AN ASSOCIATION OF TRACE ELEMENTS AND MINERALIZATION AT SUDBURY*

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ABSTRACT

The Ti, Mn, Ni, V, Co and Ga concentrations in 330 samples of norite taken adjacent to mineralized areas in the Sudbury basin, have been determined spectrographically. A pattern in the behaviour of the concentration as the distance from the mineralized areas increased is revealed, and is characteristic for each element.

The area known as the Sudbury basin is formed by an elliptical ring, the outcrop of a norite-micropegmatite instrusive said to be of Keweenawan age. It is approximately 37 miles long from northeast to southwest, and 17 miles wide from northwest to southeast. The width of this outcrop varies from a maximum in the south range of slightly less than 4 miles to a minimum in the north range of slightly less than 1 mile. The dip of the intrusive is inward for the most part; on the southern boundary however, it is vertical or steeply dipping outward in some places. An assumed average inward dip of 38° gives a calculated thickness of $1\frac{1}{4}$ miles for the intrusive.

The lower, or outside portion of the intrusive is commonly known as norite, but has also been referred to as quartz gabbro, diorite or quartz diorite. The composition varies somewhat, but the difficulty of naming the rock is due to the rarity of completely fresh specimens.

Walker (1897) suggested that the present relative position of the norite and the micropegmatite is due to "gravitative differentiation" of homogenous magma, intruded as a flat sill and folded after solidification to its present shape. Phemister (1925) thought that the two portions of the intrusive may have been emplaced at different times, the magma for each intrusion perhaps coming from the same underground reservoir after differentiation, and the second intrusion occurring before the complete solidification of the first had taken place. Knight (1917) was of the opinion that the intrusive is in the form of a ring-like mass injected around a down faulted block, now preserved within the igneous outcrop, and Yates (1948) says "that a large syncline, existing previously, controlled the position and shape of the norite. The apparent differentiation is more likely a form of 'deuteric alteration,' the initial crystallization taking place at the outer margins with the gases and more residual acid solutions collecting near the upper part, with just enough leak-

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age of the convex roof to allow continued movement of residual altering solutions upward. The intense granitization of the agglomerate and tuffaceous cover is good evidence of such escape."

Chemical analyses and specific gravity determinations summarized by Collins (1934) do not indicate any significant differentiation in the norite.

The nickeliferous orebodies of the Sudbury district are found at the lower edge of the norite, or in "offsets" in the older rocks below the norite. The mineralization in these bodies is in the form of pyrrhotite, chalcopyrite and pentlandite, with minor amounts of arsenides and rare sulphides. Gold and silver occur native and as tellurides, and metals of the platinum group are found. Selenium is recovered from the ore, though selenium minerals are rare. Galena, marcasite, sphalerite, violarite and some silver minerals occur in late stage veins (Yates, 1948).

The ore is always associated with quartz diorite, either replacing it or occurring in other rocks close to it, with the exception of the Levack orebody, where a granite breccia takes the place of quartz diorite. The quartz diorite is petrologically similar to the norite, but the exact relationships between the two rocks are not known. The sulphides are found massive and disseminated, when massive they may occur in stringers in shattered and brecciated country rock of any description.

The various theories of genesis of the ore deposits range from those of Coleman (1913) and others who favour separation of an immiscible sulphide melt and its segregation, to those of Knight (1917) and others, who postulate a hydrothermal replacement of the country rock by the ore minerals. Bateman (1917) suggests that the sulphides were injected in a molten condition into their present position after separation from the norite magma, and Yates (1948) classifies the deposits as epigenetic replacement bodies, in part high temperature hydrothermal, and in part deep seated contact metamorphic. There appears to be agreement on the fact that the mineralization is genetically related to the norite.

In order to determine the nature of any association of trace elements and mineralization, samples were taken in areas close to orebodies, and analysed spectrographically.

As norite is adjacent to all the orebodies sampled and was considered more homogenous with respect to its primary trace element content than sedimentary beds or lava flows, all samples were taken from the norite.

Sampling was commenced at some point beyond the limits of the economic orebody, and called for convenience the contact of mineralization. This contact is an arbitrary line and was fixed visually. In some cases, its position was influenced by the presence of a fault plane, the edge of a shear zone, the contact of two different rock types, or a combination of these conditions, but the main factor governing its position was the

sulphide content of the rock on either side of the line, and the rate of decrease of this amount in a direction away from the orebody. The presence of too much sulphide in the sample affects its behaviour in the arc during spectrographic analysis, so that the results obtained from these samples cannot be directly compared with the results from those samples containing little or no sulphide. The contact of mineralization was fixed so that the results from all the samples taken could be compared directly, and though visible sulphide was present in some samples, this did not amount to more than 2 per cent and did not affect the behaviour of the sample in the arc. Variations in the position of the contact of mineralization with respect to such factors as distance from the orebodies, intensity and type of mineralization, and perhaps relation to different rock types and faults are unavoidable.

Samples were taken on traverse lines run roughly perpendicular to and away from the orebodies. 20 traverses were run and a total of 330 samples were taken. It was reasoned that any variations in the trace element content of the rock due to the mineralization, would be more more pronounced closer to it, and therefore frequency of sampling was greater at the start of each traverse. Sampling was commenced 1 inch from the contact of mineralization, and the interval between samples doubled for successive pairs. Where samples were taken close together, they necessarily had to be small, but an attempt was made to take them all of approximately the same size, that is, about 2 inches diameter. As far as possible they were taken where there were no obvious local differences in the rock, and any geological features such as shears, dikes, veinlets or local accumulations of sulphides were recorded. Sampling was at such a depth to ensure that the rock had been unaffected chemically by weathering.

The samples were washed to remove all adhering material, heated for 5 minutes to red heat and quenched in distilled water, as suggested by Ahrens (1950) to facilitate grinding. About 10 grams was then ground in an agate mortar to about minus 150 mesh. 0.1 gram of sample was then weighed accurately into a sample vial, and to this was added a similar amount of spectrographically pure carbon powder as buffer, and 0.01 gram of spectrographically pure tin oxide powder as internal standard.

