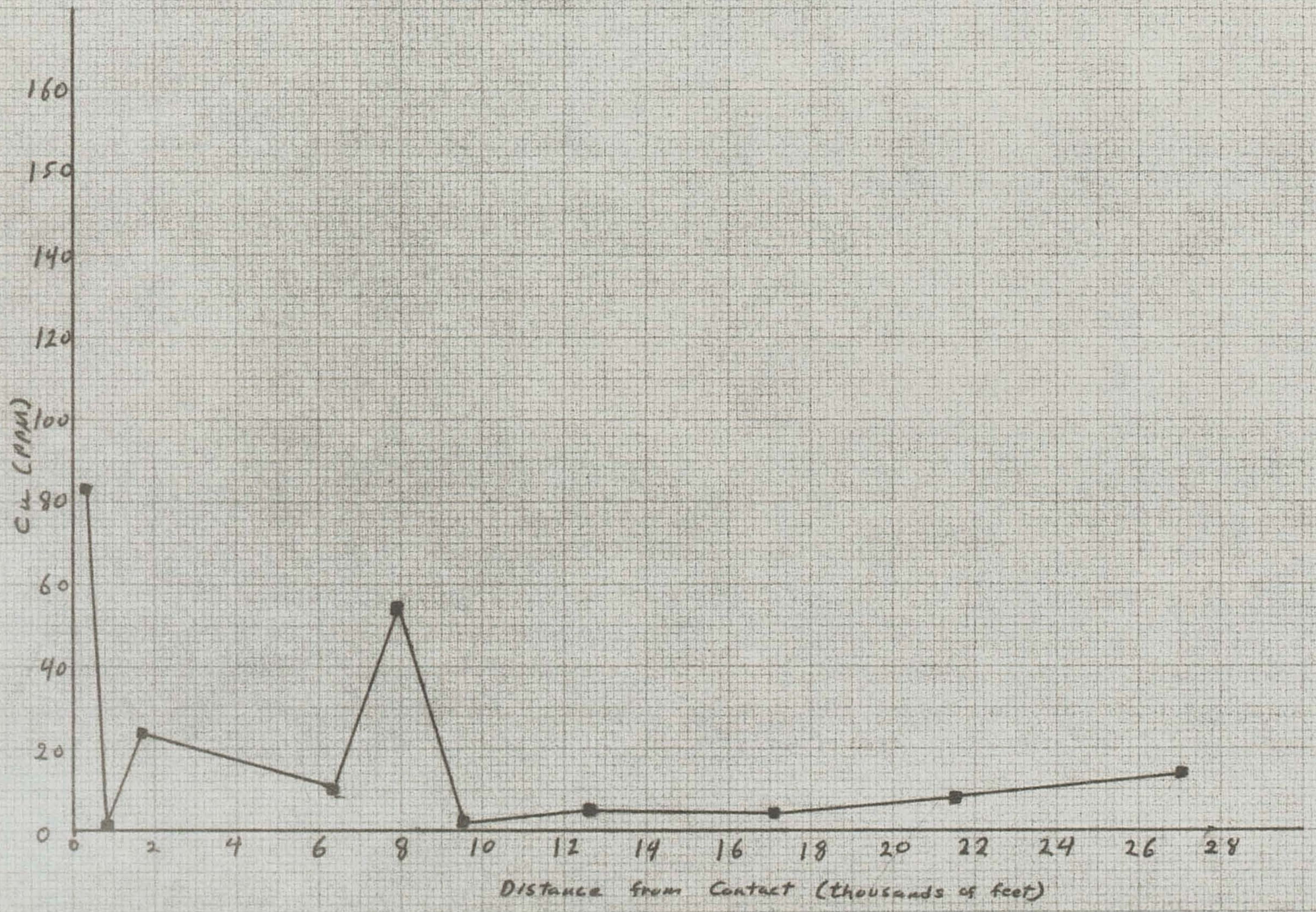

Fig 4

Figure 5
Gabbro Lake Quadrangle
Total Copper

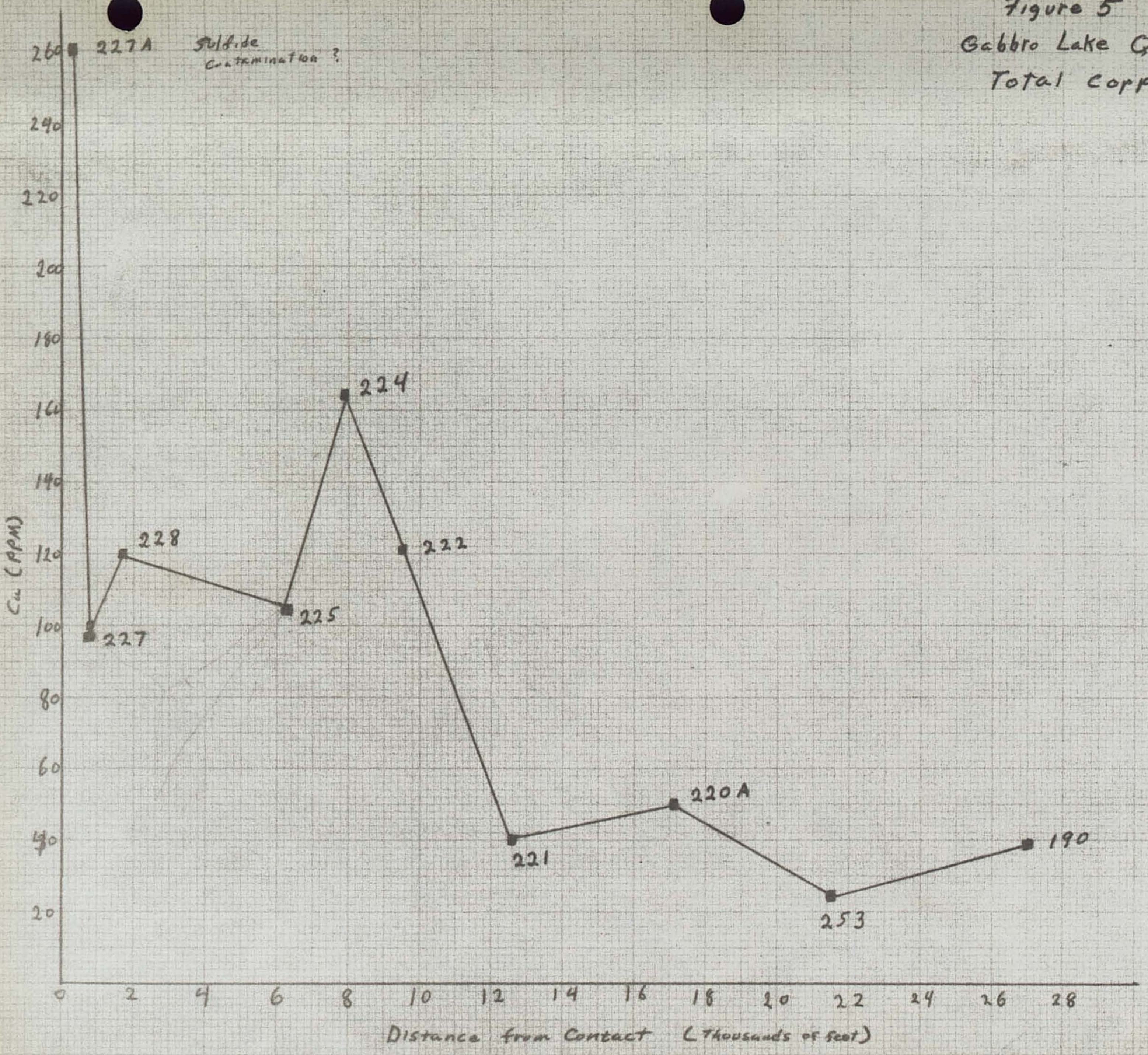

Fig 5

DISCUSSION

The profiles of the total copper content for both traverses show a generally similar pattern. This consists of a background area characterized by low copper content and an anomalous area of generally high copper content.

