

GEOLOGICAL SURVEY OF CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

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BULLETIN 130

THE COPPER CONTENT OF CANADIAN SHIELD ROCKS, RED LAKE-LANSDOWNE HOUSE AREA, NORTHWESTERN ONTARIO

R. F. Emslie and R. H. C. Holman

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By

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DEPARTMENT OF ENERGY, MINES AND RESOURCES CANADA

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PREFACE

As ore deposits become increasingly difficult to find by conventional prospecting new methods must be explored, if not to find ore deposits directly, at least to direct prospecting to the most suitable areas. This has always been the goal of economic geology but new special techniques must be developed and tested under Canadian conditions.

It has long been known that the important metals are present in minute amounts in all the rocks of the earth's crust. The purpose of the study on which this report is based is to see if these minute amounts varied significantly when examined over a wide area and if this variation could suggest where ore deposits might occur.

The investigation is far from complete and the purpose of the present report is to tell what variations have so far been found in one metal, copper, and to describe the methods being used and some of the problems.

> Y. O. FORTIER, Director, Geological Survey of Canada

OTTAWA, November 4, 1964

BULLETIN 130 — Der Kupfergehalt in Gesteinen des Kanadischen Schildes im Gebiet von Red Lake — Lansdowne House, im nordwestlichen Teil Ontarios.

Von R. F. Emslie und R. H. C. Holman

БЮЛЛЕТЕНЬ 130 — Содержание меди в породах Канадского Щита — район Лансдаун Хауз, северо-западное Онтарио. Р. Ф. Эмсли и Р. Холман

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THE COPPER CONTENT OF CANADIAN SHIELD ROCKS, RED LAKE-LANSDOWNE HOUSE AREA, NORTHWESTERN ONTARIO

Abstract

An experimental geochemical survey was made of copper in the common rocks of 43,000 square miles of the Canadian Shield in the Province of Ontario. It was based on the analyses of 7,963 samples and has shown that, (1) the mean copper content of the main rock types varies from 7 ppm in leucocratic granites to 61 ppm in basic volcanic rocks (these mean concentrations are lower than most published abundance figures for copper in similar rocks); (2) variations in the mean copper content within each rock type, considered on a regional scale, are in general insignificantly small, but there are exceptions; and (3) the distribution of the copper in each type of rock is approximately lognormal.

Résumé

On a fait sur une aire de 43,000 milles carrés du Bouclier canadien en Ontario un relevé géochimique expérimental portant sur la teneur en cuivre des roches ordinaires. L'expérience, qui est fondée sur l'analyse de 7,963 échantillons, a démontré 1) que la teneur moyenne en cuivre des principaux types de roches varie de 7 ppm, dans les granites leucocratiques, à 61 ppm dans les roches volcaniques basiques (ces concentrations moyennes sont inférieures à la plupart des valeurs publiées sur la teneur en cuivre des roches semblables); 2) que les variations dans la teneur moyenne en cuivre pour chaque genre de roche, à l'échelle régionale, sont en général sans importance, mais qu'il y a des exceptions; et 3) que la répartition du cuivre dans chaque genre de roche est à peu près normale au point de vue logarithmique.



INTRODUCTION

"For cause sufficient Mettals finde ye shall Only to be the vertue Minerall Which in everie Erth is not found, But in certaine places of eligible ground: Into which places the Heavenly Spheare, Sendeth his beams directly everie yeare And as the matters there disposed be Such Mettals thereof formed shall you see."

from an *Ordinall of Alchimy* by Thomas Norton (1477), a follower of the 'Subtil science of holy alkimy'.

Purpose and Scope of Study

During the period 1959 to 1961 the Geological Survey of Canada studied the Red Lake-Lansdowne House area, a 50,000-square-mile region of the Canadian Shield in northwestern Ontario. The main purpose of the study was to elucidate the geology of the area and to depict it on geological maps at a scale of 1 inch to 4 miles (1:253,440). These maps have been published in provisional form (Bostock, 1963; Carruthers, 1962; Donaldson, 1960, 1961; Emslie, 1961, 1963; and Jackson, 1962, 1963)¹.

As an adjunct to the geological mapping, an experimental geochemical survey over about seven eighths of the region was undertaken to investigate the distribution of several chemical elements in the principal rocks underlying the area. More specifically, the immediate objectives of the geochemical work were:

- 1. To reveal significant regional variations in the concentrations and manner of distribution of particular chemical elements within and between the principal rock types of the regions;
- 2. To compile regional geochemical maps giving basic data on the metal content of bedrock for use in mineral exploration;
- 3. To study possible correlations between regional geochemical patterns and the distribution of ore deposits.

The geochemical study was conducted by collecting specimens of bedrock from outcrops for chemical analysis in the laboratory. Analyses for copper have been completed; the results are presented and discussed in this report. A comprehensive treatment of the data, covering all three objectives outlined above, is, however, not attempted here and discussion is confined mainly to the first topic, that of regional

1

¹Names and/or dates in parentheses refer to References at end of report.

variations in the concentration of copper in the principal rocks of the region. Provisional geochemical maps showing the distribution of copper in bedrock have been published (Holman, 1964 a to g) and are not discussed here.

The completion of this study required close cooperation between the authors and minimal separate effort. Responsibility for the work is, therefore, equally shared.

Acknowledgments

The detailed geochemical work described in this paper and the series of geochemical maps already issued were made possible by the cooperation of the associated field party chiefs J. A. Donaldson, G. D. Jackson, H. H. Bostock, C. Carruthers, and R. F. Emslie, who collected many thousands of rock specimens at pre-arranged intervals along their geological mapping traverses.

Margaret A. Gilbert was responsible for the chemical analysis of the specimens.

DESCRIPTION OF REGION

The Red Lake-Lansdowne House area (Fig. 1) is a rectangular region extending for about 350 miles from east to west and 135 miles from north to south. It is principally a peneplain at a general elevation of about 1,000 feet with little relief except for a gentle downward slope of some 200 feet northwards across the region and a similarly gentle downward slope to the east.

The climate is sub-arctic, giving cool, short summers with no more than three months of mean temperatures above 50°F. Winter snowfall usually exceeds 30 inches. The area is thickly forested where drainage is adequate; elsewhere, muskegs and bogs are extensive.

Thorough scouring of the bedrock by continental glaciation has destroyed older residual soils and near-surface zones of oxidation. Glacial action has resulted also in the widespread development of drift which, in some localities, completely masks the bedrock (Prest, 1963).

The region is practically uninhabited and largely inaccessible by road.

General Geology

The geology of the region is described briefly in terms of the rock units adopted for field mapping (Table I). For such a large area these units had to be based on field and hand specimen examination, and the classification is therefore not petrographically rigorous.