The addition of an internal standard, and the closely related behaviour of standard element and unknown element during handling and and arcing, compensates for many factors likely to introduce errors. Differences in photographic material and processing will be minimized also. Unless several internal standards are used, one for each element or group of elements to be determined, it is impossible to satisfy all requirements

for the best one. It is essential that the internal standard element should be absent or present in the material to be analysed in concentrations sufficiently small so as not to interfere with the spectrographic line intensity due to the added internal standard, or present in sufficiently large concentrations that any variation in concentration will again not affect the line intensity. Tin oxide was chosen as Clauson (1947) has shown that tin is absent from the norite at Sudbury, and the oxide was a convenient medium to introduce the tin.

The relative amounts of sample, buffer and internal standard were chosen after experimental arcing had indicated that they would give suitable line intensities.

This material was then shaken for 5 minutes with two stainless steel balls of $\frac{1}{4}$ inch diameter, a method employed by Smith & Hoagbin (1946) to mix samples. After mixing, the material was introduced into a $\frac{1}{4}$ inch external diameter, center post, undercut carbon electrode, with a capacity of about 40 milligrams of sample. The powder was then moistened with a saturated solution of sugar in alcohol to "cake" it, and dried for 10 minutes. The sample was then arced under the following conditions:

> Sample electrode—anode
> D.C. arc
> Voltage—250 volts
> Current—13 amps.
> Time—90 seconds
> Arc gap—5 mm.

The spectrograph used was, an A.R.L. 2 meter grating type, with 24,400 lines per inch on the grating and a resolution of 5.2 A per mm. in the first order. Light from the arc was filtered to 12% to give a suitable exposure, and passed through a slit set at 40 microns, to give a suitable line width for densitometric determinations, all of which were made on an A.R.L. densitometer.

Eastman Kodak Spectrum Analysis Film No. 2 was used for recording the spectrum. It was developed in D-19 developer at 70° F. for $2\frac{1}{2}$ minutes. washed for 30 seconds and fixed for 2 minutes in acid fixer, washed and dried.

During handling of the sample care was taken to ensure that mechanical losses and decontamination were reduced to a minimum, and that all samples were treated identically. The similarity in the intensity of the internal standard line in practically all the samples is an indication of the similarity of arcing conditions and photographic processing which existed. When internal standard line intensity varied only slightly, and

when the intensity ratios of the trace elements, particularly gallium, varied in the opposite sense, or when internal standard line intensities varied appreciably, a repeat analysis was made.

A reproducibility test was run on one of the samples, and gave standard deviations for 16 determinations as follows:

Ga	$\pm$ 4.4%
Mn	$\pm$13.4%
V	$\pm$16.1%
Ti	$\pm$16.9%
Co	$\pm$25.7%

These values are designated very good for gallium, fair for manganese, vanadium and titanium, and poor for cobalt, by Ahrens (1950).

Intensity relationships are used in the method of spectrographic analysis involving internal standardization. In this method, a constant proportion of an element, the internal standard is added to each sample, and the intensity ratio of a line of the element to be determined, and the internal standard line chosen, is observed. Since the internal standard is present in non-variant concentration in the samples, and line intensities are proportional to concentration, other factors being equal, this ratio is proportional to the concentration of the element to be determined. To enable this relationship to be transformed into direct rather than relative concentrations, standards are used containing different but known amounts of the trace elements to be analysed for, in a matrix.

Claffy (1947) states that "it has been found . . . that the state of chemical combination of an element as well as the nature of the matrix have great influence on the intensity of spectral lines." In order to obtain reliable trace element concentrations, an attempt was made to simulate the matrix of the rock samples as closely as possible, both physically and chemically, in standards.

To obtain a suitable matrix composition, Collins' (1934) average analysis of norite from the Sudbury area was recalculated with the exclusion of TiO_2, P_2O_5, H_2O, MnO, CO_2, and S. Spectrographically pure chemicals were mixed in proportion to the recalculated analysis, and this material was used as a matrix. Calculated amounts of spectrographically pure trace element compounds were added to a portion of the matrix, such that a 1% concentration of each element resulted in the mixture. Controlled dilution of this 1% mixture by matrix material gave mixtures which were used as a set of standards.

Since all the spectrographically pure chemicals used were in the form of oxides or carbonates, and hence not physically similar to the material in the rock samples, which is mostly in the form of silicates, a fusion of the standards was made and a homogenous glass obtained. Investigation

of this material showed that both major and minor elements had been lost during the fusion, and this material was discarded.

Ahrens (1950) and Mitchell (1948) recommend sintering of the standards, and this was done at 1000° C. for 24 hours. It was found that the standards then burnt smoothly in the arc, and the spectrogram obtained resembled closely that of the average rock sample. Both powdered carbon buffer and tin oxide internal standard were added to the standards prior to arcing in the same proportions as to the samples.

Trace elements are considered to be those elements not common in the upper lithosphere, that is, all elements other than oxygen, silicon, aluminium, iron, calcium, sodium, potassium and magnesium (Rankama & Sahama, 1949). Clarke & Washington (1924) state that the "minor constituents are generally found in very small amounts, rarely more than 2 per cent for any one, or as much as 5 per cent for all of them in any one rock." They have been divided into two groups with respect to their presence in igneous rocks; those elements which form independent minerals, generally the accessory minerals, and those elements which rarely form specific minerals, but which occur in solution in other minerals of the rock (Rankama & Sahama, 1949). Some elements belong to both groups.

Goldschmidt (1937) advanced a hypothesis governing the distribution of those trace elements of the second group occurring in solution in other minerals of the rock. The partition of these elements between the silicate, sulphide and oxide phases depends on the affinity of each element for the particular phase, the relative abundance of suitable phases present, and the conditions prevailing at the time of partition. The affinity of an element for a particular phase is related to its atomic structure, its ionic structure, and its ionization potential (Goldschmidt, 1937). The presence of an element in a mineral depends, of course, on the presence of that element in the solution or melt from which the mineral crystallized, and the concentration in the mineral depends on the concentration in that solution or melt, its affinity for the particular phase, the conditions prevailing at the time of crystallization, and the atomic or ionic size of the element.

