MINOR ELEMENT DISTRIBUTION
IN SOME METAMORPHIC
PYROXENES

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OF METAMORPHIC
ORIGIN

By

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SCOPE AND CONTENTS: An investigation was made of the distribution of nineteen elements in pyroxenes of metamorphic origin, from the Grenville province of Western Quebec and Eastern Ontario. Thirty-eight pyroxenes and five amphiboles were studied. Spectrographic methods were employed to determine concentrations of B, Be, Ga, Cr, Li, Ti, Ni, Mo, Co, Cu, V, Zr, Mn, Sc, Y, Sn, Sr, Pb, and Ba. The chemistry and structure of the pyroxenes are discussed, and the minor elements are considered in the light of crystal chemistry. A comparison is made with the minor elements of igneous pyroxenes as found in the literature, and with the amphiboles examined by the writer. The location of the minor elements in the mineral structure is examined. Correlations of minor elements with colour, and with rock-type are attempted.

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Abstract

Thirty-six samples of pyroxene and four samples of amphiboles were extracted from a suite of hybrid igneous rocks, skarn rocks and pyroxenites collected from various localities in the Grenville rocks of Western Quebec. Two samples of pyroxene and one of amphibole were obtained from a skarn in Monmouth township, Ontario, making a total of forty-three specimens.

Spectrographic analyses were made for B, Be, Ga, Li, Ti, Ni, Mo, Co, Cu, Cr, V, Zr, Mn, Sc, Y, Sn, Sr, and Ba, using an air-jet method, and Li, Ga, Cu, and Pb, using a method employing an inert atmosphere of argon and oxygen.

The location of minor elements is discussed in terms of the crystal chemistry of the pyroxene group, and in terms of the known behaviour patterns of the elements in rocks and minerals. On the basis of Fairbairn's packing index and other considerations, it is concluded that the minor components are, for the most part, occupying structural sites in the mineral.

When compared with pyroxenes of igneous genesis, the pyroxenes studied are conspicuously poorer in most elements except Be, Ga, Sr, and Ba, which are at about the same level. B is richer than in igneous pyroxenes. This is explained in terms of the abundances of minor elements in the Grenville sediments. It is concluded that, just as in igneous crystallization the bulk composition of the magma influences the minor element composition of the individual minerals, so in metamorphic recrystallization the composition is determined by the country rock.

Calculations were made which show that the total minor element content of the pyroxenes studied was much less than that of igneous pyroxenes in the literature, and less than that of amphiboles of the same rocks. The method of calculation was devised so that the elements were weighted with respect to their natural abundance.

Correlation of rock-type with minor element values was attempted, with negative results. Some elements, particularly the ferrides, show a diminution in the lighter-coloured, i.e. Fe-poor specimens. Inter-element trends were investigated, with results showing some sympathetic variations among Zr, Mn, V, Ni, and Co.

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I. INTRODUCTION

In the past few years, methods of spectrographic analysis have improved in reproducibility, precision and sensitivity so that reliable quantitative analyses can be made at very low concentrations for many elements. A considerable number of analyses can be found in the literature of recent years on igneous rocks and minerals, but very few analyses are reported for metamorphic materials. As a result, the geochemistry of many elements is understood in the igneous environment, and rules have been formulated to describe and predict their occurrence under various igneous conditions, whereas for metamorphic rocks and minerals such is not yet the case.

The pyroxene family has been of interest to petrologists and mineralogists for many years, and will likely remain so for sometime to come. They are a mineral group that show wide variations with respect to chemical and optical properties, and in recent years have been extensively studied by such workers as Hess, Kuno, Muir, and Brown. They are of course a very common group of minerals and appear in a wide variety of physical and chemical environments in igneous and metamorphic rocks.

Because of their wide distribution in nature and because their major constituents are among the most common elements, much work has been done on pyroxenes by investigators working on the geochemistry of the individual elements. Most of this work concerns pyroxenes of igneous genesis, however, and very little is known of the pyroxenes of metamorphic genesis.

A study of the minor element distribution in a group of pyroxenes of metamorphic origin would provide more information on the pyroxene family of minerals, and would yield a comparison between the igneous and metamorphic members of a common mineral group. It was also hoped that such a study would lead to some conclusions regarding metamorphic crystal chemistry, and aid in the interpretation of the geology of rocks of the Grenville Series and of the Grenville skarn rocks more particularly.

In the following, discussion will be mainly limited to the monoclinic pyroxenes since no rhombic members were studied.

II. SOME FEATURES OF GRENVILLE GEOLOGY

General

The specimens analyzed in this study were collected from the Grenville province of Southern Quebec and Southern Ontario, most of the specimens coming from Quebec (only two are from Ontario). Many of the samples were collected from an area which may be regarded as typical of the Grenville, the region immediately north of the Ottawa River, in Pontiac and Gatineau counties.

The Grenville province is characterized by a distinctive group of metamorphosed sedimentary rocks. The name "Grenville Series" was first applied by Logan to metamorphosed sedimentary rocks in Grenville township, where the rocks are mainly crystalline limestones, with lesser amounts of quartzite and sillimanite gneiss. In other areas, however, either one of quartzite or sillimanite gneiss may predominate. That the rocks in the different areas of Southwestern Quebec and Eastern Ontario are contemporaneous is not yet established. Hence the name applies merely as a descriptive term covering a group of lithologically similar rocks, probably originally sandstones, arkoses, shales, limestones and some lavas.

Of the intrusive rocks in Quebec areas, anorthosites and associated rock-types are distinctive. Wilson (1924) gave the name "Buckingham Series" to certain intrusions of anorthosite, diorite and gabbro as well as some syenites, which were characterized by pink clinohypersthene. Younger than these are dykes, sills and batholiths of granite and syenite and their gneissic equivalents.

Structures are very complex and structural relationships can be satisfactorily interpreted in but a few places.

Rock Types of the Grenville

In the area north of the Ottawa River, four main lithological groups may be established, according to Dresser and Denis (1944). These are first, a series of highly metamorphosed Grenville sediments (marbles, quartzites, slates and amphibolites) which underlie a large part of the area; second, anorthosite, syenite, pyroxenic granite, pyroxenite and related rocks, all genetically related one to another; third, batholithic masses of syenite and granite; and fourth, masses consisting of diopside, scapolite and other lime-silicate minerals, formed at the contacts of the various intrusive rocks with the crystalline limestone.

The Skarns

It is from this last mentioned group that most of the pyroxene specimens studied in this investigation were taken. This group has been called the "Skarn Series" by Shaw (1955) and others. Shaw has sub-divided the Skarn Series into five members, 1) hybrid rocks such as pyroxene syenites and diorites; 2) fluorite-type skarns; 3) scapolite-augite skarns; 4) pyroxenite skarn rock; and 5) pink calcite marble-type skarn.

Certain transitional phases are observed between members of the Grenville Series, the intrusive types, and the various members of the Skarn Series, involving all the various skarn types and all members of the Grenville Series, save the quartzite. The quartzite appears to be stable under all conditions of metamorphism and metasomatism.

The Skarn Series represents an equilibrium assemblage of minerals derived during metamorphism by means of exchanges or transfer of materials. However, according to Shaw (1956), it does not seem necessary to postulate transfer or introduction of new material from outside of the skarn zone itself to account for the mineral groups found in the Skarn Series. Hence the group may represent a chemical adjustment in situ.

Pyroxene, usually as augite or diopside, occurs consistently in all five of the different skarn types, and in two principle members of the Grenville Series proper (marbles and amphibolites) they are often present. Also they are found in the hybrid igneous rocks, e.g. pyroxenic granites and tonalites, etc. The pyroxenes are thus of fairly common occurrence in the Grenville sub-province and for this reason it was felt that a study of their minor- and trace-element content would be useful in any interpretation of the origin and development of the Skarn Series; and would add to the geochemical data on metamorphic minerals.

Specimens

Thirty-eight pyroxenes and five amphiboles were studied with respect to their minor- and trace-element content.

The pyroxenes were extracted from rocks of a suite of samples of Grenville rocks collected by D.M. Shaw in the summers of 1954 and 1955 while engaged in mapping parts of Grand Calumet Island and in examining various radioactive skarn-deposits in south-western Quebec for the Quebec Department of Mines. Two samples are from the Grenville of Eastern Ontario (see Appendix I). All are believed to be of the amphibolite facies of metamorphism.

This field work provided a number of fresh specimens of all the principal rocks of the Grenville Series and of the various skarn assemblages. Twenty-three of the pyroxene specimens were extracted from scapolite-augite skarn rocks. Six specimens were taken from the metamorphic pyroxenite rocks, and five specimens of amphibole (hornblende) were extracted from pyroxene-bearing rocks and analysed for purposes of comparison. Nine pyroxene specimens were separated from the hybrid intrusive rocks of the areas studied, i.e. the pyroxene syenites and pyroxene granodiorites (see Appendix I - sample localities).