Table I

Rock Unit ¹	Rock type	Percentage of total area
2	Leucocratic granitic rocks, mainly massive	7
3	Granitic rocks, massive to weakly foliated	29
4	Porphyritic granitic rocks	8
5	Granodioritic rocks, mainly strongly foliated	17
6	Gneissic and migmatitic rocks	6
7	Basic intrusive rocks	2
10	Metasedimentary rocks: greywacke, quartzite, conglomerate, arkose, argillite: derived schist and gneiss	3
12	Metavolcanic rocks, chiefly basalt and andesite	9
	Undivided granitic and gneissic rocks	14
	Undivided metavolcanic and sedimentary rocks	5
		100

Major Rock Units Underlying Red Lake–Lansdowne House Area, and Their Relative Abundance

¹ The sequence of rocks given in the table is not intended to imply relative age. Missing rock units were used for field geological mapping but not for this survey.











The rocks of the Red Lake-Lansdowne House area are typical of much of the Superior Province of the Canadian Shield. The oldest known are metavolcanic and metasedimentary, which occur chiefly as tightly folded, synformal, and antiformal structures in long and narrow curving belts. The metavolcanic rocks (12) (see Table I) are mainly basalt and andesite, commonly pillowed, associated with minor amounts

4

of tuff and breccia. The mineral components are mainly plagioclase and hornblende with accessory magnetite, quartz, epidote, and sphene. Dacite and rhyolite are found locally in minor amounts but specimens of these rocks are not grouped with unit 12. Metasedimentary rocks (10) comprise slate, argillite, quartzite, greywacke, arkose, and conglomerate. These rocks are commonly interbedded with the volcanic sequences. Andalusite, staurolite, and kyanite have been reported from the pelitic facies of some sedimentary sequences. Sedimentary quartz-magnetite iron-formation is widespread but in small amounts; specimens of this formation are not included in unit 10. The grade of regional metamorphism shown by rock units 10 and 12 corresponds generally to the upper greenschist and lower almandine amphibolite facies.

Basic intrusive rocks (7) are mostly gabbro with some diorite. These rocks generally occur as small masses associated with the metasedimentary-metavolcanic, belts. A few small scattered ultrabasic masses are also included in this unit. Gneissic and migmatitic rocks (6) comprise a heterogeneous assemblage of banded gneisses, *lit-par-lit* gneisses, and hybrid rocks of uncertain origin. They are characterized by large variations in the abundances of quartz, plagioclase, biotite, and hornblende. Most of these rocks are probably metamorphic or metasomatic equivalents of units 10 and 12. The granodioritic rocks (5) are probably the oldest granitoid rocks in the region. They range in composition from quartz diorite to quartz monzonite. The granodiorites are characterized by a marked foliation that persists over wide areas and is usually concordant with the strike of the associated metavolcanic-metasedimentary belts. The granodiorites contain plagioclase and subordinate potash feldspar together with biotite and hornblende.

Porphyritic granitic rocks (4) are characterized by abundant phenocrysts or porphyroblasts usually of potassium feldspar. The rocks of this unit are mainly porphyritic equivalents of the granitic rocks (3). The massive and weakly foliated granitic rocks (3) are chiefly quartz monzonites and granites but include minor amounts of granodiorite and syenite. These rocks contain biotite as the most common mafic mineral together with some hornblende and minor muscovite. The leucocratic granitic rocks (2) are mainly alaskites with quartz and potash feldspar as the dominant minerals. They occur most commonly in the western half of the region. The granites of units 2 and 3 are probably the youngest granitoid rocks in the area.

Potassium-argon ages on biotites taken from seven specimens of granitoid rocks and paragneisses collected at localities scattered throughout the region range from 2340 to 2755 million years (Lowdon, 1961; Lowdon, *et al.*, 1963; Leech, *et al.*, 1963). These dates are concordant with other dates recorded from the Superior Province of the Canadian Shield and probably reflect the latest widespread metamorphism and igneous activity to affect the region, the Kenoran orogeny (Stockwell, pp. 111– 112, *in* Lowdon, 1961). Northwesterly trending diabase dykes that are especially abundant in the southeastern part of the region and Palaeozoic beds occurring at the eastern boundary are the only known younger rocks.

PROCEDURE

Specimen Collection

Because of the large area to be covered (Fig. 1), special sampling crews were not provided and rock specimens for geochemical purposes were restricted to those that could be collected by geological mapping parties without seriously impeding their progress. Wherever possible, specimens of rock weighing between two and three pounds were collected from exposed bedrock at intervals of about a mile along traverses required for geological mapping. Composite sampling was not attempted and the practice usually followed was to take a single specimen of the most representative rock. In areas where the rocks were visibly heterogeneous, such as areas of gneisses and migmatites, those rocks exposed at the outcrop were collected. Field descriptions of all specimens were recorded. Approximately 8,000 specimens were collected from this 43,000-square-mile area.

Specimen Preparation

Each specimen was split, a chip retained for reference, and the rest reduced to about $\frac{1}{4}$ -inch size in a jaw crusher. The crushed material was then ground to about 60 mesh by a rapid pass through a Braun pulverizer (rotating disk type) fitted with ceramic plates. The resulting powder was mixed by rolling on paper sheets. A 15 to 20 gram sample was then taken for fine grinding to about 200 mesh size by mechanical agitation for twenty minutes in a small ceramic ball mill on a paint mixing machine. This procedure introduces very little contamination. Salting of one sample by another was guarded against by thorough cleansing and by recording the order in which samples were processed at all stages during preparation for analysis.

Chemical Analysis Choice of Method

Ideally the method of chemical analysis chosen should be based solely on geochemical requirements of the study, but in practice a compromise must usually be sought between factors such as the availability of special facilities or instruments, special techniques developed, and the cost of analyses. For this reconnaissance study of copper in rocks, involving the analysis of a large number of specimens, a rapid, inexpensive technique was required. A high degree of accuracy was considered unnecessary provided sufficient precision was obtained to allow valid comparisons between groups of results.

Outline and Performance of Method Used

Analyses for copper in the rock samples were made with the technique described in detail by Gilbert (1959). Briefly, the method consists of:

- 1. Mixing 0.2 g of the finely ground rock with powdered potassium pyrosulphate in a test-tube and heating it in a gas flame to bring about partial fusion of the sample at red heat;
- 2. The addition of dilute hydrochloric acid and warming to dissolve the liberated copper;
- 3. Transference of a portion of this acid solution to a second test-tube and the simple addition of reagents to provide optimum conditions for the reaction of copper with dithizone reagent;
- 4. The addition of dithizone solution in carbon tetrachloride and vigorous shaking to induce reaction between the copper and dithizone;
- 5. Estimation of the amount of copper present by visually comparing the resulting colour of the carbon tetrachloride solution with those of a series of standards produced from known amounts of copper by the same procedure.

The accuracy of the method was tested by analyzing a set of twelve standard samples ten times during the course of the project. Using the procedure suggested by Craven (1954), a mean accuracy of 20 per cent was obtained for the range 30 to 200 ppm copper on the ten replicate sets of data. Suitable standards were not available for testing the method below this range, and the accuracy would probably decrease somewhat as the sensitivity limit of 5 ppm Cu is approached.