Among other factors, the state of oxidation is important in determining the amount of an element present in a mineral. Under reducing conditions, chromium will be obliged to enter the sulphide daubréelite rather than form an oxide (Goldschmidt, 1937) and possibly under oxidizing conditions, the amount of iron available for entry into pyroxene may be limited.

Atoms or ions fit into positions in a crystal structure unique for any particular mineral, that is formed during crystallization of that mineral.

The unit of this structure is comparatively rigid, and only small changes in dimensions are possible, so that atoms or ions included will be chosen, among other reasons, according to their size. This is represented by the radius of the atoms or ions, which, since atoms or ions are not solid particles, is a variable quantity depending on the coordination, nature of the bonding to adjacent atoms or ions, and the ionic charge.

The rigidity of the crystal structure is such that when diadochy takes place, as the substitution of different elements in identical positions in a crystal structure without disruption of that structure is known, the radii of the two atoms or ions involved must not vary by more than 10 to 15 per cent of the larger of the two (Goldschmidt, 1945). Rankama & Sahama (1949) raise this tolerance to about 15 per cent, but indicate that there are exceptions to this rule. Variations of temperature and pressure affect the tolerances, which are increased for increasing temperature and vice versa. The effect due to pressure is probably in the opposite sense.

Coordination and crystal structure influence diadochy in some cases. An element may substitute for another element frequently and completely in one type of structure, while doing so rarely and in limited amount in another. An example of this is given by the substitution of large amounts of aluminium for magnesium in the spinels, but the restricted substitution of aluminium and sodium for magnesium which takes place in the pyroxenes. Another example is the extensive substitution of barium for potassium in feldspars, and the limited or lack of substitution of barium for potassium in mica. There are many more examples.

When substitution takes place, the electrostatic charges in the structure must be satisfied.

The relative bond strength of two atoms or ions in identical positions in a structure is the final criterion which decides whether substitution will or will not take place at any particular time, and thus is important in fixing the sequence of incorporation of a number of elements into a structure. The atom or ion providing stronger bonds will be substituted for that providing weaker bonds preferentially (Goldschmidt, 1937).

Within allowable tolerances under prevailing conditions, for atoms or ions of similar valency charge, the larger will weaken the bond, and for atoms or ions of similar size, the larger valency charge will strengthen the bond, except where strong directed bonds may distort a structure. When a trace element replaces a major element of similar valency "camouflage" takes place, when the major element has the lower valency "capturing" occurs, and when the major element has the higher valency the replacement is known as "admission" (Goldschmidt, 1937). During

crystallization from a magma, captured trace elements will be concentrated in early crystallized minerals, or early phases of a mineral, and where these separate, in the early more basic rock fraction. Admitted trace elements will be concentrated in later crystallizing minerals and later phases of a mineral, and consequently in the more acid rock fractions. With regard to atomic or ionic size, within limits of diadochy, the smaller atom or ion will be concentrated early, and the larger one later.

This can be illustrated by the following figures, which show that scandium* (Sc^{3+} 0.83 kX), captured by magnesium (Mg^{2+} 0.78 kX) is concentrated in basic rocks, while lithium (Li^+ 0.78 kX) is admitted by magnesium and concentrated in acid rocks.

	Sc ppm.	*Li ppm.*
Pyroxenite	46[1]	
Dunite, eclogite		2.3[2]
Granite	1.3[1]	179.4[2]

[1] Goldschmidt (1934, 1937b).
[2] Strock (1936).

This concentration of the ion with the highest valency in basic rocks is also indicated by the enrichment of calcium (Ca^{2+} 1.06 kX) over sodium (Na^+ 0.98 kX) in basic igneous rocks.

	% Ca	*% Na*
Gabbro	7.85	1.85
Granite	1.42	2.58

Data taken from Daly (1933).

With regard to the similarity of charge, the smaller ion (Ni^{2+} 0.78 kX) is concentrated in basic rocks rather than the larger one (Zn^{2+} 0.83 kX).

	Ni ppm.	*Zn ppm.*
Peridotite, dunite	3160[1]	
Gabbro		90[2]
Granodiorite		200[2]
Granite	2.4[1]	

[1] Goldschmidt (1937).
[2] Lundegårdh (1948).

The changes in the iron (Fe^{2+} 0.83 kX) to magnesium ratio in igneous rocks, based on figures from Daly (1933) also show this trend.

	Fe:Mg
Dunite	0.2
Granite	4.9

* All atomic and ionic radii are taken from Rankama & Sahama (1949).

Predictions can be made on this basis as to the trends of concentrations of trace elements in differentiated igneous rock complexes, and in the minerals in those rocks. Nockolds & Mitchell (1948) studied four complexes, and Wager & Mitchell (1951) studied the highly differentiated Skaergaard intrusion. The results obtained showed the form of these trends, and confirmed the hypothesis advanced by Goldschmidt (1937) and mentioned above.

Apart from the trace elements studied quantitatively here, titanium, manganese, nickel, vanadium, cobalt and gallium, relative concentrations of chromium, silver, copper and zinc were determined. Of these, titanium and possibly nickel, copper and lead in part occur as specific minerals in the rocks, the first as ilmenite and the remainder as sulphides. The remaining elements and possibly some nickel, copper, silver, zinc and lead, do not form common rock forming minerals and are considered therefore to occur by substitution in the silicates, oxides or sulphides of the rock. The occurrence and behaviour of some of these trace elements in igneous rocks in general, and in the Sudbury norite in particular, is discussed below.

Titanium Ti^{4+} (0.64 kX)

Titanium is not classed with the trace elements by Nockolds & Mitchell (1948) or by Wager & Mitchell (1951), perhaps because it is usually determined by chemical methods in rock analysis, but by definition, it must be considered as a trace element. It is the only element here discussed which occurs mainly in the first group of the division made by Rankama & Sahama (1949), those elements which form independent minerals, generally the accessory minerals, but titanium is found in pyroxene, hornblende and biotite, besides ilmenite, titanomagnetite, sphene and rutile in igneous rocks.