A brief description of the pyroxenes from the main rock types sampled follows (Shaw, 1956):

Pyroxene syenite-granite group (the hybrid rocks). Pyroxene is nearly always present in these rocks, as dark green anhedral grains up to 5cm in diameter, but averaging 5mm. The pyroxene crystals occur in clusters showing a rude foliation. The pyroxenes usually show yellow-green pleochroism, and often irregular zoning. The pyroxene content of the rocks varies from zero to 60%.

Fluorite-rich skarns - The pyroxene in these rocks is usually dark-green to black, occurring as small anhedral grains, or, occasionally, as small prisms.

Marbles - In the marbles, the usual pyroxene mineral is diopside, usually a pale green variety, but in some places white. Dark-coloured augite is found near the contacts of igneous rocks.

Pink calcite skarn rocks - These rocks contain a pale green sugary aggregate of diopside (colourless in thin-section) that makes up twenty per cent or less of the rock. Anhedral crystals of diopside up to 2cm in diameter are often seen, however. The rock may often show a coarse banding of calcite, diopside and mica (phlogopite).

Scapolite-pyroxene rocks - The pyroxene in these rocks varies from green to black, (in thin section it is colourless to pale-green). Pleochroism is weak, and its colour is never as intense as in varieties found in the hybrid rocks. The mineral has been described as a diopsidic augite.

Pyroxenite - This refers to the rock that Wilson (1924, p.33) termed "metamorphic pyroxenite", to distinguish it from pyroxenite of igneous origin. The pyroxene is a light-green diopsidic variety composing more than 60% of the rock. It occurs as a sugary mass of rounded grains, or as aggregates of interlocking prismatic crystals.

Appendix I gives a list of the sample locations, the type of rock from which the sample was extracted, and where possible, a brief description of the geological environment.

III. ANALYTICAL METHODS

Preparation of Samples

The rock samples were crushed by hand in a steel mortar, and screened through stainless steel screens, retaining the 100-200 mesh portion for separation of the pyroxene fraction. This was accomplished by magnetic separation using the Frantz electromagnetic separator and gravity separation using heavy liquids.

The larger part of the separation work was possible on the Frantz machine. To increase the efficiency of the magnetic separation, and also to preclude the possibility of contamination from dust of the other minerals present in the rock, the screened fraction was thoroughly washed with distilled water before separation was attempted. In many cases magnetic separation was all that was necessary to produce a high purity pyroxene fraction from the rock.

In some samples, however, the magnetic susceptibility range of the pyroxene was overlapped by other minerals present in the rock (commonly amphibole, sphene or allanite). In these cases heavy liquid separations were made using tetrabromoethane and/or Clerici solution. After heavy liquid separation the pyroxene portion was carefully washed with acetone and distilled water. See section on "Purity of Samples".

Semi-quantitative Analysis

As a preliminary study, it was decided to run a series of semi-quantitative analyses on some specimens using the graphite-base standards (G - standards) made by Spex Industries, Inc. for comparison. This served as a general survey to determine which elements were present at the minor- and trace-element level, their general levels of abundance, and to choose which were suitable for more detailed observation. This survey also served as a guide for the development of a suitable quantitative method.

The semi-quantitative method adopted used mineral samples mixed with potassium sulphate and graphite in the ration 1:1:2 respectively. The mixture produced a smooth burn in the arc, yet maintaining cyanogen bands and background interference at a reasonable level. The Stallwood air-jet and a screen-filter were used.

Comparison standards were prepared using a matrix of oxides and salts mixed in a proportion approximating the gross composition of a natural pyroxene. This was mixed with "Spex-mix" (Spec Industries, Inc.) to provide 4 standards containing 1.0, 0.1, 0.01, and 0.001% respectively, of 43 of the more common elements. The standards were mixed with potassium sulphate and graphite in the same proportions as the samples. Plates were then exposed, each bearing the spectra of the standards, and a number of pyroxenes. Spectral line intensities were measured and compared with the values obtained for the standards.

The semi-quantitative study showed numerous elements to be present at the trace and minor level. Those chosen at this time for further study included, B, Ba, Be, Co, Cr, Cu, Ga, Ge, Mo, Ni, Pb, Sc, Sr, Ti, V, Zr. To these were added Li, La, and Y after further work, making a total of twenty elements.

Quantitative Analysis

i. Graphite-Palladium Method

The choice of an internal standard in analysis for a large group of elements is critical from several standpoints. Ideally the internal standard should be an element that has negligible concentration in the unknowns, a similar rate of distillation into the arc, a similar excitation potential and has readable lines in the same spectral wave-length region as the elements with which it will be compared.

Palladium is an element that makes the best compromise among these factors, and it has been used successfully for most of the elements in this analysis. The determinations were made by an air-jet method, diluting each sample with an equal weight of graphite containing 0.1% Pd. Elements determined by this method were Ba, Be, B, Co, Cr, Cu, Ga, Mo, Mn, Ni, Ti, V, Sc, Sr, Y, Zr.

The method for this group has been outlined by Shaw (unpublished paper). This method was first recommended by Ahrens (1953) and was revised by Shaw. It was subsequently adopted by the writer for reasons of its simplicity and adequate reproducibility. Before the analyses were made some test analyses were made to investigate whether the method was suitable for determination in a pyroxene-type matrix, with generally satisfactory results.

Further details of the method are given in Tables I and III. Working curves covered the range from 3 ppm to 1000 ppm. Later it was found necessary to construct additional curves, taken from other spectral lines for such elements as titanium and manganese, which occasionally were found in amounts considerably in excess of 1000 ppm.

ii. Argon-Oxygen Method

A method for determing a few more elements was later developed, (Shaw, Wickremasingh, and Yip, in press, 1958) that yielded plates free of cyanogen bands and of very low background darkness. Elements sought in this lesser group were Li, Pb and Sn. Ga and Cu were also rechecked by this method. A number of useful lines occur in the region of the cyanogen bands and are otherwise rendered useless by their presence.

This method consists of arcing the sample in an atmosphere of argon and oxygen; hence very little nitrogen is available to form cyanogen. Indium was used as internal standard, added to the potassium chloride buffer. Sample preparation, spectral parameters, development conditions and other details of this method are outlined in Table II. Spectral lines used are listed in Table IV.

A number of elements were determined more than once, using two or more lines or by using both methods. This was done in cases of high values, where a less sensitive line was chosen to measure the abundance more accurately (e.g. Ti, Mn) and in other cases was useful in checking the accuracy of the later argon-oxygen method.

TABLE I - Spectral Parameters and Development Conditions for Graphite-Palladium Method

Spectrograph	JACO 21-foot grating, Wadsworth mount, first order dispersion 5Å/mm.
Condensing optics	25 cm. focal length cylindrical lens (horizontal axis) at the slit. 6.7 cm. focal length cylindrical lens (vertical axis) 16.1 cm. from the slit. Diaphragm with 5 mm. aperture 27.5 cm. from the slit. 10 cm. focal length spherical lens 58.1 cm. from the slit. Arc located 72.5 cm. from the slit.
Slit width	30 microns.
Intensity control	7-step sector at the slit, log intensity ratio = 0.2; 1 screen.
Slit length	25 mm.; sector height adjusted for steps 3 and 4.
Electrodes	National Carbon Co. graphite ("Special" grade): sample (anode), 1/8" rod, plain crater 1/16" x 3/8"; counter-electrode, 1/8" rod.
Emulsions and range	Eastman Kodak Type S.A.1 plate, 2200-3550Å Eastman Kodak Type III-F plate, 3550-4900Å
Processing	3 minutes development in D19 developer at 20°C.; 15 seconds stop-bath; 20 minutes acid fix; 20 minutes wash.
Voltage	225 V.D.C. on open-circuit;
Exposure	Completion; 80 to 90 seconds.
Current	Started at 3 and raised to 6 1/2 amperes
Air-jet	1 p.s.i.
Sample	1 part mineral to 1 part graphite powder containing 0.1% $PdCl_2$, thoroughly ground and mixed. 15 mg put in electrode crater.
Artificial standards	Prepared from Johnson-Matthey "Specpure" compounds; (a) SC series; matrix of: SiO_2, 45%: Al_2O_3, 23%: $CaCO_3$, 22%: NaCl, 9%: Fe_2O_3, 1%; to this matrix were added "Spex-mix" (Spex Industries Inc.) containing 43 metals at 1.34% concentration and Ga_2O_3, and standards were prepared by dilution to cover the range 3.16 to 10,000 ppm; some standards at higher concentrations were arced using 2 intensity-reduction screens. (b) SLY series; matrix of: SiO_2, 50%: Al_2O_3, 20%: $CaCO_3$, 15%: NaCl, 5%: Fe_2O_3, 5%: MgO, 5%; Sc_2O_3, Y_2O_3 and

TABLE I - continued

	La_2O_3 were diluted with this matrix to give standards covering the range 10 to 1000 ppm. (c) ST series; matrix of: SiO_2, 60%: Al_2O_3, 25%: $CaCO_3$, 10%: NaCl, 5%: TiO_2, Mn_3O_4, ZrO_2, MgO and Fe_2O_3 were diluted with this matrix to give standards covering the range 0.1 to 3.16%.
Photometry	ARL photodensitometer used; galvanometer readings between 1.0 and 95 were used and background corrections applied in all cases except where 2 intensity-reduction screens had been used; clear-plate reading adjusted to 100 before each measurement; readings made on step 4 (steps numbered 0 to 8) where possible.
Exposure sequence	At least one standard exposed on each sample plate, recording 7 steps in order to check calibration curves and minimize working-curve drift; samples analyzed in triplicate, one on each of three pairs of plates.
Calibration	Calibration curves (Ahrens, 1950) were drawn using a modified two-step method (Shaw, unpublished).