Several points should be noted in comparing the two traverses. As was mentioned above, the sample interval in the Gabbro Lake traverse is considerably greater than in the Babbitt traverse. For this reason the Gabbro Lake profile does not show the details of the distribution as well. The background values are not well establish in the Babbitt traverse (2 points), but the assumption that the last 2 points in the profile represent the background value is supported by comparison with the Gabbro Lake profile. If this is the case it can be seen that both the background areas and the anomalous areas of the Gabbro Lake profile contains considerably higher values that the Babbitt profile. Presumably this is due to greater mineralization in this area.

Individual peaks in copper content were found to exist in the anomalous zone. In the Babbitt traverse these peaks are well defined by several samples in each case. This indicates that the peaks are real and not due to random variations in the rock or in the testing procedure. The origin of these peaks and their relationship to mineralization is not known.

Acid vs Total Copper Content

The acid soluble copper content is assumed to consist of copper which is not incorporated in the crystal structure of the silicate minerals, but is easily available for extraction by a relatively mild reagent. Figure 6 shows the correlation between the acid soluble copper content and the total copper content for both traverses. It can be seen that in the Babbitt traverse (Fig. 6A) there is a definite relationship between the two values. The ratio of acid to total copper (A/T) is about 0.3 ± 0.04 at a 95% confidence level, assuming a normal distribution. The variation in this value is probably due to a great extent to inherent inaccuracies in the colorimetric method employed. Figure 6B is the same plot for the Gabbro Lake traverse. It shows that the correlation between acid and total copper is extremely poor and that the acid soluble fraction has been relatively impoverished.

Evidence from preliminary exploration work seems to show that the Gabbro Lake area has a higher concentration of sulfide minerals near the contact than the Babbitt area. If this is so, the relatively low values of acid soluble copper may be related to the sulfide concentrating processes. It is possible that some type of remobilization enriched the contact areas at the expense of the easily extractable copper in the surrounding rock.

Warren and Delavault (1959) have stated that they believe the easily extractable copper fraction is more