The average titanium concentration of the Sudbury norite is 2500 ppm. This is considerably lower than values for other gabbros and norites, which range from 4200 ppm. (v. Tongeren, 1938) to 6800 ppm. (Daly, 1933). The curve drawn of the average trace element concentra-

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Description of Diagrams

The accompanying curves show the average Trace Element Concentration, in parts per million, plotted against the distance from the Contact of Mineralization, in feet, on a logarithmic scale. Data for individual samples is plotted as short horizontal lines, with the exception of high and low values, which are indicated in the boxes above the curves and which are not used in computing the averages. The length of the horizontal lines is proportional to the number of samples with the same concentration values in any one sample position, for any one element.
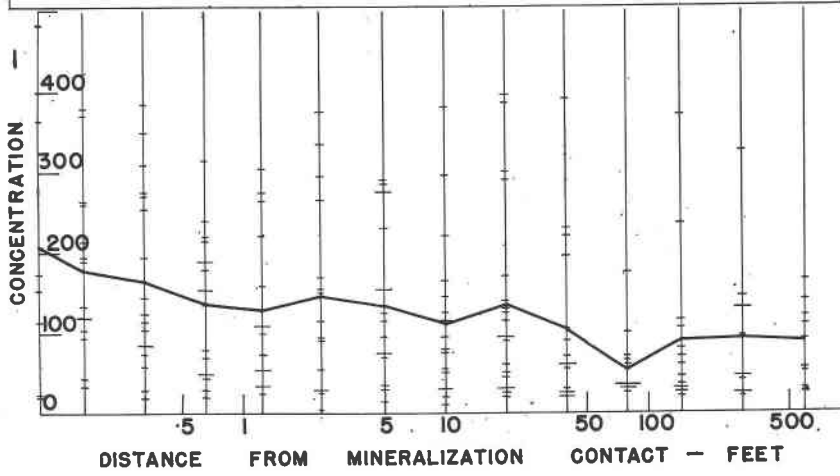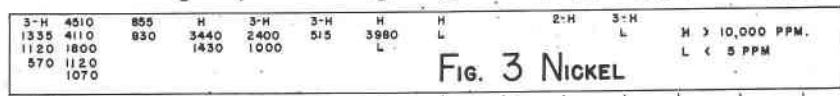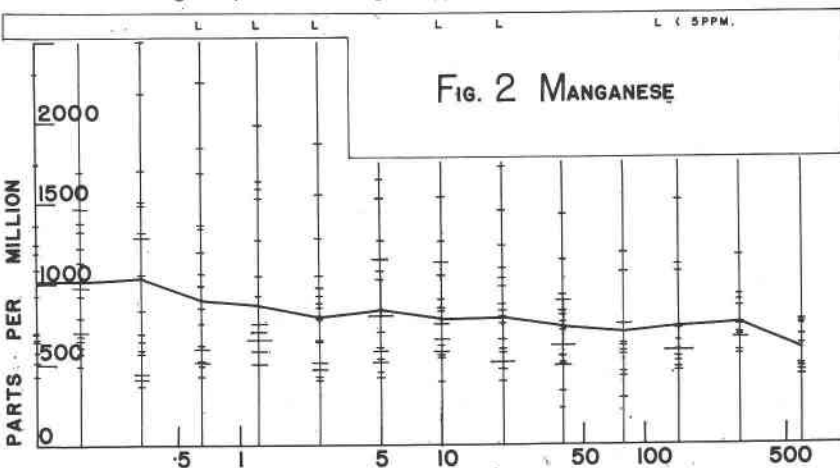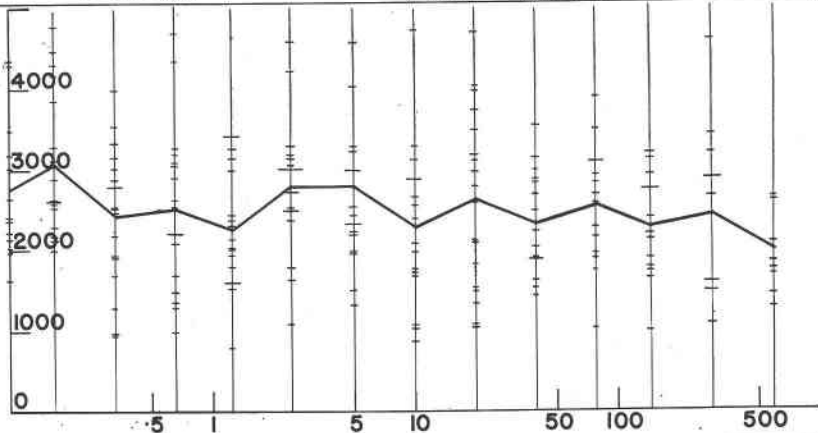
FIG. 1 TITANIUM

FIG. 2 MANGANESE

FIG. 3 NICKEL

PARTS PER MILLION

CONCENTRATION

DISTANCE FROM MINERALIZATION CONTACT — FEET

H > 10,000 PPM.

L < 5 PPM.