Appendix III gives a comparison of the values obtained in these cases, and a note explaining on what basis the accepted values were chosen.

Sensitivity and Precision

Listed in Table III are the relative error "E" for each analysis line, and the range of the line, for the graphite palladium method. The sensitivity of each line is in all cases, for purposes of this discussion, the lower limit of the range, since standards of each element were made as low as 1 ppm. The sensitivity of a line refers to how much of a given element is required to produce a measurable blackness on the plate for the spectral line in question.

TABLE II - SPECTRAL PARAMETERS AND DEVELOPMENT CONDITIONS for Argon - oxygen Method

Spectrograph	JACO 21-foot grating, Wadsworth mount, first order dispersion 5Å/mm.
Condensing optics	25 cm. focal length cylindrical lens (horizontal axis) at the slit. 6.7 cm. focal length cylindrical lens (vertical axis) 16.1 cm. from the slit. Diaphragm with 5 mm. aperture 27.5 cm. from the slit. 10 cm. focal length spherical lens 58.1 cm. from the slit. Arc located 72.5 cm. from the slit.
Slit width	30 microns.
Intensity control	7-step sector at the slit, log intensity ratio = 0.2, no screens.
Slit length	4 mm.; sector height adjusted for steps 4, 5, 6.
Electrodes	National Carbon Co. graphite ("Special" grade): sample (anode), 1/8" rod, plain crater 1/16" x 3/8"; counter-electrode, 1/8" rod.
Emulsion and range	Eastman Kodak Type S.A.1 plate, 2900-4250Å.
Processing	3 minutes development in D19 developer at 20°C.; 15 seconds stop-bath; 20 minutes acid fix; 20 minutes wash.
Voltage	225 v.D.C. on open-circuit;
Exposure	90-100 seconds (completion of alkalies).
Current	6 amperes.
Atmosphere	Argon and oxygen in proportion 1:1 at total pressure of 5 p.s.i.
Sample	5 parts mineral, 1 part graphite and 4 parts KCl containing 0.025% In_2O_3, thoroughly ground and mixed - about 15 mg put into electrode crater.
Artificial standards	Prepared from Johnson-Matthey "Specpure" compounds; matrix of: SiO_2, 45%: Al_2O_3, 23%: $CaCO_3$, 22%: NaCl, 9%: Fe_2O_3, 1%: Li, Cu, Ag, Pb, Sn and Ga were mixed (as oxides) with this matrix and diluted to give standards ranging from 3.16-1000 ppm.
Photometry	ARL photodensitometer used; galvanometer readings between 1.0 and 95 were used and background corrections applied in all cases except where 2 intensity-reduction screens had been used; clear-plate reading adjusted to 100 before each measurement; readings made on step 4 (steps numbered 0 to 8) where possible.
Exposure sequence	At least one standard exposed on each sample plate, recording 7 steps in order to check

TABLE II - continued

calibration curves and minimize working-curve drift; samples analyzed in triplicate, one on each of three pairs of plates.

TABLE III - Spectral Lines, Range and Relative Error for Graphite Matrix Method

Spectral Line	Relative Error (E) for Triplicate Analysis	Range of Line
B 2497.733Å	19.4%	3-1000 ppm
Be A-2348.610 *	22.8	3-1000
Be B-3131.072 *	14.0	<1-1000
Ga A-2943.637	12.4	3-1000
Cr 4254.346	13.5	3-1000
Ti B 3354.635	11.4	30-1000
Ti C 3321.588	7.5	.03- 3%
Ti D 3346.728	5.9	.03- 3%
V B 3185.396	10.3	10-1000
Mo 3193.973	11.6	1-1000
Ni 3414.765	8.4	1-1000
Co 3453.505	9.0	1-1000
Cu 3273.962	14.6	<1-1000
Zr A 3391.975	13.6	10-1000
Mn C 3212.884	8.5	.03- 3%
Mn D 3258.413	10.0	.03- 3%
Sc 4246.829	11.3	3-1000
Y 3216.682	12.7	3-1000
Sr 4607.331	13.2	3-1000
Ba 4554.042	12.6	1-1000
Pd 3258.780	Standard Lines	
Pd 2476.418		

* Standard Line Pd 2476.418 used with these lines
Standard Line Pd 3258.780 used for all others.

Working curves were calculated by a regression analysis method.

Wave lengths of lines are those given by Harrison et al. (1939).

TABLE IV - Spectral Lines and Ranges for Argon-Oxygen Method

Spectral Line	Range of Line
Ga B 2943.637 Å	1-1000 ppm
Ga C 4172.056	3- 100
Sn 3175.019	10-1000
Li 3232.610	100-1000
Cu B 3273.962	10- 100
PbA 3683.471	10- 300
Pb B 4057.820	10- 300
In 3256.090 (Standard Line)	

Working curves not calculated by regression analysis.

The method of calculating the precision is that used by Shaw (1954), and described in Mood (1950, p.300). It is given as relative error "E", expressed as a percentage, and is derived as follows:

Let n = number of replicates of analysis,
K = concentration of element,
x = log K
$\bar{x}$ = mean value of x
x_i = value of x for the replicate i
s = standard deviation of x, estimated from the

formula $$s^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i\right)^2}{n}\right]$$

$s_{\bar{x}}$ = standard error (error of arithmetic mean)
defined by $s_{\bar{x}} = \frac{s}{\sqrt{n}}$

Then, E = relative error of concentration

$$= \frac{\text{antilog } (x+s_{\bar{x}}) - \text{antilog } (x-s_{\bar{x}})}{\text{antilog } \bar{x}} \times 100$$

$$= \frac{s_{\bar{x}}}{\bar{x}} = \frac{s}{\sqrt{n} \times \bar{x}}$$

multiplied by 100 to express as a percentage.

The precision has not been calculated for the lines used in the argon-oxygen method. According to Shaw, Wickremasinghe and Yip (1958), the reproducibility is entirely adequate and the sensitivity is sufficient, as shown in analyses of standard granite G1 and standard diabase W1.

IV - THE PYROXENES, - THEIR COMPOSITION, STRUCTURE AND CRYSTAL CHEMISTRY

Description of Structure

The pyroxenes constitute one of the most important groups of igneous and metamorphic rock-forming silicates. They are composed, in the main, of the most abundant elements in the earth's crust, potassium excepted. The major constituents are oxygen, silicon, magnesium, iron, calcium, and sodium. These are present in widely varying proportions and lesser amounts of titanium, aluminium, lithium and manganese serve to set apart various end members as separate mineral species.

A study of the atomic structure of the group (Warren and Biscoe, 1931; Bragg, 1937) shows that the fundamental building block is the SiO_4^{-4} tetrahedron. The tetrahedra are arranged parallel to the c axis in chains, each one sharing oxygen atoms with tetrahedra immediately above and below, so that the ratio of silicon to oxygen is, instead of one to four, one to three.

The individual chains are linked to each other in the a and b crystallographic directions by cations, the linkage in the b direction being closer than in the a direction, so that the chains are disposed in sheets parallel to the (100) plane, (Warren, 1930; Bragg, 1937).

The disposition of these chains governs the orientation of the (110) cleavage planes that occur in all pyroxenes at the characteristic 87^0 angle. Warren (1930) has shown that the difference in cleavage of pyroxenes and amphiboles is due to the difference in form of their Si-O chains. The cleavage is parallel to c; presumably it is more difficult to break through the Si-O bonds than through the cation-O bonds that hold the chains together. Since the Si-O chains in amphibole are longer in the b direction, the diagonal cleavage planes occur at an angle closer to the b direction, explaining the 56° -124° cleavage in amphiboles.

In the case of monoclinic pyroxenes, under discussion here, the individual chains, then, are linked laterally by cations, each of which is surrounded by six 'active' oxygens, i.e., oxygens with only one bond to a silicon atom. Each active oxygen is linked to two cations. For example, in the case of diopside,$CaMgSi_2O_6$, which may be considered a type structure of the monoclinic pyroxenes, each active oxygen ion would be linked to one Ca ion and to one Mg ion. Calcium, however, because of its greater size, also has as near neighbours two of the inactive oxygen atoms, i.e., those forming links in the Si-O chains, and is thus in eight-fold co-ordination with respect to oxygen ions. Magnesium, being smaller is only in six-fold co-ordination. This difference in size, with its consequent difference in co-ordination number is, of course, the factor that separates the various cations into the various co-ordination groups X, Y and Z in the monoclinic pyroxenes. X and Y iohs are the cations joining the Si-O chains. The Z positions are the tetrahedral positions, usually occupied by silicon, but often by other ions in four-fold co-ordination.