Some doubt was felt about the efficiency of the partial fusion of the sample with potassium pyrosulphate for extracting all the copper from the rock samples. This possible source of inaccuracy was examined by selecting 15 specimens of granite giving a range of copper content commonly found in that type of rock, and analyzing them for copper, first using the pyrosulphate fusion and second with a hydrofluoric-perchloric acid attack to bring about complete decomposition of the rock. Fifteen specimens of basic volcanic rock were similarly selected and analyzed in the same way. The results obtained by these two procedures are given in Table II.

The relationship between the two sets of results obtained from each rock specimen was examined by performing a linear regression of copper extracted by $K_2S_2O_7$ on copper extracted by HF/HClO₄, it being assumed that the HF/HClO₄ treatment gave the truer results. The data points and the fitted regression lines are plotted on Figures 2 and 3 together with the 95 per cent confidence limits. The narrow 95 per cent confidence belts on both Figures 2 and 3 indicate close agreement between the two extraction methods. The slopes of the regression lines show, however, that the pyrosulphate method gives slightly lower results than the hydrofluoric-perchloric acid attack, but that the difference is very small, especially below 100 ppm copper. For this reason it was considered unnecessary to apply a correction. For practical purposes, therefore, the two sets of results can be considered the same, and the pyrosulphate fusion method can be regarded as an efficient extractor of copper from these rocks.

Table II

				the second s
	1	2	1	2
Specimen	ppm Cu	ppm Cu	ppm Cu	ppm Cu
	Copper ext graniti	racted from c rocks	Copper ext basalti	racted from c rocks
1	44	42	520	475
2	2	8	80	58
3	22	22	6	6
4	12	14	6	10
5	10	12	36	42
6	1	2	62	52
7	42	42	140	135
8	6	10	80	85
9	34	32	22	26
10	34	38	80	74
11	12	16	64	66
12	20	20	80	90
13	2	4	160	165
14	68	72	20	16
15	200	180	32	30
and the second of the second se				

Comparison of Copper Extracted from Rocks 1) by Complete Digestion, with Hydrofluoric and Perchloric Acids, and 2) by Potassium Pyrosulphate

The precision of the analytical technique was measured to assess the amount of variance introduced into the grouped geochemical data by analytical error (Shaw, 1961). Sets of 25 specimen powders were selected from each of four of the rock units 3, 5, 6, and 12, so as to cover the general range in the copper content of each unit. Small portions were taken from each specimen powder, arranged in a random order, and analyzed. This process was repeated three times giving the replicates A, B, and C listed in Table III. An analysis of variance of the data was performed and is summarized in standard form in Table IV. Estimates of the analytical variance obtained in this way range from 1.8 to 8.1 per cent of the total variance (Table V). The largest value, 8.1 per cent for rock unit 3, is mainly the result of two specimens that gave replicate values of 42, 46, 105 and 4, 46, 8, which must be due to gross error. It seems likely that the variance due to chemical analysis rarely contributes much more than 5 per cent to the total variance.



FIGURE 2. Linear regression of the relationship between the amount of copper extracted from granitic rocks by the K₂S₂O₇ and HF/HClO₄ methods.

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FIGURE 3. Linear regression of the relationship between the amount of copper extracted from basic volcanic rocks by the K_2S_2O7 and HF/HClO4 methods.

Table III

Replicate Determinations (in ppm) for Copper from Suites of 25 Specimens taken from Four Rock Units

Rock Unit 3																								
Replicate A	12	44	4	42	00	22	14	12	10	42	10	32	7	5	4	38 1	9	4 21	4	4	4	4	72	180
Replicate B	18	46	10	40	9	26	20	10	4	46	14	34	4	4	00	10	0	8	*	4	46	7	68	150
Replicate C	16	50	12	44	S	24	14	18	00	105	14	30	ŝ	∞	ŝ	36	1 1	2	2 10	50	00	7	99	150
Rock Unit 5																								
Replicate A	46	56	4	12	9	18	18	26	10	34	4	9	105	4	24	10	8		4	74	18	36	18	12
Replicate B	42	99	7	14	4	24	22	30	18	36	18	10	105	13	30 1	4	0		4	95	20	40	24	16
Replicate C	46	56	80	14	10	16	20	16	18	34	12	9	105	ŝ	24	[4]	0 3	0	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	70	12	40	22	18
Rock Unit 6																								
Replicate A	90	120	16	10	20	32	90	18	40	16	10	32	76	10	6 10	1 00	0 3	4 4	4	135	34	170	210	12
Replicate B	95	110	12	10	28	36	95	22	42	14	20	38	60	16	10 6	56 1	6 3	4 5	2	130	40	140	190	18
Replicate C	74	145	12	14	22	30	100	2.6	40	10	24	36	84	20	8	50 1	6	8 4	5	120	34	60	190	18
Dock Huit 12																								
Replicate A	270	38	475	58	9	270	52	370	130	28	10	155	42	52 1	35 8	35 2	6 9	0 17	4 66	6	100	165	16	30
Replicate B	270	48	450	74	9	270	64	340	125	85	10	145	40	58 1.	30 8	30	6 0	0 1/	0 66	90	100	06	20	32
Replicate C	270	30	500	74	ŝ	230	38	360	120	20	10	140	24	44 1	55	18	6 9	0 8	5 50		100	165	∞	58

Procedure

Table IV

Analysis a	of Variance on Replicate Determinations for Copp	er from Suites
	of 25 Specimens Taken from Four Rock Uni	ts

Source	Sum of Squares	df	Mean Square
Rock Unit	3		
Between specimens Within specimens Total	80,019 4,743 84,762	24 50 74	3,334.1 94.9
Rock Unit	5		
Between specimens Within specimens Total	. 43,855 . 919 . 44,774	24 50 74	1,827.2 18.4
Rock Unit	6		
Between specimens Within specimens Total	. 181,717 . 6,097 . 187,814	24 50 74	7,571.5 121.9
Rock Unit	12		
Between specimens Within specimens Total	. 949,811 . 11,861 . 961,673	24 50 74	39,575.4 237.2

Table V

Summarized Analysis of Variance Data on Replicate Copper Determinations, Showing Component Due to Chemical Analysis

Rock Unit	Estimate of Population Variance Sp ²	Estimate of Analytical Variance _{Sa²}	$\frac{s_a^2}{s_a^2+s_p^2} \times 100$
Massive granites	1,079.7	94.9	8.1%
Foliated granodiorites	602.9	18.4	3.0%
Gneisses and migmatites	2,483.2	121.9	4.7%
Basic volcanic rocks	13,112.7	237.2	1.8%

ANALYSIS OF THE DATA

General Considerations

Regional variations in the concentrations of trace elements in rocks are likely to follow complex patterns. This complexity may, in general, arise from the interaction among such factors as:

Lithology of the host rock acting as a primary control, for example, the preference of nickel for basic rocks;

Structure imposed on the host rocks, which may influence the nature and localization of metamorphic changes;

Age of the host rock, especially with respect to metallogenic epochs;

Metamorphism, including all epigenetic effects causing elements to migrate on a regional scale;

Older patterns, whose origins are partly obscured or destroyed by subsequent events, e.g., 'ghost stratigraphy' in granitic batholiths; and

Other patterns, possibly purely random or beyond explanation in terms of known geology.