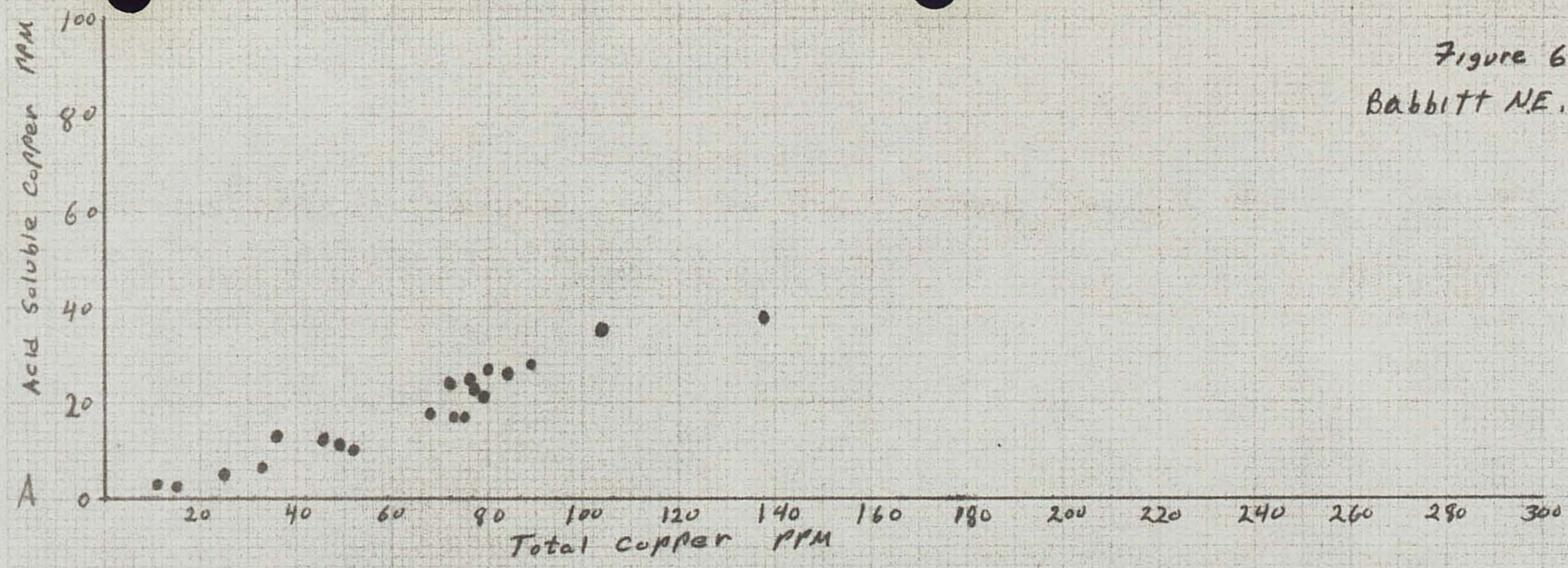

Figure 6A
Babbitt N.E. Quadrangle

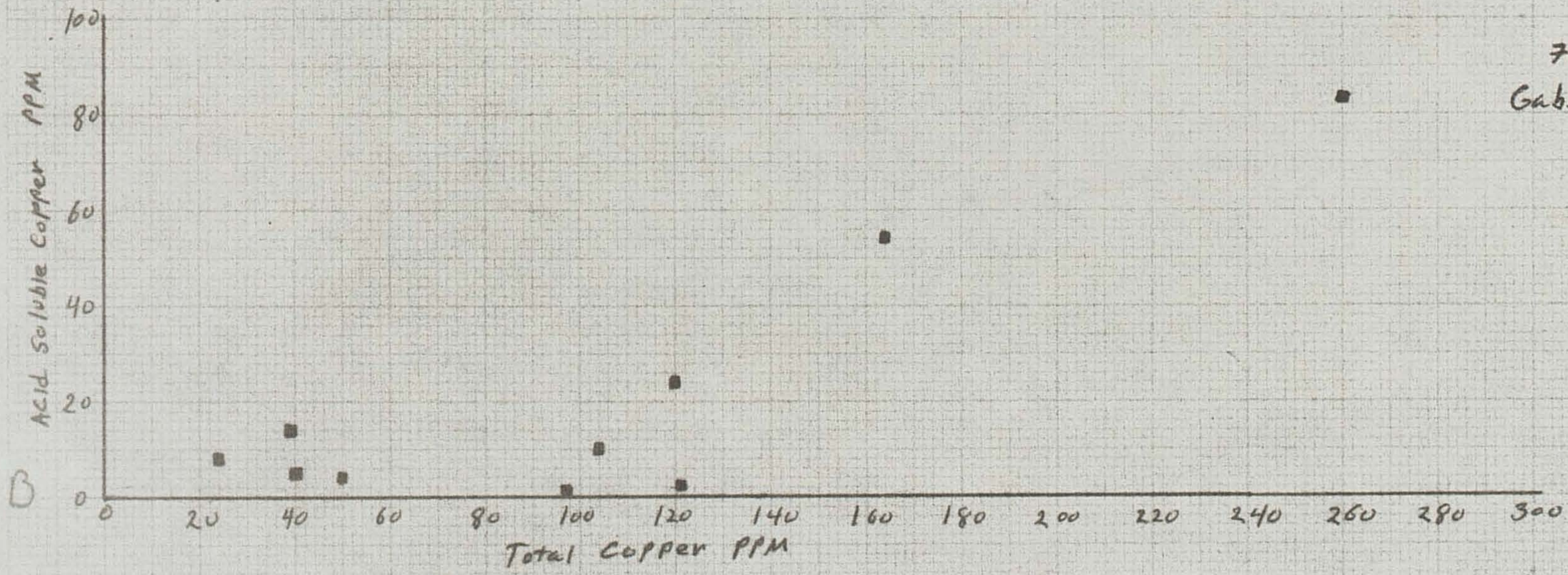

Figure 6B
Gabbro Lake Quadrangle

0 20 30 40

closely related to mineralized zone than the total copper content. They believe that the large variation in the average total copper content of igneous rocks may make total copper anomalies indistinguishable from background variation. Their work was concerned with characterizing the copper content of an igneous body with a few samples to determine its relative mineralization with respect to other similar bodies. They showed good correlation between areas of known mineralization and their results. They did not report any analysis for total values.