Warren and Biscoe (1931) suggested as a general formula for pyroxenes $\underline{X_m Y_{2-m} Z_2(O,OH,F)_6}$, where m tends to be zero or or unity. For this general expression, m would be unity for the diopside-hedenbergite series or acmite-jadeite series, and would be zero, or approaching zero, for the orthorhombic pyroxenes (e.g. enstatite, $Mg_2Si_2O_6$) and pigeonites.

In a few monoclinic members, only Y cations are present, (i.e., m=0). These are the non-calcic, clinopyroxenes, clinoenstatite, clinohypersthene, and clinoferrosilite. The pyroxenes investigated are, however, all calcic monoclinic members and discussion will be confined to them.

It should be recalled that even in the case of the formula $Y_2 Z_2O_6$ many other small ions including X size ions, are present in small but significant amounts. Therefore, the general formula is still applicable to both orthorhombic and monoclinic members of the group.

There are no pyroxenes of the formula-type X X Z_2O_6, of course. The reason for this is that the larger size of an extra X ion would force the lattice to crystallize in a different space-group (e.g. triclinic wollastonite, $CaSiO_3$).

Common Species

In the general formula of Warren and Biscoe (1931) there are, then, only three possible situations for any given cation. This may be summarized as follows, (for major elements):

Symbol	Co-ordination	Ionic Radius	Ions
Z	4	$.35-.64A^{\circ}$	Si^{+4}, Al^{+3}, Ti^{+4}
Y	6	$.65-.90A^{\circ}$	Mg^{+2}, Fe^{+2}, Fe^{+3}, Al^{+3}, Li^{+1}, Ti^{+4}
X	8	$.90-1.22A^{\circ}$	Ca^{+2}, Na^{+1}, Mn^{+2}

The common types involving these elements are:

Diopside	$Ca\ Mg\ Si_2O_6$
Hedenbergite	$Ca\ Fe\ Si_2O_6$
Augite	$Ca\ (Mg,Fe,Mn)\ Si_2O_6$ with $Mg\ FeSi_2O_6$ and $(Al,Fe_2)\ O_3$ -(after Winchell, 1951)[1]

Winchell (1951) uses the term "polyaugite" to include this group. Augite is the most common pyroxene in igneous and metamorphic rocks, and for this reason Winchell (1951, p.404) feels that an inclusive name is required to cover these subspecies. In Winchell's reference, all of the pyroxenes investigated by the writer would be considered polyaugites.

Most of the pyroxenes in this study are ferroaugites. These occupy the area shown in Fig. 1, taken from Winchell (1951), after Hess (1941). The augites themselves may be considered the 'general case" of the clinopyroxenes, since they contain all of the major elements found in pyroxenes, to a greater or lesser degree, and thus exhibit a wide variety of valence and bonding relationships in the mineral structure. The augites are among the most important mafic constituents of igneous and metamorphic rocks.

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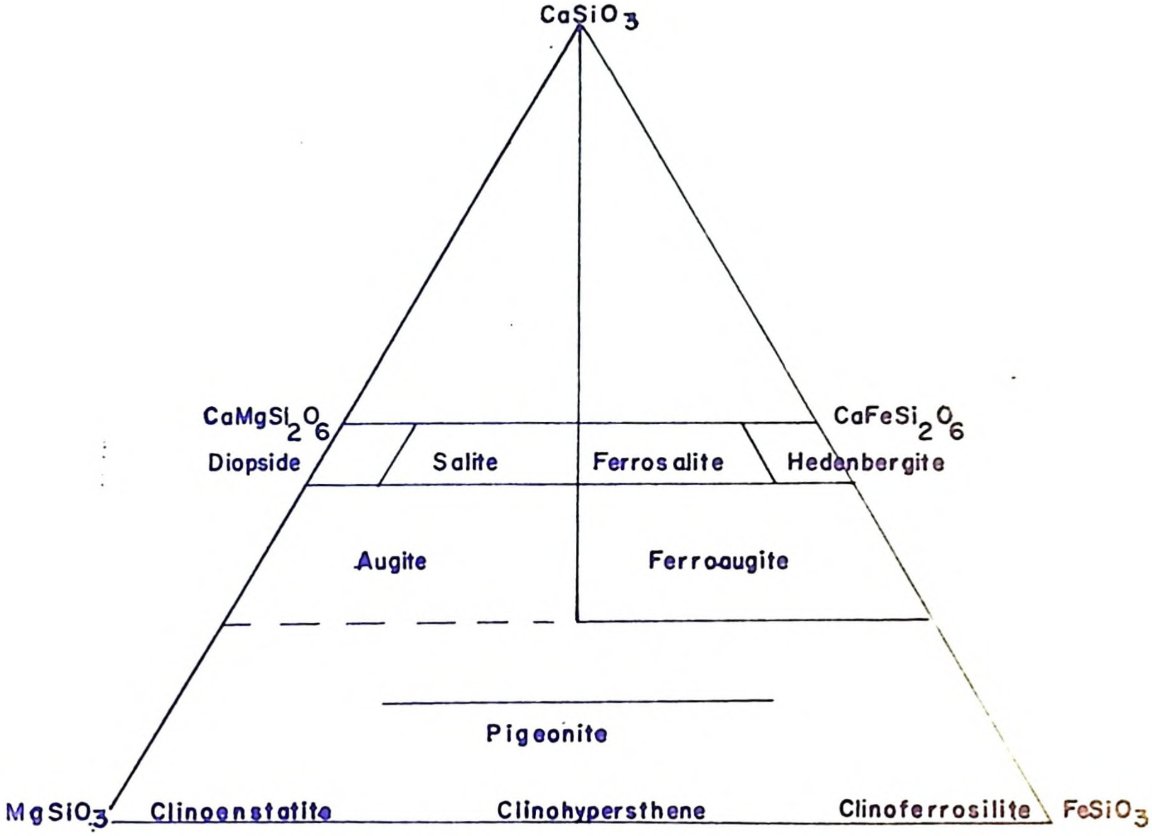
[1] Rankama and Sahama (1950) give augite the formula $CaNaFe_2Mg_6(AlFe_2Ti)_2(Al_2Si_{14}O_8)$

Fig. I- NOMENCLATURE of the COMMON CLINOPYROXENES.
(after Hess, 1941)



Two less common varieties of the polyaugite group are acmite ($NaFeSi_2O_6$) and jadeite ($NaAlSi_2O_6$). Acmite is also known as aegirine.

Spodumene ($LiAlSi_2O_6$) forms a special case. It is restricted to the pegmatitic stage, and since there are no known varieties intermediate between it and the rock-forming pyroxenes, it is of little interest in the present study.

Two other less common end members are also known - schefferite - a manganese pyroxene, $MnSiO_3$, and jeffersonite, a manganese zinc pyroxene.

Many other variety names, usually based on colour or texture, are also recognized.

Some authors (e.g., Ford, 1932) used to include wollastonite ($CaSiO_3$), rhodonite ($MnSiO_3$) and pectolite ($HNaCa_2(SiO_3)_3$) as triclinic pyroxenes, although they are crystallographically quite different from the orthorhombic and monoclinic varieties. Larsen and Berman (1934) suggested the name "pyroxenoid" for minerals of this group.

Bonding and Valence

In the pyroxenes, complex relationships attend the replacement and substitution of the major elements. Since these elements affect the minor element abundances, it is necessary to consider their bonding and valence associations.

The simplest type of clinopyroxene would be the type $Ca(Mg,Fe)\ Si_2O_6$. In this case, the X and Y cations are of equal valence and the Z cation (silicon) is in four-fold co-ordination within the Si-O tetrahedron. Here the substitution of, say, Ni for Mg and Mn for Fe represents a small degree of variation, since the substituting cations are of similar size and equal valence. A slightly more complex bonding is utilized to derive the alkalic pyroxenes (jadeite, acmite, and spodumene). In these cases the pair of bivalent cations is replaced by a univalent (Na^+,Li^+) and a trivalent (Fe^{+3}, Al^{+3}), thus maintaining electrical balance in the structure. This is a coupled replacement. The relationship becomes more complex when a substitution takes place within the Si-O tetrahedron; tri-valent aluminium may do this, as may titanium or germanium to a more limited degree (see below). Electrical balance will be established if, 1) the sum of cation charges per formula group is twelve, to balance the -12 charge of the six oxygen atoms, 2) there are two cations in the X and Y positions for each two in Z positions.

Al plays an important part in the formation of pyroxenes. According to Rankama and Sahama (1950), in the alkalic members and in diopside-hedenbergite series Al can substitute for Si in the Si-O tetrahedra to only a very limited degree - 2-3%. In augite, however, Al appears to be capable of replacing one quarter of the Si sites. Electrical balance is maintained by introduction of Al into some of the six-fold sites as well. This was shown by Segnit (1951) in studies of artificial pyroxenes, who also showed that such a substitution caused a decrease in unit cell dimensions. The largest amount of Al substituting for Si in any pyroxene in the literature is 27.6% in a pyroxene from a xenolith described by Dixon and Kennedy (1933). Hess (1949) feels that under normal circumstances there is an upper limit beyond which substitution of Al for Si does not take place, because of the greater radius of the Al ion, without serious distortion of the structure. This upper limit he places at about 12%.