Studies of each of these factors are desirable but would require much more geochemical and geological information than is now available for the Red Lake– Lansdowne House area. For this reason, discussion of the data given in this paper will not be comprehensive but confined mainly to one controlling factor, the lithology of the host rock. It was indeed assumed that the effects of lithology would be of paramount importance and required assessing before the other factors listed could be considered.

To investigate the control of lithology over the distribution of copper a distinction was sought between:

- 1. Variations in the concentration of the element within each rock unit; and
- 2. Differences in the concentration of the element between rock units.

The study of these two effects was approached by arbitrarily dividing the data into seven major groups or samples, each corresponding to one of the seven map areas A, C, D, E, F, G and H (Fig. 1). Each of these samples was further divided according to the eight lithological units of Table I. Division of the data in this manner gave a total of 49 sub-samples (Table VI), not 56 as might be expected because not all eight rock units are present in each of the seven areas. The figures for the copper content of each of these 49 sub-samples were then examined for significant differences by the application of some simple statistical procedures.

Table VI

Deals type				Map-	areas			
	A	С	D	Е	F	G	Н	Total
2 3 4 5 6 7 10 12	297 480 90 250 51 92 84	159 325 49 13 245 29 29 29 102	 662 364 390 40 81 234		 214 28 234 160 33 83 148	273 22 223 39 71 12 35		456 2616 615 1811 700 413 420 932
Total	1344	951	1771	967	900	675	1355	7963

Number of Specimens in Each of the 49 Sub-samples

Computations

The following statistical computations were performed on the copper data for each of the 49 sub-samples.

- 1. Computation of arithmetic means and standard deviations for the arithmetic data.
- 2. Construction of histograms and cumulative frequency diagrams to examine the form of the distributions.
- 3. Transformation of the data to logarithms to improve the assumption of normality.
- 4. Computation of geometric means and standard deviations on the logarithmically transformed data.
- 5. Test of the means for lack of homogeneity by a one-way analysis of variance (F test).
- 6. Determination of the particular means contributing to the inhomogeneity by applying the 'q' statistic (Dixon and Massey, 1957).

$$q = \frac{w}{\frac{s_n \sqrt{n}}{\sqrt{n}}}$$

where w = range of means being compared

 $s_p = pooled$ standard deviation

n = total number of individuals in the sample

Because (n) varies with each map-area, (no) is used (Snedecor, 1956, p. 269),

where $n_0 = \frac{1}{a-1} \left(n - \frac{\Sigma n_i^2}{n}\right)$ where $n_i =$ number of individuals in each sub-sample

here $n_i =$ number of individuals in each sub-sample

a = number of sub-samples being compared

The value of (q) (at the 95 per cent level) is obtained from tables (Dixon and Massey, 1957, p. 440). The quantity $q(s_p/\sqrt{n_0})$ is computed and compared with the observed (w). Whenever (w) exceeds $q(s_p/\sqrt{n_0})$ a significant difference in the means is indicated.

Computations 1, 3, and 4 were made by an electronic computer from information on data processing cards; computations 5 and 6 were made on a desk calculator.

DISCUSSION OF RESULTS

Variations of Copper Content Between Rock Units

The arithmetic means of the copper concentrations for each of the 49 sub-samples are given in Table VII together with grand mean for each rock unit for the whole region. The grand means indicate gross differences between the copper content of all rocks, with the exception of the three groups of granitic rocks (2), (3), and (4). Grand means vary from a minimum of 7 ppm Cu in the leucocratic granite (2) up to a maximum of 61 ppm in the basic volcanic rocks (12). Similar gross differences in copper contents are shown by the 49 sub-samples whose means range from about 6 ppm Cu in the granitic rocks up to about 71 ppm in the basic rocks. These marked differences between the copper contents of the rock units were taken to be sufficiently self-evident not to need statistical verification.

This evident correlation between, copper content and rock type and the strong preference of copper for the more basic rocks is in accordance with the known geochemistry of copper (Goldschmidt, 1954).

One problem that appeared was that of assigning a true figure for the copper content of specimens containing less than 5 ppm, the sensitivity limit of the analytical method. An arbitrary figure of 2 ppm was assumed and used in the calculations, but subsequent examination of the data suggests that 3 ppm would have been a better choice. It was not however considered worth repeating the calculations because the substitution was found to produce negligible change in the means and to have no effect on the statistical tests applied.

The results of this study expressed more generally as means for acid, intermediate, and basic rocks together with comparable recent published figures are shown in Table VIII. It is interesting to observe that the mean copper contents of rocks from the Canadian Shield appear to be, on the whole, much lower than those of approximately equivalent rock groups presented by Sandell and Goldich (1943), and Vinogradov (1956 and 1962), but more closely resemble those of Turekian and Wedepohl (1961). It should be noted that the more recent abundance figures are lower than the earlier ones, a trend observable in recent reviews of both the Russian and Western literature.

Assessment of the significance of the differences between the mean copper contents of these Canadian Shield rocks and those of rocks from elsewhere shown in Table VIII is not a simple matter. Sampling procedures and methods used to derive the abundance figures quoted need to be considered together with the problems inherent in comparing geochemical data from areas vastly different in size before valid comment is possible.

Table VII

						Map-area	as			Grand
	r	Kock types	A	С	D	Е	F	G	H	Mean
2	ī		6.29	6.94	-	_	_	_	_	6.52
2	s		10.14	9.42	—	—		—	-	_
	x		9.32	9.57	6.35	8.16	6.27	8.93	8.38	8.06
3	s	•••••	12.13	14.80	7.65	10.95	6.75	15.90	15.32	_
	x		8.33	10.82	7.92	30.55	11.21	7.05	9.63	8.88
4	s		8.08	12.44	9.90	47.21	19.94	10.01	17.49	_
	x		9.72	7.46	10.04	10.13	11.01	11.52	10.62	10.40
5	s		12.00	8.03	11.50	14.79	18.94	16.99	24.87	_
	x		_	13.50	_	17.56	22.63	19.28	18.41	17.55
6	s		_	19.75	—	31.70	27.67	21.08	10.53	_
	$\bar{\mathbf{x}}$		36.20	36.21	57.48	54.74	67.64	49.69	69.37	56.11
7	s		45.62	35.43	57.47	45.32	91.05	63.24	100.91	_
	x		48.60	34.48	26.62	23.48	33.17	12.00	29.48	33.09
10	s		73.45	32.00	33.99	30.32	33.99	13.67	31.05	_
	x		69.86	57.58	56.06	55.67	61.21	49.09	71.28	61.24
12	s		109.13	58.11	53.47	61.99	64.17	47.84	85.13	_

Arithmetic Means and Standard Deviations of Copper Concentrations (ppm) in the 49 Sub-samples

Standard deviations calculated arithmetically for the 49 sub-samples show an obvious tendency to be numerically equal to the corresponding arithmetic mean for copper (Table VII). This arises from the strongly positive skew of the copper distributions, a feature discussed later. For examples of cumulative frequency curves *see* Holman (1964 a–g).