H > 10,000 PPM.
L < 5 PPM

3-H	4510	855	H	3-H	3-H	H	H	2-H	3-H
1335	4110	930	3440	2400	515	3980	L	L
1120	1800		1430	1000		L	
570	1120						
	1070						
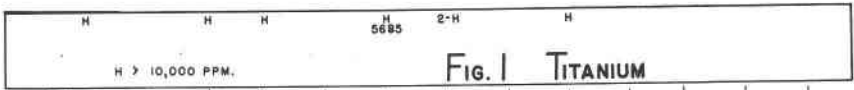
FIG. 4 VANADIUM

840   1385   795
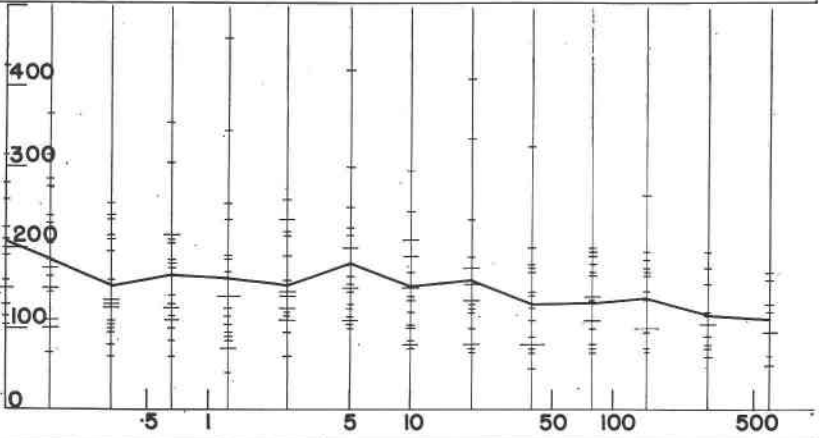
FIG. 5 COBALT

250   L   135   2-L   175
235   L
145
L < 5 PPM

PARTS   PER   MILLION
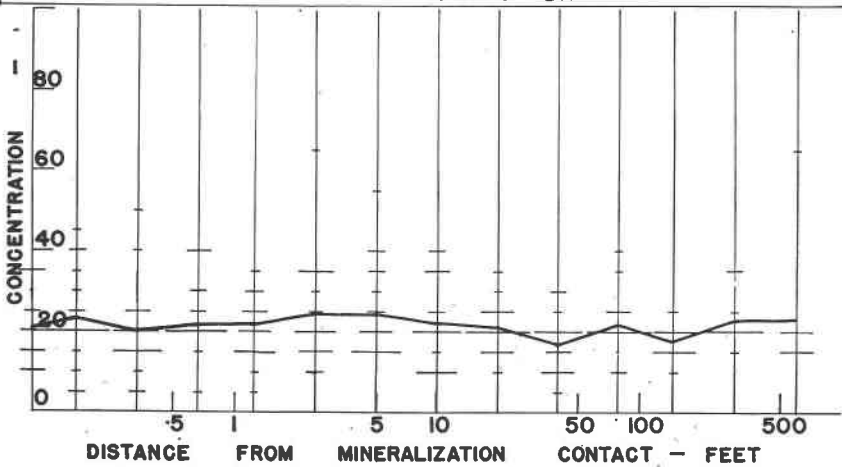
FIG. 6 GALLIUM

2-L
L < 5 PPM
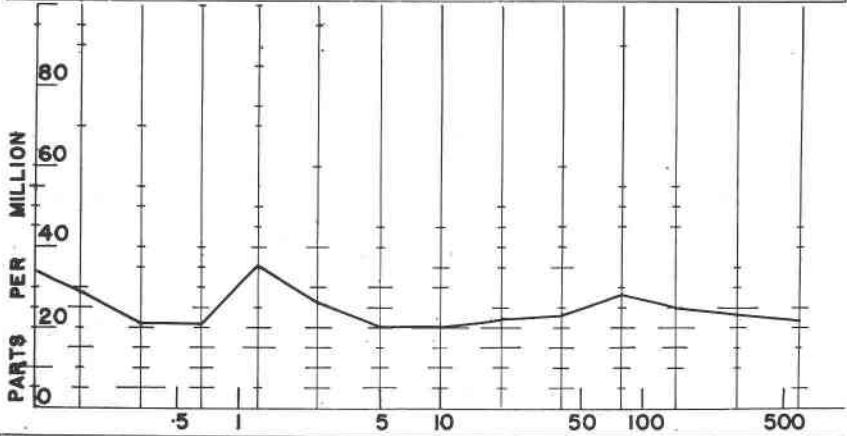
CONCENTRATION

DISTANCE   FROM   MINERALIZATION   CONTACT — FEET

tion for each sample position against distance from the contact of mineralization (Figure 1), shows that the titanium concentration decreases as the distance from the contact of mineralization increases. When a similar curve is drawn for samples from each individual traverse, though the titanium concentration decreases overall as the distance from the contact of mineralization increases, there is usually a pronounced peak 10 to 20 feet from the start of the curve, which often coincides with a peak drawn in the curve drawn for vanadium. This peak is present in sample position 9 in the average curve, and would be more obvious if 2 high values were suppressed in each of sample positions 6 and 7, these 4 values being among the 7 highest recorded for titanium.

Manganese Mn^{2+} (0.91 kX)

Specific manganese minerals do occur in igneous rocks, but they are of minor importance. Manganese commonly occurs in silicates and oxides; sulphides are relatively free of manganese.

Manganese occurs mainly as the diavalent ion (Rankama & Sahama, 1949), and can substitute for iron (Fe^{2+} 0.83 kX), calcium (Ca^{2+} 1.06 kX), magnesium (Mg^{2+} 0.78 kX) and sodium (Na^+ 0.98 kX), the first being the most common substitution. Data from Daly (1933) and Otto (1936) indicate that manganese is concentrated in early differentiates, but that the manganese to iron ratio remains fairly constant throughout differentiation. However, Nockolds & Mitchell (1948) and Wager & Mitchell (1951) show that while the manganese to iron ratio remains fairly constant, manganese tends to concentrate in late differentiates. Work by Landergren (1948) shows that the manganese to iron ratio increases in acid rocks.

Manganese can occur in all of the primary minerals present in the Sudbury norite. Data concerning its distribution between these minerals is poor, but it occurs in plagioclase and biotite from a diorite according to Nockolds & Mitchell (1948) as follows:

	ppm.
Plagioclase	80
Biotite	100

and in

Plagioclase	50
Pyroxene	2700

in an olivine free gabbro (Wager & Mitchell, 1951)

The manganese content of the Sudbury norite, 825 ppm., is also below that of other norites and gabbros which range from 1000 ppm. (Otto, 1936) to 3100 ppm. (v. Tongeren, 1938). In Figure 2 is illustrated the

curve drawn for the manganese concentration versus the distance from the mineralization contact. The concentration shows a steady decrease in value as the distance increases, and this is similar to the majority trend as observed for the individual traverses.