Table I shows some of their results. The values in nonmineralized areas are on the order of 1 to 5 ppm while areas near mineralization are considerably higher. It would be very interesting to have total copper analysis of these specimens to determine the relationship of the total copper content to mineralization. Also it would be useful to known how the copper content of rocks associated with mineralization varies with distance from the mineralized areas.

In comparing the present study with that of Warren and Delavault one should keep in mind that their work was done on diorites and the mineralization was probably metasomatic, while this paper is concerned with basic gabbros and magmatic segregation deposits. Also the testing procedures are different and would probably give different results on the same sample.

Table I

TRACE CU. CONTENT OF SOME DIORITIC STOCKS AND BATHOLITHS IN BRITISH COLUMBIA

(Aqua Regia Soluble Fraction)

(Warren 1959)

Supposed Non-Mineralized Areas	Mineralized Area Nearby	
2	52	
5	60	
4	18	
1	130 - Guichon Qtz. Diorite	
1	3 - not related to mineralization	
1	20	
2	9	
2	32, 20	Bethlehem Qtz. Diorite
	50, 45, 7	
	110, 18	

Keeping this in mind, there are two interesting points that can be made. In the Gabbro Lake traverse, acid soluble copper is a poor indicator of the known mineralization but the total copper profile shows a definite high near the mineralized contact. The other point is that both acid soluble copper and total copper show considerable variation depending on where the samples were taken in the same intrusive. Therefore one might come to different conclusions as to the mineral potential of this intrusion depending on the location of the samples.

Snyder (1959) has done some interesting work in the Duluth Gabbro. He has determined the total copper content of olivines, pyroxenes, and plagioclase in the Gabbro Lake area by spectrographic analysis. The results in general show an increase of copper in the various minerals near the mineralized contact. It would be of interest to know the relationship between these values and those for whole rock obtained by the same method.

CONCLUSIONS

The results obtained in the South Kawishiwi intrusion open up some interesting possibilities for the use of whole rock geochemical analysis of metal contents as a guide to mineralized zones. It is clear that the trace metal content is related to mineralization, but the determination of the exact nature of this relationship requires further study before any definite conclusions can be reached as to the effectiveness of the method.

Gross has shown that a systematic increase in radioactivity and silica content in Dome Stock, Red Lake, Ontario is related to concentration of gold ore. Fig. 7 is a contour map of the stock showing this relationship.

That this type of pattern may exist in the South Kawishiwi intrusive with respect to copper is suggested by the difference in the general level of trace copper between the Babbitt and Gabbro Lake traverses. If so a grid system of samples should be analyzed to outline favorable areas.

The problem of the existence of peaks in the profiles which are not related to known mineralization was mentioned in an earlier section. If it is assumed that these are not directly related to mineralization, it can be speculated that they are due to petrological reasons. Perhaps some mineral such as olivine or pyroxene has an affinity for copper and the peaks are due to rhythmic layering of these minerals in a high copper region. A combination of petrographical study of the mineral composition of the rocks and analysis of mineral fractions similar to Snyder's work might throw some light on the question.

In any case more geological work is required so that geochemical data can be more closely related to the geological situation. Interpretation of this data would then be more relevant.