Table VIII

Region	Acid rocks	Intermediate rocks	Basic rocks	Author
North American rocks	16	38	149	Sandell and Goldich (1943)
World-wide rocks	30	35	149	Vinogradov (1956)
	10 (low Ca granitic rocks)	30 (high Ca granitic rocks)	87 (basaltic rocks)	Turekian and Wedepohl (1961)
	20	35	100	Vinogradov (1962)
Present study	8 (grand mean of rock units 2 and 3)	10 (grand mean of rock unit 5)	60 (grand mean of rock units 7 and 12)	

Comparison of Mean Copper Contents of Canadian Shield Rocks (Present Study), with Published Data for Igneous Rocks

Forms of the Frequency Distributions

Histograms and cumulative frequency curves constructed from the data show distributions with a pronounced positive skew for most of the 49 sub-samples. This feature may be explained by considering the probable mode of occurrence of copper in the rocks.

Krumbein (1955) and Griffiths (1960) have shown that frequency distributions for minerals present in rocks as rare grains are positively skewed, and it has been further suggested by Rodionov (1961) that chemical elements contained in such rare minerals will give similar types of frequency distributions. Frequency distributions of grains of minerals that are abundant in rocks, on the other hand, are known to be binomial in samples of a fixed size (Chayes, 1949; Chayes and Fairbairn, 1951). One might expect, therefore, that the continuous variation in concentration of a chemical element present in abundant discrete mineral grains, which themselves show a symmetrical binomial distribution, would have a normal distribution (Vistelius, 1960).

Thus it might be inferred from the positively skewed distributions of copper found in rocks from the Red Lake–Lansdowne House area that the metal is probably present mainly as small and rare grains or as a component of a rare mineral. Work on the geochemistry of copper by Goldschmidt (1954) and others, suggests that the metal is present in rocks as a sulphide, probably chalcopyrite. The inference that copper is mainly present as discrete grains of a sulphide scattered throughout the rock is supported by the virtually complete extraction of copper by potassium pyrosulphate, previously referred to in the section on analytical technique. Total release of the metal would not have been achieved were it mostly contained within the lattices of common rock-forming minerals such as quartz, feldspar, or the mafic constituents because these are largely unattacked by potassium pyrosulphate.

Biotite and feldspar separated from granitic rocks of the Red Lake-Lansdowne House area were found to contain negligible proportions of the total copper in the rock (Vollrath, 1964). Vollrath's data indicate that a significant portion of the copper may occur in magnetite, also a rare constituent of these rocks. This disagrees with the results of Azzaria (1963), who found that most of the copper in the Deloro granite is contained in the feldspar.

Calculations indicate that enough chalcopyrite to account for the average amount of copper in the rocks of the Red Lake–Lansdowne House area would not contribute more than about 0.001 to 0.1 per cent to the volume of the rock. It is unlikely, therefore, that chalcopyrite grains would be readily visible either in hand specimens of these rocks or in thin sections. Nevertheless, a study by Newhouse (1936) of sulphide occurrences in common igneous rocks did reveal the presence of chalcopyrite in many granitic rocks and in most basic rocks. Recent work by Parry and Nackowski (1963) has shown that the high copper contents of some biotite concentrates from quartz monzonites were due to chalcopyrite.

For statistical computation—such as the analysis of variance—to be valid it is necessary that the distribution of the data be approximately normal or that steps be taken to stabilize the variance. Bartlett (1947) has shown that the variance of a strongly skewed distribution can be stabilized by transformation to a logarithmic scale and at the same time this generally tends to normalize the distribution. Transformation of the copper data to logarithms (base 10) seemed to give distributions that are approximately normal. Rigorous testing for normality was however not attempted because (i) the distributions at the lower ends were truncated by the limit of analytical sensitivity, and (ii) the unlikelihood that natural distributions of elements in rocks over large areas can be described by a simple mathematical function (Miller and Goldberg, 1955; Vistelius, 1960). All the following calculations on the copper contents were made using the logarithms (base 10) of the concentrations.

Variations in Copper Content Within Rock Units

The arithmetic copper means for single rock units do not show, on the whole, the large differences found between means for the different rock units (Table VII). Thus, with a few exceptions, for a given rock unit there appears to be remarkably

little variation in the mean copper content from area to area. With such small differences in means, it is difficult to recognize by simple inspection of the figures any significant variations that may be present. An objective approach to this problem was attempted by carrying out a one-way analysis of variance in the copper content (log_{10}) of each rock type, for the seven areas.

The analysis of variance data for each of the eight rock types is given in standard form in Table IX. The shown calculated values for 'F' indicate inhomogeneities, at the 95 per cent level, in the mean copper content of the following five rock units,

- (3) massive to weakly foliated granitic rocks¹
- (4) porphyritic granitic rocks
- (6) gneisses and migmatites¹
- (7) basic intrusive rocks
- (10) metasedimentary rocks¹.

¹ Also significant at the 99 per cent level.

Table IX

Analysis of Variance Data for Copper in the Rock Units of the Red Lake-Lansdowne House Area

Source	Sum of Squares	df	Mean Square	F
	Rock Unit 2			
Between map areas Within map areas	0.09267 63.89021	1 454	0.09267 0.14072	0.66n.s.
Total	63.98288	455		
	Rock Unit 3			
Between map areas Within map areas	8.03129 461.37891	6 2609	1.33854 0.17684	7.571
Total	469.41020	2615		
	Rock Unit 4			
Between map areas Within map areas	2.24768 108.56847	6 608	0.37461 0.17856	2.102
Total	110.81615	614		
	Rock Unit 5			
Between map areas Within map areas	2.29738 386.59543	6 1804	0.38289 0.21429	1.77n.s.
- Total	388.89281	1810		

Source	Sum of Squares	df	Mean Square	F
	Rock Unit 6			
Between map areas	7.45149 182.58933	4 695	1.86287 0.26271	7.091
Total	190.04082	699		
	Rock Unit 7			
Between map areas Within map areas	4.37185 133.35065	6 406	0.72864 0.32844	2.222
Total	137.72250	412		
	Rock Unit 10			
Between map areas	6.02978	6	1.00496	3.511
Total	124.37317	419	0.20034	
	Rock Unit 12			
Between map areas Within map areas	2.58958 285.92529	6 925	0.43159 0.30910	1.40n.s.
Total	288.51487	931	1	

Table IX (cont'd)

¹ Significant at 99% level

² Significant at 95% level

n.s. Not significant at 95% level.

To determine which of the means were contributing to the inhomogeneity, the q-statistic was used as described earlier. The results of this test are given in Table X and show which of the 49 sub-samples contributed to the inhomogeneities of the means either by low or high copper contents.