It has been shown that manganese concentrates in late differentiates, and if differentiation had taken place in the norite, it would be expected that the manganese concentration would rise as the distance from the bottom of the norite, that is, the contact of mineralization in every case, increased.

Nickel Ni^{2+} (0.78 kX)

Nickel occurs primarily in four ways in igneous rocks, in silicates, sulphides, oxides and rarely in iron-nickel alloys. The most important method of occurrence is in silicates, where nickel is camouflaged by magnesium (Mg^{2+} 0.78 kX) and is concentrated in early formed olivine, orthopyroxene and clinopyroxene, and to a less extent in amphibole (Vogt, 1923). In sulphides, nickel is present in pentlandite and pyrrhotite in larger amounts than in associated pyrite (Gavelin & Gabrielson, 1947); in pyrite and pyrrhotite, nickel presumably replaces iron, the atomic radii being identical (1.24 kX). In oxides, nickel is found in magnetite and ilmenite, perhaps as the nickel spinel trevorite, in solid solution.

Nickel is distributed in the lithosphere in the following manner:

	ppm.
Silicate meteorites	3300[1]
Peridotite	3160[2]
Gabbro	158[2]
Diorite	40[2]
Granite	2.4[2]

[1] Goldschmidt (1937a).

[2] Goldschmidt (1937).

It is seen that nickel is concentrated in early basic rocks, and it occurs in these rocks substituting for magnesium. However, the nickel to magnesium ratio is also enhanced in these early crystallates, despite the identical ionic size and valency (Wager & Mitchell, 1951). Goldschmidt (1944) states that nickel has a tendency to homopolar bonding in compounds, which increases the bond strength and consequently is responsible for the preferential concentration with respect to magnesium in early crystallates.

Nickel is present in hypersthene, augite and biotite from a diorite, as shown by Nockolds & Mitchell (1948) in the following amounts:

	ppm.
Plagioclase	—
Hypersthene	300
Augite	200
Biotite	150

and in pyroxene, ilmenite and magnetite from an olivine free gabbro (Wager & Mitchell, 1951),

	ppm.
Plagioclase	—
Pyroxene	50
Magnetite	50
Ilmenite	100

Nickel may also occur in hornblende; these minerals are all present in the norite sampled.

The average of the three most frequently occurring values for the nickel concentration of the Sudbury norite is 25 ppm., and this figure gives a more representative measure of the nickel content of the rock away from the mineralized areas. The average of all the analyses is 240 ppm. Both of these values are within the range of the nickel content of other norites which is from 0.2 ppm. (Lundegårdh, 1947) to 350 ppm. (Vogt, 1923).

Figure 3 shows that the nickel content of the norite decreases as the distance from the contact of mineralization increases, and finally levels off at a value of about 80 ppm. This trend is similar to the trends displayed by the individual traverses which often show in addition, one or more high values not present in the average curve.

These high values, which are most prominent and numerous close to the mineralization contact, are probably due to the incorporation of nickeliferous pyrrhotite or pentlandite particles in the sample, as they are often associated with visible sulphide. Chemical analyses of the norite and the sulphide separated therefrom showed that while the nickel in both the rock, determined spectrographically, and the nickel in the sulphide, determined chemically, varied in the same sense, there was no relation between the nickel and sulphur contents of the rock, the latter also determined chemically. Visible pyrite and chalcopyrite in some samples indicates that the sulphur is not all associated with pyrrhotite or pentlandite.

A spectrographic analysis for nickel in the acid resistant portion of the heavy mineral fraction of six samples chosen from the beginning, middle and end of two traverses, showed that there was little variation in the nickel content of this portion of the norite from these traverses. This portion of the heavy mineral fraction of the rock was found to con-

sist mainly of pyroxene and amphibole, and the results obtained showed that there had been no segregation of nickel rich, or early crystallizing pyroxene or amphibole in the area covered by these traverses.

Vanadium V^{4+} (0.61 kX)

Vanadium occurs extremely rarely in igneous rocks in a distinct mineral, ardennite, a member of the epidote group, and it must therefore be sought in the other minerals of the rocks. It probably exists as the quadrivalent ion, and in that state would be captured by aluminium (Al^{3+} 0.57 kX) or iron (Fe^{3+} 0.67 kX), and camouflaged by titanium (Ti^{4+} 0.64 kX). According to Wager & Mitchell (1951) vanadium exists as the trivalent ion (0.65 kX) and is camouflaged by ferric iron. Leutwein (1941) suggests that the ferric ion would be reduced to the ferrous ion, as trivalent vanadium is a strong reducing agent, and replacement could not then take place.

Nockolds & Mitchell (1948) show that vanadium is concentrated in the first crystallized biotite, in muscovite, ilmenite, and to a less extent in pyroxene and amphibole. Wager & Mitchell (1951) find that it is similar to chromium in its behaviour and shows a preference for magnetite, ilmenite and pyroxene in that order. Other authors are in accord with this, and the association of vanadium with magnetite, ilmenite and rutile to a less extent, is common.

When vanadium substitutes for titanium or ferric iron, it should be concentrated preferentially in the earliest crystallates. Predictions with regard to its behaviour when substituting for aluminium cannot be made, as relative bond strengths due to ionic size and valency are in opposition.

Vanadium can occur in all the primary minerals of a norite. Nockolds & Mitchell (1948) show that vanadium distribution is as follows in a diorite:

	ppm.
Plagioclase	20
Hypersthene	100
Augite	200
Biotite	400

and Wager & Mitchell (1951) give the following data for an olivine free gabbro:

	ppm.
Plagioclase	10
Pyroxene	100
Magnetite	800
Ilmenite	300

The vanadium concentration in the Sudbury norite is 165 ppm. This

is between the lowest value of 50 ppm. (Sahama, 1945) and the highest of 350 ppm. (Lundegårdh, 1947) for other gabbros and norites.