In many cases in recalculation of the mineral formula from analyses, Al is found to be in Z positions. However, analyses turn up when there is insufficient (Si + Al) to accommodate the Z positions, calculated on the basis of six oxygen atoms. Barth (1931) was one of the first to notice this, and he concluded that titanium was entering the oxygen tetrahedron. Upon subsequent work with artificial pyroxenes he concluded that $CaMgTi_2O_6$ was miscible up to ten mole percent in $CaMgSi_2O_6$. Dixon and Kennedy (1933) describe a similar situation, as did Wager and Deer (1938) for pyroxene No.12 of the Skaergaard intrusion, and Muir (1951) shows this to be true for four other clinopyroxenes of the Skaergaard, (Nos. 10, 11, 13, 14). Owing to the difference in size of Si and Ti ions, this replacement is strictly limited.

There has been some question as to the valence state of titanium in silicate minerals, and pyroxenes more particularly. Kunitz, (1936) states that Ti^{+3} replaces Al^{+3} in titanaugite, but it is not clear that he excludes the possibility of the presence of Ti^{+4} replacing Si^{+4}. Dittler (1929) suggests that Ti^{+3} may occur in natural silicate, but Segnit (1953) doubts that such conditions may occur on a large scale in nature because of the difficulty of co-existence of Fe_2O_3 and Ti_2O_3 at elevated temperatures. Segnit believes that the quadrivalent titanium is most often present, and his work with synthetic minerals showed that such a substitution for silicon was possible for up to approximately 6% of Si positions. Kuno (1955) also reports Ti^4 in the Z group in natural pyroxenes he investigated. Segnit concludes, however, that in natural pyroxenes, Ti would, under conditions of excess alumina, preferentially seek the Y position.

There are cases reported by Kuno (1955), in some subcalcic augites, of Fe entering the oxygen tetrahedron. Kuno cites ten analyses from Japanese volcanic rocks where this is the case and Muir (1951) reports three of the Skaergaard clinopyroxenes where such is the case (Nos. 11, 13, and 14). Hess (1949) also reports an analysis where Fe^{+3} is required to complete the Z group in the calculated formula. That Fe^{+3} can go into the tetrahedral position was first shown by Faust (1936). Several instances of Fe-bearing feldspars, both natural and synthetic have been reported by Rosenquist (1950), Kuno (1950) and Wager and Mitchell (1951) and others. Segnit (1953) claims to have synthesized pyroxenes of this type, and he places the upper limit of possible solid-solution at about 5%. The ionic radii Ti^{+4} and Fe^{+3} are indeed similar, but their ionization potentials and other physico-chemical properties no doubt have a major influence upon the possibility of this replacement.

Crystal Chemistry

The clinopyroxenes, particularly augites, show a considerable tolerance for minor and trace elements of wide variety. Those found in the present study include B, Be, Ga, Cr, Li, Ti, Ni, Co, Cu, V, Zr, Mn, Sc, Y, Sn, Sr, Pb, and Ba. It is worthwhile to consider where these may be located in the mineral structure.

With respect to size, the minor elements may be readily divided into three groups, that is, those most likely to occupy X, Y, and Z sites respectively.

The X sites, normally occupied by Ca and Na, would be the sites occupied by the larger ions; those suitable from a size standpoint would include Y, Sn, Sr, Pb and Ba.

The Y sites are largely occupied by Mg, Fe^{+2}, Fe^{+3}, Al and in spodumene, by Li. This group covers the range of ionic radius from .65 to .90 A°, and includes the larger number of the transition group of elements, and hence it is in the Y sites that there is the greatest opportunity for the accommodation of foreign elements. From consideration of their radii we could expect Ga, Cr, Li, Ti, Ni, Mo, Co, Cu, V, Zr, Mn, Sc, Y and Sn to be suitable in this group. All of these ions, in their common valence states, are well within the empirical 15% size range of the Mg^{+2} and Fe^{+2} (.66 A° and .74 A° respectively). It is this structural position that offers most opportunity to the greatest number of foreign elements for admission into the lattice.

The intratetrahedral (Z) sites are, of course, occupied by Si and Al in the main. Only a few ions are suitable by virtue of size to occupy the centre of this rigid unit to any degree. These are Ti, Ge, Ga, B, and Be.

Although size is a factor of considerable importance in considering the admissibility of a given ion into a structure, several factors appear to be operative in harbouring minor elements in a crystal-lattice.

In the foregoing discussion the views of Goldschmidt are used as a general estimate of suitabilities of different elements for various locations. Goldschmidt's view was that the two deciding factors in the substitution of trace elements were that the guest element be of similar size and valency to the major element. He suggested an empirical 15% tolerance in ionic radius as a limiting factor and suggested that an ion of like charge was not always required as long as electrical balance was maintained in the structure, as for instance by a coupled replacement.

In some cases, however, these postulates do not always hold (e.g. Shaw, 1954), and other factors have been sought to explain the distribution of the minor elements.

Ahrens (1952, 53) considers the ionization potential to be the most important property governing the distribution of an element, and suggested that elements of similar ionization potential are diadochic. There are exceptions to this, however.

Ringwood (1955) and Ramberg (1952) examined minor element incorporation from the standpoint of electronegativity and bonding properties of compounds. Ringwood states (p.193) that "diadochy takes place between ions of similar electronegativity, and whenever diadochy is possible between two ions of different electronegativity, the ion with the lower En will be preferentially incorporated because it forms a stronger and more ionic bond".

Ramberg viewed the silicates as a series of compounds of increasing polymerization with respect to oxygen in the Si-O links and found that they form a series from orthosilicates (SiO_4^{-4}) to tectosilicates ($(Si,Al)O_2^{n-}$). Those early in the series prefer small cations of high charge, (Mg, Fe) and those at the end of the series prefdr large low-charged cations (Na,K) and show a greater propensity for the substitution of Si by Al in the Si-O network. From this viewpoint, one would expect the single-chain inosilicates, i.e. the pyroxenes to show a moderate amount of replacement of Si by Al, which is the case, and to distinguish less decidedly in their choice of cations than the orthosilicates on one hand or the tectosilicates on the other. This in fact appears to be the case in the pyroxenes studied, recalling the variety of foreign substances found.

Crystal chemical arguments of this sort have in the past been mainly concerned with the formation of igneous minerals. In igneous minerals, suitable ions are incorporated into a structure with which their physico-chemical properties are in accord, without regard to the problem of transport of ions to the site; these explanations postulate free movement of ions in the magma solution, allowing a high degree of selectivity bounded by the properties of each ion and its concentration in the magma.

Such is by no means the case in the genesis of metamorphic minerals. While some movement takes place, indeed, must, if only on the intra-granular scale, the migration of ions is greatly impeded in the metamorphic rocks. The selection of cations is, of course,governed by the same chemical laws, but the availability of metallic ions is governed largely by the composition of the rock in situ, so the case is different from that of crystallization from a practically homogeneous magmatic solution.

Table V lists some physical and chemical constants for the elements discussed on this thesis. Valency and co-ordination are standard values. Ionic radius (R) and ionization potential are those given by Ahrens (1952). Electronegativity values (En) are those of Fyfe (1951) and lattice energy contribution factors (Ek) are those given by Doerffel (1953), after Fersman.

TABLE V - SOME PHYSICAL AND CHEMICAL CONSTANTS OF THE ELEMENTS ANALYZED

Element	Co-ord.	R	Ip	En.	Ek
Si^{4}	4	.42	45.1	1.8	2200
Al^{3}	4,5,6	.51	28.4	1.5	1270
Mg^{2}	6	.66	15.03	1.2	538
Fe^{3}	6	.64	-	1.8	2330
Fe^{2}	6	.74	16.24	1.65	543
Na^{1}	8	.97	5.12	.90	115
Ca^{2}	8	.99	11.87	1.0	448
K^{1}	8	1.33	4.34	.80	92
B^{3}	3,4	.23	37.9	2.0	1535
Be^{2}	4	.35	18.21	1.5	678
Ga^{3}	6	.62	30.7	1.6	1335
Cr^{3}	6	.63	96.0	1.5	1220
Li^{1}	6	.68	5.39	1.0	141
Ni^{2}	6	.69	18.2	1.7	558
Mo^{4}	6	.70	-		
Co^{2}	6	.72	17.4	1.7	551
Cu^{2}	6	.72	7.72	1.0	538
V^{5}	4	.59	65.0	1.8	3870
V^{4}	5	.63	48.5		
V^{3}	6	.74	26.5	1.35	1360
Zr^{4}	6	.79	34.0	1.4	2005
Mn^{2}	6	.80	122.0	1.4	2330
Sc^{3}	6	.81	24.8	1.3	1190
Y^{3}	6	.92	20.0	1.2	1010
Sn^{2}	(6)	.93	14.6		

TABLE V - continued

Element	**Co-ord.**	**R**	**Ip**	**En.**	**Ek**
Sn^4	6	.71	55.7	1.65	2025
Sr^2	8	1.12	11.03	1.0	384
Pb^2	8	1.20	39.0	1.1	423
Ba^2	8	1.34	10.0	0.85	346

Sources are given in text.