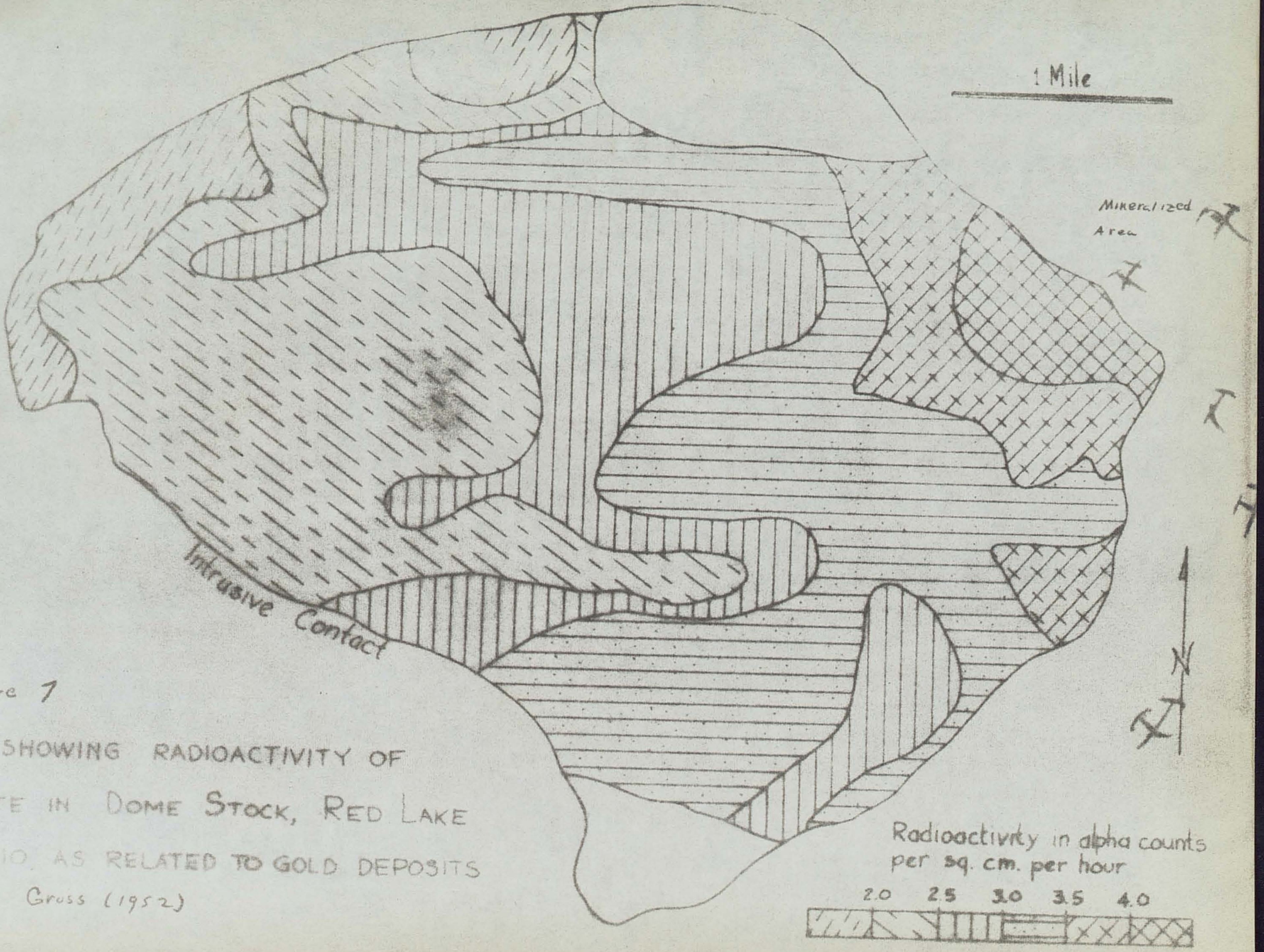

Figure 7

MAP SHOWING RADIOACTIVITY OF GRANITE IN DOME STOCK, RED LAKE ONTARIO AS RELATED TO GOLD DEPOSITS

Gross (1952)

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APPENDIX I

Babbitt Traverse

Sample	Acid Sol. Cu (ppm)	Total Cu (ppm)	Approximate distance from contact
17	35	104	1,500
11	26	84	2,100
18	27	80	2,350
19	13	36	2,900
3	25	76	3,000
20	21	79	3,500
21	5	25	4,250
10	11	49	5,200
9	18	68	7,250
8	23	77	8,300
7	17	75	8,550
4	24	72	8,700
2	10	52	10,400
647	12	46	10,600
5	6	33	11,550
614	17	73	12,800
615	28	89	13,200
616	38	138	13,900
624	3	11	18,900
6	2	15	21,000

Gabbro Lake Traverse

227A	83	260	300
227	1	97	650
228	24	120	1,700

Sample	Acid Sol Cu	Total Cu	Distance
225	10	104	6,320
224	54	164	7,900
223	2	121	9,540
221	5	40	12,600
220A	4	50	17,100
253	8	24	21,500
10[illegible]	14	39	27,100