The curve represented in Figure 4 shows that the vanadium concentration of the norite decreases as the distance from the mineralization contact increases, but an obvious feature is the peak present in sample position 9. This peak is obvious in the curves drawn for individual traverses, and frequently coincides with the titanium peak mentioned above. An inspection of the titanium to vanadium ratios for the individual traverses, shows that it is remarkably constant throughout any one traverse. This obvious association of titanium and vanadium is emphasized further by the similarity of the titanium to vanadium ratio of 2 rock samples and of the ilmenite separated from them, all determinations being spectrographic. This would indicate that probably the vanadium occurs mainly in ilmenite or perhaps associated with titanium in other minerals.

As mentioned above, when vanadium substitutes diadochally for titanium, it should be concentrated in the earliest crystallites of any mineral containing both elements. The lack of systematic variation in the titanium to vanadium ratio with respect to the position of the samples in the traverses, shows that these relatively vanadium rich early crystallites have not been separated and concentrated preferentially in any portion of the norite covered by the traverses. This evidence of lack of differentiation is confirmed by the similarity of the concentration of nickel in the pyroxene and amphibole along a traverse, and by a study of the distribution of manganese in the norite, as discussed above.

Cobalt Co^{2+} (0.82 kX)

The occurrence of cobalt in igneous rocks is similar to that of nickel, with the exception that no iron-cobalt alloys are known. It is camouflaged by iron (Fe^{2+} 0.83 kX) and is concentrated in early crystallizing fractions (Nockolds & Mitchell, 1948, Wager & Mitchell, 1951). Sandell & Goldich (1943) found that the trend between basic and acid igneous rocks shown by the cobalt to magnesium ratio is more apparent than that shown by the cobalt to iron ratio, and is linear over a wide range. This trend is, however, opposite to that expected by Goldschmidt's theory, which predicts that cobalt, being the larger ion, would be concentrated in the later differentiates with respect to magnesium. Nockolds & Mitchell (1948) show that the cobalt to magnesium ratio is highly variable, and no definite trend is apparent.

On account of its smaller size, the nickel ion would be expected to concentrate relative to cobalt in early differentiates, for despite the fact that these two elements replace different major elements, they occur in the same structural positions. This has been found to be the case by

Goldschmidt (1937), Lundegårdh (1947) and Wager & Mitchell (1951).

Cobalt is preferentially concentrated in pyrite rather than pyrrhotite in any one association of these two sulphides (Gavelin & Gabrielson, 1947), but comparisons between these sulphides from different occurrences cannot be made. In oxides, cobalt occurs in both magnetite and ilmenite (Wager & Mitchell, 1951) and in both oxides and sulphides, presumably replaces iron.

Cobalt is found in all the primary minerals which occur in the norite studied. It is present in the minerals of a diorite according to the following data (Nockolds & Mitchell, 1948):

	ppm.
Plagioclase	15
Hypersthene	100
Augite	70
Biotite	50

and in minerals from an olivine free gabbro as follows:

	ppm.
Plagioclase	—
Pyroxene	60
Magnetite	80
Ilmenite	100

(Wager & Mitchell, 1951). Cobalt also occurs in hornblende.

Cobalt is found in norites and gabbros in concentrations between 25 ppm. (Lundegårdh, 1947, Sahama, 1945) and 80 ppm. (v. Tongeren, 1938). The average concentration in the Sudbury norite is 30 ppm.

Figure 5 shows that the average cobalt concentration for the various sample positions plotted against the distance from the contact of mineralization, is quite uniform, but there are some erratic high values. These high values are a feature of the curves drawn for the cobalt concentration versus distance from the mineralization contact for the individual traverses, and often coincides with extremely high nickel values, though occasionally the latter occur without the former. These high values are thought to be due to the presence of cobalt bearing sulphide in the sample, perhaps nickeliferous pyrrhotite or pentlandite, though some of this material must be cobalt free, or perhaps pyrite associated with the pyrrhotite or pentlandite. Most of the pyrite in the rock, however, is cobalt free.

Gallium Ga^{3+} (0.62 kX)

Gallium does not form independent minerals in rocks, and the similarity in size between the gallium ion and the aluminium ion (0.57 kX) indi-

cates that camouflage of gallium by aluminium will take place. This happens in both 4-fold and 6-fold coordination positions (Rankama & Sahama, 1949) as is shown by the occurrence of a synthetic gallium spinel (Barth & Posnjak, 1931) and a synthetic compound formed by replacing aluminium by gallium in the feldspar structure (Goldsmith, 1950). However the larger size of the gallium ion indicates that it should be relatively concentrated in later differentiates of an igneous magma. This has been shown to be the case by Wager & Mitchell (1951), Goldschmidt & Peters (1931) and others, but this trend is only indicated in hornblende and biotite in the Caledonian plutonic rocks studied by Nockolds & Mitchell (1948), and is not apparent in the rocks as a whole, which show a comparatively non-variant gallium to aluminium ratio between acid and basic rocks. Wickman (1943) explains that the constancy of this ratio is due to the fact that gallium may be camouflaged by chromium (Cr^{3+} 0.64 kX) and iron (Fe^{3+} 0.67 kX) and admitted by titanium (Ti^{4+} 0.64 kX), and will thus occur in chromite, magnetite and ilmenite, which he assumes are early crystallizing minerals in a differentiation sequence. Thus gallium may be concentrated without reference to aluminium in basic rocks, by association with these oxides, and it is concentrated in acid rocks relative to aluminium by direct substitution. A suitable combination of these circumstances results in a roughly invariant gallium to aluminium ratio throughout a differentiation sequence. That gallium occurs in magnetite and ilmenite has been shown by Wager & Mitchell (1951), but its presence in chromite has yet to be determined.