V - EXPERIMENTAL RESULTS

The analysis results are listed in Table VI. Explanatory footnotes are given on the following page.

Although the lines used for determining Sn and Mo were quite sensitive, (sensitivities 3 ppm and 1 ppm respectively) Sn and Mo were not found at a measurable level in any analysis, although in a few cases they were faintly visible. For the sake of completeness, they have been retained in the analysis table. Lanthanum was also looked for in all samples, but was not observed.

Lithium, measured on the 3232.610 Å line, was rather insensitive, the lower limit of sensitivity being at 30 ppm. Hence, although traces may be present, in most cases it appears to be absent. However, it attains fairly high values in four analyses (see table).

Lead has a sensitivity of 3 parts per million on both lines used. It is frequently visible, and measurable, but its dy-value[1] in many cases is below the usable part of the working curve.

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[1] dy= relative intensity ratio
= Y analysis line - Y internal standard line
= $\log I_A - \log I_s = \log I_A/I_s$,

where I is the intensity of the spectral line Log.I values are obtained from galvanometer readings by conversion using a calibration curve and a calculating board of the type described by Honerjäger-Sohm and Kaiser (1944). Conventionally, $y = o$ when A (galvonometer reading) is 10 for the fourth step.

Hence in many cases it is listed as only being present at trace level. ("Trace level", symbolized in the table by "tr", in all cases means that the element is present, but at a level lower than the lowest significant point on the working curve).

Ti and Mn are the most abundant trace elements present. These elements were both measured on more than one line, and the value chosen and listed in Table VI was selected as the most appropriate (see Appendix II and accompanying notes). The higher level of titanium and manganese is in line with their greater terrestrial abundance.

The analysis results of the 5 amphiboles are given in the lower section of the table. Generally speaking, higher concentrations of elements are attained in the amphibole from a given rock sample than from the pyroxene. This is discussed on a subsequent page.

TABLE VI - ANALYSIS RESULTS

	B^3	Bo^2	Ga^3	Cr^3	Li^1	Ti^4	Ni^2	Mo^4	Co^2	Cu^2	V^3	Zr^4	Mn^2	Sc^3	Y^3	Sn^2	Sr^2	Pb^2	Ba^2
R	.23	.35	.62	.63	.68	.68	.69	.70	.72	.72	.74	.79	.80	.81	.92	.93	1.12	1.20	1.34
S	3	1	3	3	30	1	1	1	1	1	3	10	3	3	3	3	3	3	1
Pyroxenes																			
Q-3	16	3.0	14	42	*	209	34	*	30	3.5	39	60	2810	9.2	8.0	*	70	*	5
Q-7	9	1.5	6.2	205	*	612	39	*	45	1	30	40	730	28	4.5	*	72	tr	2.6
Q-11B	16	1.8	6.4	tr	*	234	10	*	10	1.5	23	68	950	tr	7.4	*	86	*	30
Q-12B	17	1.5	8.8	24	*	437	11	*	10	2	29	32	1020	tr	13	*	100	*	12
Q-13B	8	1.5	5.6	tr	*	300	2.8	*	8	1.0	14	16	950	tr	<5	*	99	tr	12
Q-16B	13	1.5	10.0	52	*	164	32	*	22	3.6	40	26	1500	7.8	6.8	*	78	tr	44
Q-16D	24	1.6	9.6	46	*	223	27	*	20	2.0	42	28	1550	8.4	30	*	94	*	5
Q-19D.S13	15	tr	11.3	20	*	165	13	*	9	15	23	21	940	3.0	4.8	*	82	*	2.5
Q-19D.S14	17	tr	*	15	*	233	6	*	5	tr	9	20	605	tr	13	*	60	*	3
Q-24C	13	8.9	13	10	*	315	31	*	18	3.5	30	55	2180	6.5	8.6	*	48	*	15
Q-25	15	1.1	11	20	*	214	8	*	9.5	2.0	35	19	930	5.0	6.2	*	17	tr	13
Q-27	17	2.7	5.6	tr	*	178	3.2	*	9.4	4.0	14	16	915	tr	4.0	*	59	*	13
Q-30	13	1.0	11	11	*	150	1.7	*	5.2	4.0	8	12	730	2.0	8	*	52	15	20
Q-31A	33	tr	11	32	*	241	6	*	4.5	3.7	8	15	785	tr	13	*	34	50	6.5
Q-31B	42	1.0	9	29	*	231	3	*	4.5	3.0	9	18	870	tr	6.2	*	41	*	21
Q-31C	24	1.3	13	120	*	860	9	*	6.0	3.1	33	36	810	15	27	*	38	*	15
Q-34	27	2	5.6	25	*	165	2	*	8	2.8	19	23	780	1	8.6	*	38	343	17
Q-64A	21	4.3	6.7	51	*	420	3.4	*	9.5	5	76	38	1540	23	<5	*	59	tr	8.4
Q-69B	13	6.5	12	52	*	310	13	*	10	1	45	58	2200	15	8.6	*	47	tr	44
Q-73J	15	11	*	46	*	285	4.5	*	6	tr	16	54	1900	<2	20	*	450	216	11
Q-85	31	tr	27	tr	*	350	1	*	4.5	47	10	50	590	tr	6.6	*	123	*	31
Q-87B	17	tr	11	44	*	160	24	*	19	1.5	36	29	1010	9.4	7.4	*	94	tr	6
CA-30	16	1.8	7.3	tr	*	320	15	*	27	4	39	58	890	11	3.5	*	74	59	30
CA-44	15	3.6	8	36	*	190	3.5	*	14	7.4	44	35	1620	12	10	*	96	16	1.9
CA-45	20	2.8	9.4	36	*	165	24	*	29	1	32	38	2300	5.2	3.5	*	52	tr	5.6
CA-46	13	9.1	18	30	*	235	27	*	29	2.7	47	60	1790	10	<5	*	51	tr	3.9
CA-47	16	19	20	44	*	165	10	*	16	4	27	39	2840	10	11	*	64	15	8
CA-49	6.9	5.4	6.4	47	*	220	8.5	*	20	2	67	42	1500	12	18	*	90	*	5.3
CA-53	12	4.3	8	tr	*	200	9.6	*	18	2.5	41	67	1850	6.3	tr	*	74	tr	6
CA-56	17	tr	23	15	*	480	1	*	9	3.7	27	41	1070	4.7	4.1	*	92	*	1
CA-63A	26	2	16	43	*	230	17	*	15	1.5	32	32	1390	5.5	9.0	*	120	tr	10
CA-65	19	4.3	12	36	*	313	10	*	17	>500 (1)	42	45	1460	10	11	*	120	tr	29
CA-74	27	tr	16	16	*	390	31	*	26	tr	46	56	1500	12	8.2	*	84	*	10
CA-76	12	5.9	26	tr	116	930	29	*	30	9	63	66	955	23	tr	*	47	*	8.2
CA-92B	14	9.1	7.4	26	*	290	22	*	18	1.5	57	41	1880	14	4.5	*	88	tr	5.2
CA-105	14	1.5	*	tr	*	163	1	*	5.5	1.5	6.8	10	1290	tr	16.4	*	78	30	1.5
ON3A	14	1.0	19	tr	81	710	2.8	*	4.3	8.4	34	28	1020	48	tr	*	48	tr	26
ON6A	89	9.0	19	15	*	260	12	*	8	3.5	16	43	1530	2.6	23	*	36	tr	tr
Amphiboles																			
Q-7	25	tr	22	116	*	645	45	*	25	<1	54	43	720	23	12	*	262	*	20
CA-47	20	6	47	15	153	710	15	*	22	<2	38	44	2170	5.4	18	*	52	tr	12
CA-76	19	tr	62	tr	*	1190	50	*	35	8.2	86	71	710	5.4	18	*	52	*	st
CA-92B	27	14	24	24	137	590	27	*	22	4.6	68	117	1790	5.4	6.7	*	52	*	33
ON-3A	29	4.5	21	tr	*	660	2	*	5	3.4	40	50	1000	tr	9.2	*	56	*	13

Footnotes are given on the following page.

Notes on Table VI

Values are given in parts per million (ppm).

All analyses were made in triplicate, and the mean was taken as the most acceptable value.

Due to the logarithmic scale employed in constructing the working curve, all values have three significant figures. For example, 12.3ppm has the same significance as 1230 ppm.

An asterisk denotes that the element was sought, and found not present.

Trace amounts, symbolized by "tr", means the element was observed but at a level below the lowest significant point on the working curve.

"St" -(strong) - signifies that the amount present was greater than could be measured on the line used, i.e., the line was too sensitive.

Less than (<) is used where the concentration was below a measurable level on one or two of the three replicates, so that a mean of the three replicates could not be calculated.