It will be seen from Figure 4 that significantly high mean copper contents occur in the massive or weakly foliated granites (3) in the adjacent areas A and C (Fig. 1). Significantly high copper means occur, also, in the porphyritic granitoids (4) of area E and in the gneisses and migmatites (6) of area F. Metasedimentary rocks (10), on the other hand, are significantly low in copper in both areas E and G. No significant inhomogeneities in the means were detected in the leucocratic granites, granodiorites, basic intrusive rocks, and metavolcanic rocks.

A comparison can be made between the results of the analysis of variance, described above, and variations shown by the arithmetic means (Table VII and Fig. 4).

Considering first the massive to slightly foliated granitic rocks (3) it will be seen that although the arithmetic means show only a very small variation, i.e., from 6.3 to 9.6 ppm Cu, the analysis of variance indicates the means of 9.3 ppm and 9.6 ppm from areas A and C, respectively, are significantly higher than the other five. The mean copper contents of the porphyritic rocks (4) show little variation, 7 to 11 ppm, except for a grossly high mean of 30 ppm in area E; confirmed, of course, by the analysis of variance. Strongly foliated granodiorites (3) have very uniform mean copper contents and form a homogeneous set according to the analysis of variance. Basic intrusive rocks (7) are also inhomogeneous at the 95 per cent level according to the analysis of variance, but although means vary from 69 ppm for area H down to 36 ppm in both areas A and C, the q-test fails to isolate a single mean contributing significantly to the inhomogeneity.

D. 0. 01 /	MAP AREAS See Figure 1						
UNIT	А	С	D	E	F	G	Н
2	n	n	n	n	n	n	n
3	h	h	n	n	'n	n	n
4	n	n	n	h	n	n	n
5	n	n	n	n	h	n	n
6	n	n	n	n	n	n	n
7	n	n	n	n	n	n	h?
10	n	n	n	1	n	1	n
12	n	n	n	n	n	n	n

Not significant......n Significantly highh Significantly low........

FIGURE 4. Rock units in each map-area that have anomalous mean copper contents according to the analysis of variance and q-test.

Table X

q-Test Data

				Rock Unit 3			
	x	x-0.58602	x-0.61906	x-0.62651	x-0.62680	x-0.66288	x-0.72619
A	0.73545	(0.09203) 0.14943	(0.08894) 0.11639	(0.08519) 0.10894	(0.08011) 0.10865	(0.07327) 0.07257	(0.06113) 0.00926
С	0.72619	(0.08894) 0.14017	(0.08519) 0.10713	(0.08011) 0.09968	(0.07327) 0.09939	(0.06113) 0.06331	
E	0.66288	(0.08519) 0.07686	(0.08011) 0.04382	(0.07327) 0.03637	(0.06113) 0.03608		
D	0.62680	(0.08011) 0.04078	(0.07327) 0.00774	(0.06113) 0.00029			
G	0,62651	(0.07327) 0.04049	(0.06113) 0.00745				
F	0.61906	(0.06113) 0.03304					
н	0.58602						

Rock Unit 4

	x	x-0.58215	x-0.65432	x-0.68517	x-0.70546	x-0.73237	x-0.77754
E	1.06445	(0.22251) 0.48230	(0.21504) 0.41013	(0.20597) 0.37928	(0.19370) 0.35899	(0.17716) 0.33208	(0.14781) 0.28691
С	0.77754	(0.21504) 0.19531	(0.20597) 0.12322	(0.19370) 0.09237	(0.17716) 0.07208	(0.14781) 0.04517	
A	0.73237	(0.20597) 0.15022	(0.19370) 0.07805	(0.17716) 0.04720	(0.14781) 0.02691		
F	0.70546	(0.19370) 0.12331	(0.17716) 0.05114	(0.14781) 0.02029			
D	0.68517	(0.17716) 0.10302	(0.14781) 0.03085				
н	0.65432	(0.14781) 0.07217					
G	0.58215						

Rock Unit 6

	x	x-0.84784	x-0.85783	x-0.90859	x-0.98129		
F	1.10405	(0.17208) 0.25621	(0.16183) 0.24622	(0.14801) 0.19546	(0.12349) 0.12276		
G	0.98129	(0.16183) 0.13345	(0.14801) 0.12346	(0.12349) 0.07270			
н	0.90859	(0.14801) 0.06075	(0.12349) 0.05076				
E	0.85783	(0.12349) 0.00999					
С	0.84784						

Rock Unit 7							
	x	x-1.31863	x-1.30337	x-1.33855	x-1.49362	x-1.50133	x-1.52988
H 1.:	55180	(0.31863) 0.24989	(0.30793) 0.24843	(0.29494) 0.21325	(0.27737) 0.05818	(0.25292) 0.05047	(0.21166) 0.02192
1.:	52988	(0.30793) 0.22797	(0.29494) 0.22651	(0.27737) 0.19133	(0.25292) 0.03626	(0.21166) 0.02855	
D 1.5	50133	(0.29494) 0.19942	(0.27737) 0.19796	(0.25292) 0,16278	(0.21166) 0.00771		
3 1.4	49362	(0.27737) 0.19171	(0.25292) 0.19025	(0.21166) 0.15507			
3 1.3	33855	(0.25292) 0.03664	(0.21166) 0.03518				
1.:	30337	(0.21166) 0.00146					
1.:	30191						
			1	Rock Unit 10			
	x	x-0.78862	x-1.03180	x-1.16882	x-1.25461	x-1.25838	x-1.2949

(0.27201)

0.18894

(0.25581) 0.12617

(0.23396) 0.08956

(0.19520) 0.08579 (0.25581) 0.10315

(0.23396) 0.04038

(0.19520) 0.00377

(0.23396) 0.09938

(0.19520) 0.03661

(0.19520)

0.06277

Table X (cont'd)

For each rock unit, the map-area means are listed in order of decreasing size and the differences between each pair are tested against the computed value of $q(sp/\sqrt{n_o})$. Observed differences that exceed the calculated value are blocked out above and to the left in the body of the table.

(0.28399) 0.32596

(0.27201) 0.26319

(0.25581) 0.22658

(0.23396) 0.22281

(0.19520) 0.13702

(0.29386) 0.56914

(0.28399) 0.50637

(0.27201) 0.46976

(0.25581) 0.46599

(0.23396) 0.38020

(0.19520) 0.24318

1.35766.....

1.29499.....

1.25838.....

1.25461.....

1.16882.....

0.78862.....

Δ

С

H

F

D

E

G

The means for the metasedimentary rocks (10) are dissimilar and show a range from 12 to 49 ppm Cu. The analysis of variance finds the means of 12 and 23 ppm from areas E and G, respectively, to be significantly low, but does not rate the mean of 49 ppm from area A as significantly high. The means from the metavolcanic rocks (12) vary over a fairly wide range, from 56 ppm in areas E and F to 71 ppm in area H. Nonetheless the analysis of variance shows this set of means to be homogeneous.