Among the primary minerals occurring in the norite at Sudbury, gallium is to be found in feldspars, pyroxene, amphibole, biotite, magnetite and ilmenite. Nockolds & Mitchell (1948) show that the distribution in a diorite is as follows:

	ppm.
Plagioclase	30
Hypersthene	1
Augite	8
Biotite	12

and in an olivine free gabbro, Wager & Mitchell (1951) show the following distribution:

	ppm.
Plagioclase	50
Pyroxene	—
Magnetite	30
Ilmenite	3

The average gallium concentration of the Sudbury norite is 20 ppm.,

which agrees with the other figures of 20 ppm. (Sahama, 1945) and 35 ppm. (v. Tongeren, 1938) for gabbros and norites.

The curve of the average gallium concentration values versus the distance from the contact of mineralization (Figure 6), shows that there is very little variation in the gallium content of the rock. Owing to the high reproducibility of the gallium analyses, small variations in the values would be significant. Thus the gallium concentration is seen to be low close to the mineralization, to rise to the sixth and seventh sample positions, to fall to a low between the tenth and twelfth sample positions and to rise again. This is the trend exhibited by the majority of the individual traverses, but as with them, does not appear to be related to the trends of any of the other trace elements.

Chromium Cr^{3+} (0.64 kX)

Chromium occurs in rocks as chromite, rarely as chrome spinels, and in silicates. The most important occurrence is in silicates, where chromium is camouflaged by aluminium (Al^{3+} 0.57 kX) and iron (Fe^{3+} 0.67 kX), and apparently captured by magnesium (Mg^{2+} 0.78 kX) and iron (Fe^{2+} 0.83 kX).

Chromium appears to be highly concentrated in early differentiated silicates (Wager & Mitchell, 1951; Nockolds & Mitchell, 1948 and Goldschmidt, 1937). That it shows a distinct preference for pyroxene rather than olivine is indicated by Wager & Mitchell (1951), but the high concentration reported by Goldschmidt (1937) in dunite and that by Sahama (1945) in "ultrabasics" appears contradictory. Perhaps the abundance in pyroxene may be explained by the presence of chrome diopside.

Chromium may be present in all the ferromagnesium minerals in norite, but it is not found in plagioclase. In a diorite (Nockolds & Mitchell, 1948) it occurs as follows:

	ppm.
Plagioclase	—
Hypersthene	200
Augite	1500
Biotite	800

and in an olivine free gabbro (Wager & Mitchell, 1951) as follows:

	ppm.
Plagioclase	—
Pyroxene	—
Magnetite	800
Ilmenite	300

Chromium intensity ratios, proportional to the chromium concentration, vary similarly to the manganese concentration in the Sudbury

norite, that is, for the most part, the chromium concentration decreases as the distance from the mineralization contact increases.

Copper Cu^{2+} (0.83 kX)

Copper has a strong affinity for sulphur and occurs in igneous rocks mainly as the sulphide chalcopyrite, but probably replaces iron in minerals containing that element, and sodium (Na^+ 0.98 kX) in plagioclase feldspars. It occurs in apatite but is not found in the potash feldspars (Nockolds & Mitchell, 1948).

According to Sandell & Goldich (1943) copper is concentrated in early crystallates. Wager & Mitchell (1951) show that copper concentrates towards the end of differentiation, but add that the possible reason for this late concentration in the case they studied is that insufficient sulphur was present to remove all the copper in the early precipitated sulphides, though the sulphur content of the rock under discussion (500 ppm.) is close to the average given by Goldschmidt (1937a) and Clarke & Washington (1924).

Vogt (1923) shows that the copper content of ores associated with norite is higher than that of those associated with more basic rocks. This would indicate that the copper content of a magma increases as differentation proceeds.

Copper generally appears to be absent from hornblende (Nockolds & Mitchell, 1948), but is present in all the other primary minerals which may occur in norite.

	ppm.
Plagioclase	—
Hypersthene	150
Augite	100
Biotite	300

are the amounts present in minerals from a diorite (Nockolds & Mitchell, 1948) and

	ppm.
Plagioclase	15
Pyroxene	50
Magnetite	30
Ilmenite	50

is present in the minerals from an olivine free gabbro (Wager & Mitchell, 1951).

There is apparently no trend in the copper concentration of the Sudbury norite, and the values obtained show that the copper distribution is spotty and erratic.

Lead, Zinc and Silver

Lead is present in only nine samples and zinc occurs in four of these. Silver generally occurs in the samples containing lead, but it is present in other samples. The samples containing lead have a high copper content and often a high nickel content, suggesting that the lead may be present as the sulphide. These elements are too sparsely distributed to be of any but general interest, and the values are too erratic.

Summary

There appears to be then, associated with the mineralization which produced the orebodies, a relative concentration of titanium, vanadium, manganese, nickel and chromium adjacent to the mineralized zone, which decreases as the distance from the zone increases. There is a slight peak concentration in the case of titanium and vanadium away from the mineralized zone, but overall along the traverse, the concentration of these two elements decreases. Gallium is depleted close to the mineralized zone and concentrated further away. The cobalt content of the rock appears to be unaffected with relation to the mineralized zone. Copper concentration is erratic and is probably primarily due to chalcopyrite disseminated throughout the rock. Silver, lead and zinc are not present in a sufficient number of samples for conclusions to be drawn regarding their association with mineralization.

The variation of these trace elements is certainly associated spatially with the mineralized zones, and thus the orebodies. It seems probable that the variations in the trace element concentrations are caused by agencies connected with the emplacement of the sulphide mineralization, but this has not been proven, and perhaps the distribution of these trace elements in the present manner took place after mineralization. It is likely that the concentration of the trace elements is additive, and not due to their rearrangement in the rock, but this is only surmise.

Despite the fact that the samples were taken from widely varying locations around the Sudbury basin, and that all of the orebodies with which they were associated may not have been formed by the same processes (Davidson, 1948, Yates, 1948), there is no distinction between the results from one traverse and any other. There are also no great differences in the trace element content of samples from different locations.

The distribution of the manganese and nickel and the constancy of the titanium to vanadium ratio shows that there has been no significant differentiation of those portions of the norite covered by this sampling.

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