Radii (R), expressed in Ångstrom units, are those given by Ahrens (1952) for ions in six fold coordination.

Sensitivity (S) is that given in Tables III and IV.

Elements Be, Ga, Ti, Mn, and Pb were measured on two or more lines for all samples. Values for each line used, and the accepted value are given in Appendix III.

(1) - This high copper concentration probably due to contamination.

VI - DISCUSSION

Comparison with Crustal Abundances

Table VII shows a comparison of the mean abundances of minor elements found in the pyroxenes with the abundances of these elements in the crust of the earth, or as it is conventionally expressed, in the average igneous rock. The values in the pyroxenes are given as a mean of the determinations made. The sources of the crustal abundance values are given in the last column.

Only two elements are significantly concentrated - B and Mn. The manganese content can be readily related to the amount of iron present in pyroxenes. Boron is discussed in a later section.

Most of the elements are greatly attenuated in the pyroxene structures, by as much as twice to twenty times, compared to the average crustal levels.

One cannot expect, of course, that the abundances of minor elements in pyroxenes will approach the abundances in the crust of the earth. The concentration of elements in a mineral structure are governed by rules far more complex than the general availability of elements in nature. It is of interest, however, to note the extent of the less common elements in the pyroxenes, and the crustal abundance figures from the literature offer a convenient frame of reference for comparison purposes.

TABLE VII - Crustal Abundance of the Elements, and their Mean Value in the Grenville Pyroxenes

Element	Average in all pyroxenes analysed	Crustal Abundance (Average Igneous Rock)	Source of Figures in Col. 3
B	17.7	3	Goldschmidt and Peters, 1932
Be	3.5	2	Sandell, 1952
Ga	10.3	20	Fleischer, 1955
Cr	31.3	100	Shaw, 1954
Li	--	29	Degenhardt, 1957.
Ti	331	4400	Green, 1953
Ni	13.5	80	Rankama and Sahama, 1950
Mo	--	1	Kuroda and Sandell, 1954
Co	12	23	Rankama and Sahama, 1950
Cu	2.9	70	Rankama and Sahama, 1950
V	31.2	100	Shaw, 1954
Zr	37.7	156	Degenhardt, 1957
Mn	1348	1000	Green, 1953
Sc	8.5	15	Shaw, 1954
Y	8.9	40	Fleischer, 1955
Sn	--	2	Onishi and Sandell, 1957
Sr	80.4	450	Turekian and Kulp, 1956
Pb	(19.6)	15	Wedepohl, 1956
Ba	11.2	250	Green, 1953

Sample Purity

In spite of reasonable precautions, it was impossible to exclude all foreign grains from some pyroxene fractions during their separation. This is especially true with respect to minerals with similar magnetic susceptibility and/or specific gravity, such as amphiboles, zircon, and allanite. In the heavy liquid separations small numbers of foreign grains may remain in the pyroxene fraction notwithstanding agitation of the suspension. These could have an effect upon results; for instance, sphene and zircon might affect Ti and Zr results significantly. Another possibility that cannot be overlooked concerns the inclusion of one or more metals as an included sulphide or oxide phase. In some samples, such as those from some pyroxenite rocks, the possibility of included galena exists. (Wilson, 1924).

To answer the question of whether the minor element content of the pyroxenes was influenced substantially either by the presence of foreign grains, or by inclusions of intergrowths within the mineral grains, the analysis fractions were examined under a binocular microscope. The results are tabulated in Appendix II. Column 1 gives estimated percentage of foreign grains as counted under a graticule in the microscope. Figures in Column 2 are the percentages of grains showing intergrowth and iron staining. The degree and extent of the alteration are listed in Column 3.

The percentage of foreign grains is in most cases negligible. In only two cases does it exceed 1% of the sample and in most cases is less than one grain in every five hundred. For most elements this amount will not make a large difference upon the analysis results. For instance, if the impurity amounts to 1% of biotite, a mineral containing many minor elements, and supposing that some element is enriched 11 times with respect to pyroxene, this will raise the content by 10%, which for most elements is of the order of the range of experimental error (see Table III). For such elements as Ti and Y a different situation obtains, however. Suppose that one grain in every thousand, or .1%, is sphene. The content of titanium in sphene is approximately 25% by weight. If all the titanium found in a particular analysis were derived only from sphene, it would be present in the sample at a level of 250 ppm, a considerable figure in view of the titanium figures shown in the analysis results (Table VI). A similar, but less serious, situation exists with yttrium in sphene and allanite.

However, samples in which allanite and sphene were detected do not show Y and Ti values appreciably different from apparently "pure" fractions. It appears that foreign grains do not affect results as much as might be anticipated. Samples Q64A, Q87B and CA44, for instance, which show a higher foreign grain content than most other specimens, do not show anomalous analysis results, although it might be argued that the results have less significance.

Intergrowths were observed in only three cases, where they occurred in 1 to 2% of the grains. The foreign mineral (usually biotite) constituted only about 10% of a grain, and so constituted a small fraction of the total sample volume. In eleven samples some iron staining was evident, usually affecting less than 5% of the sample grains.

Alteration of the grains was observed in only five of the samples, and took the form of a dusty, light green or grey, very fine, clay-like material adhering to the edges of grains and less often in cleavage fractures of individual grains. A small percentage of grains is affected in these cases (see Appendix II) and alteration has attacked no individual grain to an extent any greater than 5% of its volume, and this appears to be a generous estimate. In view of the fact that such a small percentage of sample volume is affected, and that the composition of the alteration product would not be expected to differ as largely from the fresh grains as, say, a foreign grain would, alteration can have only a very small affect upon analysis results.

Of the four sources of contamination, i.e., foreign grains, intergrowths, staining by solutions and the effect of altered grains, that most likely ~~are~~ to make a difference to the results appears to be the inclusion of small amounts of foreign grains. A comparison of Table VI and Appendix II, however, seems to indicate that this has had little effect on results.

Location of Minor Elements

There are five possible locations for the minor elements.

These are:

i. in foreign grains.

ii. in inclusions and intergrowths in the pyroxene grains.

iii. in voids in the lattice structure.

iv. in an absorbed and/or adsorbed phase, developed during crystal growth.

v. within the crystal structure, occupying structural sites.

In the section on purity of samples, the possibility of contamination by foreign grains and the possibility of inclusions or intergrowths interfering with analysis values was discussed. At that time it was concluded that of the four sources of contamination discussed, i.e., foreign grains, inclusions, altered grains and stained grains, the most important source was foreign grains. However, it was considered that these might produce anomalous results in certain cases only: presumably results in these cases will have less significance for some elements.

It may then be suggested that some of the elements are present in lattice voids. In the chain structure of pyroxenes these voids would be in the form of channel-ways parallel to the _c_ crystallographic axis. Fairbairn (1943) worked out the concept of "packing index" of a mineral to account for some of its physical, optical and chemical properties; and showed that refractive index,hardness and density increased with the packing index.

The packing index is defined as V_i/V_u x 10 where

V_i= total volume of ions in unit cell, and

V_u= volume of the unit cell.

The index of most minerals lies between 4.0 and 7.0, or in other words, for most minerals, ions occupy from 40 to 70% of the mineral volume, the rest being space.

The packing indices of the pyroxene minerals vary from 5.5 to 6.0, most being 5.9.

Fairbairn suggests that those minerals with a lower packing index will be able to contain more ions, and ions with larger radii, in the lattice spaces than those with higher indices. Pearson (1955) showed that among three chemically analogous minerals of different packing indices (andalusite, kyanite and sillimanite), there was no preferential distribution of minor elements, from which he concluded that the minor elements occupied lattice sites. There are no chemical analogues of the pyroxenes that have different packing indices for which minor element analyses are available, however, so that a comparison of this type cannot be made. A comparison can be made with the amphiboles studied. The amphiboles are chemically analogous to the pyroxenes, and their packing indices are very similar, covering the same range and most having the index of 5.8 or 5.9.

But they have a significantly higher trace element content; both in total and with respect to all but a few of the individual elements. Since the main difference between amphiboles and pyroxenes is not a difference in chemical content, nor of packing (insofar as the packing index is concerned), but in structural bonding, this would indicate that the emplacement of minor elements in chemical analogues is at least as dependent on structure as it is on lattice voids. The corollary of this is that in the pyroxenes, and in the amphiboles also, most, if not all, of the minor elements are probably occupying structural sites.

De Vore (1955) has proposed that most, or at least a large part of minor element content does not occupy regular lattice sites, but occurs on growth surfaces, imperfections and structural dislocations within the crystal, through a mechanism of adsorption. He claims that as O ions in hornblende, for instance, become more polarizable through the replacement of Si by Al, the cations of higher polarizing power, such as Ti, Zn, Cr, Co, Ni, and Cu should increase also. Co, Cr, Ni, and Cu, however, do not increase. DeVore proposes adsorption as an alternative to direct substitution. The argument is based on the bonding relationships of silicates as expressed by Ramberg. DeVore has used the case of co-existing minerals, hornblende, biotite, and garnet, which may not be a general case. Also, his argument is restricted to a few elements. That elements can be carried in an adsorbed phase to a considerable degree is quite possible, but there is no way of knowing with certainty that they do.