Appendix 2

[redacted]

Operator's Chart

Field Test for Acid Soluble Copper
2-2' - Biquinoline

Ref.: Canney & Hawkins - Cold Acid Extraction from Soils and Sediments, 1958
Eco. Geol. Pp. 877-886

1. Place 0.2 gms. of sample in culture tube.
2. Add 1 ml cold 6N (1:1) HCl and shake 30 sec.
3. Add 10 ml buffer, and 2 ml biquinoline reagent.
4. Cap tube, shake vigorously 30 seconds.
5. Allow to stand until immiscible isoamyl alcohol layer separates.
6. Compare with standards.

Standards

1. Add 0, 0.2, 0.4, 0.8, 1.5, 3 and 6 micrograms copper to screw cap culture tubes.
2. Add 1 ml 6N HCl and continue with step 3 above.

NOTE: Keep standards stoppered to prevent evaporation of the organic solvent (and resultant intensification of color). Standards are good for several weeks.

Reagents

Buffer Solution:

Dissolve - 400 g. sodium acetate
100 g. sodium tartrate
20 g. hydroxylamine hydrochloride

in 1 liter of demineralized water. Test a 10ml sample with 1 ml of reagent (shake 2 min.) to check for contamination.

Biquinoline Reagent - (0.02%, weight per vol.)

On a hot plate warm 0.2 gms. of 2,2' biquinoline in 900 ml isoamyl alcohol (use well ventilated area away from open flame).

NOTE: Solution should be colorless; if yellow should be discarded.

H.Cl. 6N. Add 500 ml conc HCl to 500 ml demineralized water.

Standard Copper Solution - (100 micrograms Cu per ml.)

Dissolve 0.2 g. Cu $SO_{4.5}H_2O$ in a small vol. of 0.1 N HCl, dilute to 500 ml with 0.1 N HCl.

Prepare more dilute solution as required.

School of Mineral & Metallurgical Eng.
University of Minnesota

Appendix 3

[redacted]

Operator's Chart

Field Determination of copper - biquinoline.

1. Fuse 0.1 g. sample with 0.5 g. $KHSO_4$. Cool melt on side of tube.
2. Add 3 ml 1+1 HCl, place in hot water bath until melt is broken up.
3. Dilute to 10 ml. with water; mix.
4. Transfer 1 ml. aliquot to screw cap culture tube. (Use 2.5 ml. where cu. anomaly is low.)
5. Add about 50 mg. solid $NH_2OH.HCl$, and shake occasionally until dissolved.
6. Add 10 ml. buffer, 2 ml biquinoline in isoamyl alcohol, screw cap on culture tube, then shake for 30 seconds.
7. Allow to clear, then compare with standards.

Standards

1. Add 0, 0.2, 0.4, 0.8, 1.2, 1.6, 2.5, 4.0, 7.0, and 10 micrograms of copper to screw cap culture tubes.
2. Add 1 ml 1+1 hydrochloric acid and 2 ml. water.
3. Continue with step 5 above through step 7.

8\. Keep slightly stoppered to prevent loss of organic solvent, but do not keep screw cap on too tightly as it may not be reopened too easily.

Reagents

Buffer solution - Dissolve 400 g. of sodium acetate, 100 g. of potassium sodium tartrate and dilute to 1 liter with water.

Biquinoline solution - On a hot plate warm 0.2 g. of 2, 2' biquinoline in about 900 ml. isoamyl alcohol. Cool, and make up to 1 liter with isoamyl alcohol.

Ref: Rapid Field and Laboratory Method for the Determination of Cu. in Soil and Rocks - Geol. Surv. Bull. 1036-A

Note - If reading is high, best to use a smaller aliquot (say 0.5 ml) and get color into more sensitive range.

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Wallen, D.A., 1967,
Cu distribution in the South Kawishiwi intrusion of the Duluth complex.

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Wallen, D.A.
1967

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300
MADE IN U.S.A.