It is apparent from this comparison between variations in the arithmetic means and the results from the analysis of variance, that absolute variations between means may not necessarily be good criteria for recognizing significant changes in copper content. Consideration of the manner of grouping of the means, revealed by the analysis of variance, may be a more valid guide. This is illustrated by the example

Discussion of Results

of the basic intrusive rocks (7) which give a homogeneous set of means even though they vary widely from 36 to 69 ppm (Table VII). Massive to slightly foliated granites (3), on the other hand, are anomalously high in copper in two areas notwithstanding a very small range of means from 6.3 to 9.3 ppm. It is interesting to note that all highs occur in granitoid rocks.

Statistical testing by analysis of variance and the use of the q-test has provided an objective way of isolating sample units giving anomalously low or high means for copper, but the results so obtained must be used with caution as they may be strongly influenced by the vagaries of sampling. The term sampling is used here to cover not only specimen collection but, also, the grouping of samples by geological description, geographic location, or other methods.

Without discussing the subject exhaustively, it is apparent that the following interrelated factors are likely to affect the mean copper contents found in the sub-samples and may be responsible, in part, for the inhomogeneities observed:

- 1. the number of specimens included in each sub-sample,
- 2. the non-random technique of collecting the specimens,
- 3. the areal extent of each rock type,
- 5. inhomogeneities in each of the rock types,
- 6. size and shape of the geographic units considered, and
- 7. operator differences in classifying specimens.

Each area arbitrarily used in this study to subdivide the data represents a rectangular area of 6,000 square miles. On this scale, the copper content of most major rock types in the Red Lake–Lansdowne House area appears to be remarkably uniform. This degree of homogeneity might not have been found if a different shape or size of unit area had been used. Relatively small scale variations in copper content, for instance, are likely to be averaged out over very large areas and remain undetected unless the size of the unit area is reduced appropriately. Great disparities between the actual areas underlain by a particular rock type in each unit area may have a similar effect.

The system of collecting specimens in the field used in this study was, for reasons mentioned earlier, largely the most expedient and has resulted in an irregular grouping which is not truly random. Non-random location of sample stations may contribute considerable bias to the grouped data, although it is hoped that this undesirable effect has been considerably diminished by the large number of specimens collected.

Variations in mean copper content may arise, also, from grouping dissimilar rocks together as a single rock unit, but a certain degree of generalization is inevitable in geological studies and will depend on the scale of the project. As already mentioned, specimens collected for the Red Lake–Lansdowne House project were classified lithologically by visual examination of the hand specimens and field outcrops only. More precise petrological identification could not be attempted, nor was it considered desirable to use too many finely distinguished rock units at this reconnaissance stage of the project. Much the same problem arises from the lack of a simple criterion for distinguishing between similar looking rocks of different age.

CONCLUSIONS

The analysis of 7,963 specimens of bedrock collected from a 43,000-square-mile region of the Canadian Shield indicates the following relationship between the mean copper content and the principal rock types:

Leucocratic granites	7 ppm Cu
Slightly foliated and massive granites	8
Porphyritic granitic rocks	9
Foliated granodiorites	10
Gneiss and migmatite	18
Metasedimentary rocks	33
Basic intrusive rocks	56
Basic volcanic rocks	61

From this it will be seen that the mean copper content shows a general increase from acid to basic rocks, which is in accordance with the known geochemistry of copper.

It is interesting to note that the mean copper content of the major rocks of the region is considerably lower than the figures generally given for equivalent rocks on a world-wide basis. These differences cannot be readily accounted for by systematic analytical error, nor by losses due to weathering because the rock specimens appeared to be relatively fresh.

The distribution of copper in the rocks is approximately lognormal and this is thought to be due to its occurrence mainly as discrete grains of chalcopyrite.

Large scale or regional variations in copper content within rock units were investigated by arbitrarily dividing the region into seven rectangular areas, each of about 6,000 square miles. The mean copper content of each major rock unit for each of the unit areas was calculated, and these sets of means were tested statistically for homogeneity by the analysis of variance and the q-test. This investigation shows that:

- 1. No statistically significant variation at the 95 per cent level, in mean copper content, on the scale examined, occurs within the metavolcanic rocks, leucocratic granites, or granodiorites;
- 2. Inhomogeneity of the means occurs in the basic rocks. Although the qtest fails to distinguish which of the means is significantly different, it suggests that the mean for area H may be unusually high;
 - 3. Statistically significant high mean copper concentrations occur in massive to slightly foliated granites in the two adjacent areas A and C (Fig. 1);
- 4. A statistically significant high mean copper content occurs in the porphyritic rocks of area E;

- 5. A statistically significant high mean copper content occurs in the gneisses and migmatites of area F; and that
- 6. Statistically significant low mean copper concentrations occur in the metasedimentary rocks of the two adjacent areas E and G.

It cannot be assumed that the statistically significant variations are entirely due to geological causes, because the results are affected by both sampling and analysis. Analytical errors are fairly simple to measure and have been shown to be relatively small, generally contributing no more than about 5 per cent to the total variance. The effects of sampling, as already discussed briefly, because of their complexity are not so easily studied and need further investigation.

The scope of this paper has been restricted mainly to an examination of the copper data to determine whether large scale variations in copper concentrations occur in the principal rocks. Our present knowledge of the region is insufficient to allow a thorough assessment of the geological significance of these regional results and their possible correlation with ore-bearing zones.

Progress in the utilization of geochemical methods for exploration purposes urgently requires studies based on the sampling and analysis of rocks and minerals associated with known base-metal deposits. These investigations should not be restricted to the ore-forming metals alone, but should include a comprehensive suite of elements chosen as indicators of different chemical environments. Only in this way will it be possible to establish a meaningful frame of reference for interpreting geochemical data obtained in virgin territory. At present there are barely sufficient data to evaluate reliably even the order of magnitude of many element concentrations to be expected in rocks and minerals associated with orebodies, although the work of Parry and Nackowski (1963), for example, provides some valuable data for biotites in the Basin and Range province of the United States.

Table XI

	Whole rock	Biotite
Granite 1		
Sample A	45	400
Sample B	53	410
Granite 2		
Sample A	45	800
Sample B.	50	840

Comparison of Zinc in PPM Determined on Whole Rock and Biotite for Two Granite Masses in Area D

The fact that trace elements occur in rocks in different ways suggests that a single sampling technique will not necessarily be universally applicable. The results of this present study, for example, indicate, in agreement with earlier workers, that

the bulk of the copper occurs in rocks as small grains of chalcopyrite. In this case the only practical way of determining the copper is by analysis of the whole rock, and this will be so whenever the element sought occurs as rare minute mineral grains. Zinc, on the other hand, as shown by Putman and Burnham (1963) and by our own investigations, appears to be contained almost entirely in ferromagnesian minerals. In such cases, for example the determination of zinc in granites, the analysis of separated biotite would provide a more useful measure of zinc for comparative purposes. There is little doubt that anomalous zinc concentrations in granites and other rocks could be established much more efficiently and reliably by analyzing biotite rather than the whole rock. Some results for zinc obtained on two granite masses in map-area D given in Table XI illustrate this point. Analyses on the whole rocks show little difference between the two granites yet the zinc contents of the biotites differ by a factor of two. Furthermore, our preliminary investigations suggest the zinc content of biotites from a particular rock mass to be relatively uniform so that differences could be established with comparatively few specimens. Mineral analysis has the obvious advantage of eliminating variations in zinc contents as determined on whole rocks by changing mineral composition. For similar reasons, lead, which is generally thought to be present in igneous rocks mainly in feldspars, might better be determined on a few feldspar concentrates rather than by many whole rock analyses.