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Plate 1

Sample points
Circled in red

SUBJECT TO CORRECTION

BABBITT NE QUADRANGLE
MINNESOTA
7.5 MINUTE SERIES (TOPOGRAPHIC)

MGS
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Report

Wallen, D.A
1967

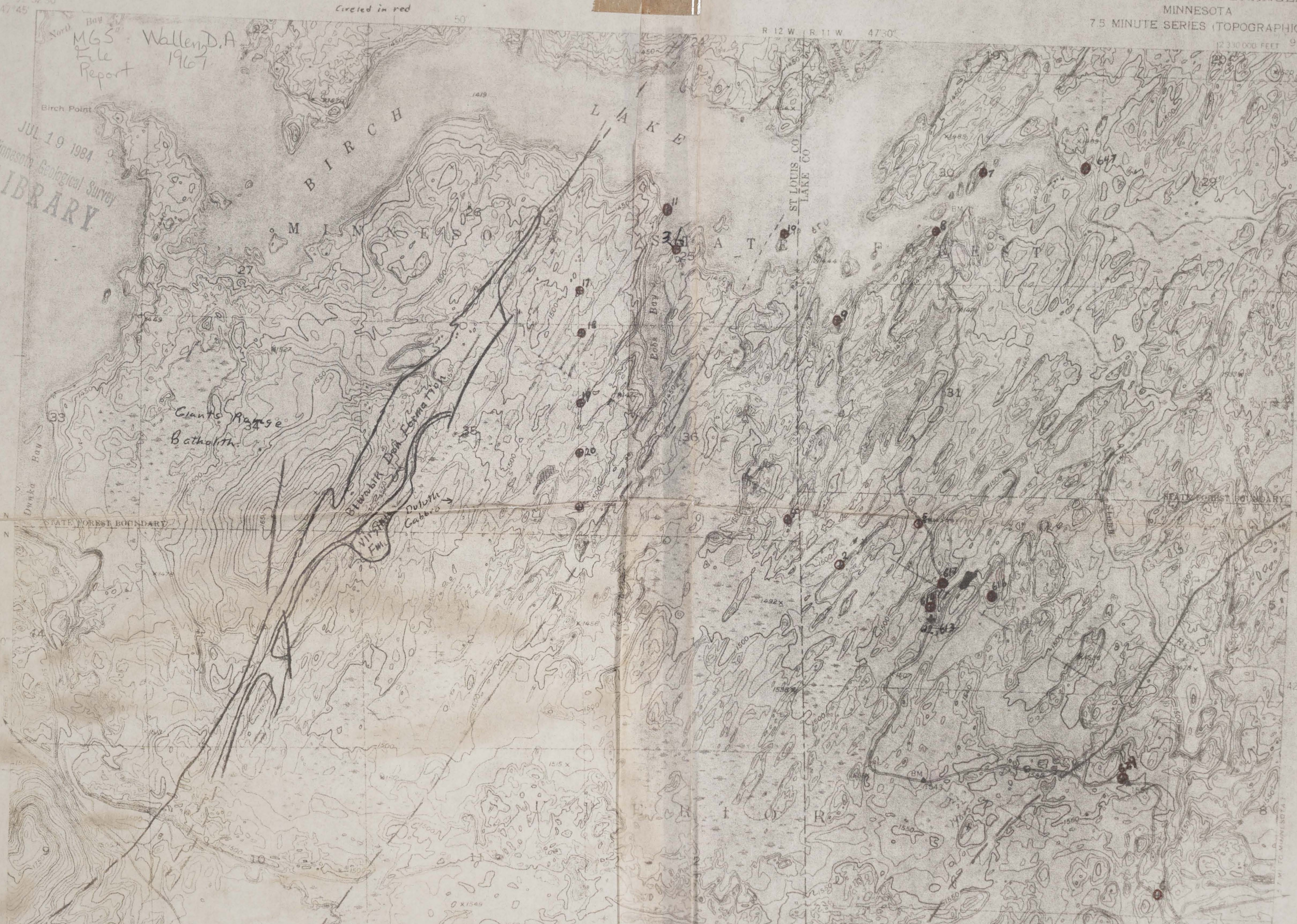

Plate 20

Gabbro Lake Traverse

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