The statistical analysis of copper data collected in this study has indicated that measurable differences occur both between and within several principal rock units on a regional scale throughout part of the Canadian Shield. Although the economic significance of these results cannot be interpreted at this stage, they would seem to be sufficiently important to warrant further study.

REFERENCES

Azzaria, L. M.

1963: A study of the distribution of traces of copper, lead, and zinc in the minerals of a Precambrian granite; Can. Mineralogist, vol. 7, pp. 617-630.

Bartlett, M. S.

1947: The use of transformations; Biometrics, vol. 3, pp. 39-52.

Bostock, H. H.

1963: Geology, Lansdowne House, Ontario; Geol. Surv. Can., Prel. Ser. Map 4-1962.

Carruthers, C. A.

1962: Geology, North Caribou Lake, Ontario; Geol. Surv. Can., Prel. Ser. Map 18-1961.

Chayes, F.

1949: A simple point counter for thin section analysis; Am. Mineralogist, vol. 34, pp. 1-11.

Chayes, F., and Fairbairn, H. W.

1951: A test of the precision of thin-section analysis by point counter; Am. Mineralogist, vol. 36, pp. 704-712.

Craven, C. A. U.

1954: Statistical estimation of the accuracy of assaying; Trans. Inst. Min. Met., vol. 63, pp. 551-563.

Dixon, W. J., and Massey, F. J.

1957: Introduction to statistical analysis; 2nd ed., McGraw-Hill.

Donaldson, J. A.

1960: Geology, Trout Lake, Ontario; Geol. Surv. Can., Prel. Ser. Map 58-1959.

1961: Geology, North Spirit Lake, Ontario; Geol. Surv. Can., Prel. Ser. Map 50-1960.

Emslie, R. F.

1961: Geology, Lake St. Joseph, Ontario; Geol. Surv. Can., Prel. Ser. Map 51-1960.

1963: Geology, Wunnummin Lake, Ontario; Geol. Surv. Can., Prel. Ser. Map 1-1962.

Gilbert, M. A.

1959: Field and laboratory methods used in geochemical prospecting by the Geological Survey of Canada. No. 1, Laboratory methods for copper, lead and zinc; *Geol. Surv. Can.*, Paper 59–3.

Goldschmidt, V. M.

1954: Geochemistry; ed. by A. Muir, Clarendon Press.

Griffiths, J. C.

1960: Frequency distributions in accessory mineral analysis; J. Geology, vol. 68, pp. 353-365.

Holman, R. H. C.

- 1964a: Geochemistry (copper in bedrock), Lake St. Joseph, Ontario; Geol. Surv. Can., Prel. Ser. Map 50-1963.
- 1964b: Geochemistry (copper in bedrock), North Spirit Lake, Ontario; Geol. Surv. Can., Prel. Ser. Map 51-1963.

Holman, R. H. C. (Cont'd)

- 1964c: Geochemistry (copper in bedrock), North Caribou Lake, Ontario; Geol. Surv. Can., Prel. Ser. Map 52–1963.
- 1964d: Geochemistry (copper in bedrock), Wunnummin Lake, Ontario; Geol. Surv. Can., Prel. Ser. Map 53-1963.
- 1964e: Geochemistry (copper in bedrock), Miminiska, Ontario; Geol. Surv. Can., Prel. Ser. Map 54–1963.
- 1964f: Geochemistry (copper in bedrock), Lansdowne House, Ontario; Geol. Surv. Can., Prel. Ser. Map 55–1963.
- 1964g: Geochemistry (copper in bedrock), Fort Hope, Ontario; Geol. Surv. Can., Prel. Ser. Map 56-1963.

Jackson, G. D.

1962: Geology, Miminiska, Ontario; Geol. Surv. Can., Prel. Ser. Map 8-1961.

1963: Geology, Fort Hope, Ontario; Geol. Surv. Can., Prel. Ser. Map 6-1962.

Krumbein, W. C.

1955: Experimental design in the earth sciences; Trans. Am. Geophys. Union, vol. 36, pp. 1-11.

Leech, G. B., and others.

1963: Age determinations and geological studies (including isotopic ages-Report 4); Geol. Surv. Can., Paper 63-17.

Lowdon, J. A.

1961: Age determinations by the Geological Survey of Canada: Report 2, Isotopic ages; Geol. Surv. Can., Paper 61–17.

Lowdon, J. A., and others.

1963: Age determinations and geological studies (including isotopic ages-Report 3); Geol. Surv. Can., Paper 62-17.

Miller, R. L., and Goldberg, E. D.

1955: The normal distribution in geochemistry; Geochim. et Cosmochim. Acta, vol. 5, pp. 111-123.

Newhouse, W. H.

1936: Opaque oxides and sulphides in common igneous rocks; Bull. Geol. Soc. Amer., vol. 47, pp. 1–52.

Parry, W. T., and Nackowski, M. P.

1963: Copper, lead, and zinc in biotites from Basin and Range quartz monzonites; *Econ. Geol.*, vol. 58, pp. 1126–1144.

Prest, V. K.

1963: Surficial geology, Red Lake-Lansdowne House area, northwestern Ontario; Geol. Surv. Can., Paper 63-6.

Putman, G. W., and Burnham, C. W.

1963: Trace elements in igneous rocks, northwestern and central Arizona; Geochim. et Cosmochim. Acta, vol. 27, pp. 53-106.

Rodionov, D. A.

1961: On the lognormal distribution of the elements in igneous rocks; *Geochemistry* (English trans.), No. 4, pp. 366–369.

Sandell, F. B., and Goldich, S. S.

1943: The rarer metallic constituents in some American igneous rocks, II; J. Geology, vol. 51, pp. 167–189.

Shaw, D. M.

1961: Manipulation errors in geochemistry; Trans. Roy. Soc. Can., vol. 55, ser. 3, pp. 41-55. Snedecor, G. W.

1956: Statistical methods; 5th ed., Iowa State College Press.

Turekian, K. K., and Wedepohl, K. H.

1961: Distribution of the elements in some major units of the earth's crust; Bull. Geol. Soc. Amer., vol. 72, pp. 175–192.

Vinogradov, A. P.

- 1956: The regularity of distribution of chemical elements in the earth's crust; *Geochimya* (A.E. R. F. Lib. Transl. 795)
- 1962: Average content of chemical elements in the chief types of igneous rocks of the crust of the earth; *Geochimya*, No. 7.

Vistelius, A. B.

1960: The skew frequency distribution and the fundamental law of geochemical processes; J. Geology, vol. 68, pp. 1–22.

Vollrath, J. D.

1964: A geochemical study of four Precambrian granites in northwestern Ontario; Ottawa, Carleton University, unpubl. M. Sc. thesis.

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