Two factors lead one to think that the foreign elements are occupying lattice sites. First, the small amounts of foreign elements present. The stability of a trace element in a mineral governs to a large extent the concentration that the element may achieve for a given energy level. When a certain maximum level of concentration is exceeded, the mineral structure becomes unstable and breaks down. In igneous pyroxenes, however, the amounts of most minor elements are twice to twenty times as great as in those examined by the writer. If these amounts do not exceed the stability limit of the structure, presumably the amounts found in the minerals studied are well below the tolerance limits of the structure, and could be accommodated occupying lattice sites.

Also, the concentrations of the various elements vary in terms of their suitability as lattice-occupying ions. Barium and strontium illustrate this. Strontium, which shows considerable coherence with calcium, has a mean concentration of approximately 80 ppm. But barium, which also has similarities to calcium, is present at a much lower level, approximately 11 ppm, because it is much less suitable in terms of replacing calcium in a lattice due to its excessively large size.

Geochemistry of the Elements

Boron - Boron figures are subject to greater error than most other elements; accuracy and reproducibility of the figures are not as satisfactory.

The mean boron concentration in the metamorphic pyroxenes determined by the author is 17.7 ppm, the range lying from 5 to 50 ppm. Its small diameter requires a low co-ordination number, hence it replaces silicon in the Si - O tetrahedron. The degree of substitution remains small, however, because of the difference in size between the two ions. According to Goldschmidt, when the boron concentration is too low for formation of boron minerals, it probably substitutes for silicon, and this is probably its most important geochemical role.

Boron is seldom mentioned in mineral analyses in the literature, and even when listed it is frequently described as absent or trace. The element is concentrated in pyroxenes by an average factor of 5.9 over its crustal abundance in the samples examined. Goldschmidt and Peters showed that it is much more abundant in the sedimentary cycle than in the average igneous rock, being present in sandstones up to 30 ppm, and in shales to an extent of 300 ppm. Therefore, the abundance of boron may be a reflection of the sedimentary origin of the rocks studied. This may also be true in part of the hybrid igneous rocks (pyroxene diorites, etc.). Goldschmidt reports a case (1954, p.247) near Harzburg, Germany, where an intrusive granite has taken up boron from the surrounding sediments.

Boron has a very high mobility, due to its small size and the volatility of its compounds. It is seldom trapped in even hydroxyl-bearing minerals. For this reason, boron concentrations around intrusive bodies, frequently explained in terms of magmatic emanations, may, in fact, sometimes be a result of the mobilization of boron already in the country rock, according to Goldschmidt. He claimed that in most cases development of tourmaline in contact zones can be explained in these terms. Such may be the explanation for apparently high boron concentrations in the minerals analysed. It should be pointed out, however, that there is no evidence of which the writer is aware to preclude the boron's being of magmatic origin.

Scapolite-bearing rocks are often high in boron content, according to Goldschmidt, and this has been related to the introduction of chlorine.

Beryllium - Beryllium is a rare element; Sandell (1952) gives its terrestrial abundance as about 2 ppm, and its concentration in sedimentary rocks is of the same order (see Rankama and Sahama, 1950, p.447). Igneous pyroxenes show abundances of 2 to 10 ppm. Nepheline bearing rocks are often higher in Be than others. Goldschmidt reports an aegirine bearing 360 ppm Be from a nepheline syenite pegmatite. Most Be in the crust is carried in trace amounts in micas, alkali feldspars and nepheline, according to Rankama and Sahama (1950). The mean in the pyroxenes examined is 3.5 ppm, and in the amphiboles it is slightly higher, at 4.8 ppm.

Because of its ionic size (.35 Å), Be readily replaces Si in the Si - O group, in fact, some beryllate compounds have structures analogous to silicates (Goldschmidt, 1954). Because of the deficient electronic charge of Be, a coupled replacement would be necessary for its introduction. The fact that Be is never found in quartz has been explained by there being no other ions available to balance the deficient charge of the Be ion.

Gallium - Gallium, whose mean value is 10.3 ppm in the pyroxenes examined appears to be at the same level as in igneous pyroxenes. The mean value is less than that for the amphiboles studied, and less than the crustal abundance figure of 20 ppm given by Fleischer (1955).

Gallium has long been known to show a close association with aluminium, with which it shows many physical and chemical similarities, as demonstrated by its occurrence in feldspars, feldspathoids and metamorphic aluminosilicates.

The amphiboles analysed by the writer, which were all a dark variety of hornblende containing more Al than the pyroxenes, show a greater average Ga-content. This would seem to demonstrate that Ga is replacing a major constituent in the crystal lattice.

It is also possible, however, for Ga^{+3} to replace Fe^{+3} and this mechanism is responsible for Ga in chromite and magmatic iron oxides (Rankama and Sahama, 1950). This has not been considered to be of importance in silicates by most workers. It is interesting to note that in lighter coloured samples, those likely to be lower in Fe content, that there is usually less Ga present.

In the six major element analyses of the specimens made available to the writer, the Al_2O_3 content is low, varying from .95% to 1.49%, but total Fe oxide varies from 1.9% to 18.1%. In these analyses, Ga shows little or no association with Al; if anything it shows a weak relationship to the Fe^{+3} content.

Sample	Q-3	Q87B	ON-6A	Q19D.S-13	Q31A	Q19D.S-14
Colour	black	dark green	dark green	green	green	light green
Al_2O_3%	1.49	1.31	1.41	1.29	1.02	.95
FeO%	14.51	8.49	4.36	3.89	2.66	1.51
Fe_2O_3%	3.64	1.72	2.17	.80	.88	.41
Ga (ppm)	14	10.5	19	11.3	11	ND

It is clear, however, that no safe conclusion concerning the relationship of Al, Fe and Ga can be drawn from so few figures.

<u>Chromium</u> - Chromium occasionally attains a high level in pyroxenes; chromium diopsides, called endiopsides, are reported bearing up to 2% Cr. Thus it is reasonable to assume that the Cr present is in the crystal lattice.

Analyses of the different pyroxenes gave results varying from zero to 50 ppm, occasionally being as high as 200 ppm, considerably less than the average crustal figure of 100 ppm (Shaw, 1954), but about the same as the amphiboles examined. The values for igneous pyroxenes are considerably higher, ranging usually from 200 to 2,000 ppm.

Geochemically, Cr shows greatest similarity to Fe^{+3} and Al^{+3}, probably replacing Fe^{+3} with greater ease than it does Al^{+3}. The low level of Cr in the analysed samples suggests, in view of the high chromium values obtained in igneous pyroxenes, that little was available during metamorphic readjustment. This may be true in a predominantly limestone terrain, recalling the abundances of Cr reported for sediments - 2 ppm in carbonate rocks (Rankama and Sahama, 1954, p.623), and 110 ppm in pelitic rocks (Shaw, 1954).

Lithium - Lithium shows greatest geochemical coherence with magnesium, although some of its chemical properties (valence, Ip and Ek values), are quite similar to those of sodium, which is, however, some 30% larger. It is only found present in two of the pyroxenes studied, so an average value would be meaningless. Lithium is reported in igneous pyroxenes (Strock, 1936; Howie, 1955; Wager and Mitchell, 1951) usually up to 50 ppm, but Strock reports some pyroxenes far in excess of this - 1,600 ppm in a ditroite rock from Norway. It is likely that any lithium in the Grenville rocks would be contained by the mica minerals, since lithium does not enter carbonate structures to any significant extent (Horstmann, 1957).

Titanium - Although the concentration factor of titanium is low with respect to its crustal abundance it is, next to manganese, the most abundant element analysed spectrochemically. The average titanium value is 330 ppm, or .075 times its average crustal abundance of 4,400 ppm. Its range is from 150 to 1,000 ppm.

The titanium concentration in the pyroxenes is considerably lower than in the amphiboles analyzed which average 757 ppm, and is much lower than igneous pyroxenes, where the range of values, obtained from several sources, is usually of the order of 1,000 to 16,000 ppm. Titanium can become a major constituent in pyroxenes: Lebedev and Lebedev (See Rankama and Sahama, 1954, p.560) report a titanaugite bearing 8.97% TiO_2.

Titanium has been discussed in an earlier section with respect to its status in the pyroxene structure. In the samples studied titanium would occupy six-co-ordinated positions in the structure, replacing ferric iron, magnesium and possibly aluminium in the augitic specimens. Cases where Ti is reported to occupy tetrahedral positions have already been discussed and require no amplification here.

Titanium must occupy lattice sites in the pyroxene structure: if augites bearing several percent of TiO_2 show only one phase present, it is reasonable to assume that concentrations of the order of 300 ppm can be readily accommodated in lattice sites.

Nickel - The nickel figures for the metamorphic pyroxenes vary over a limited range from about 5 to 40 parts per million, the mean figure being 13.7 (see Table VI). This is considerably less than the crustal abundance figure of 80 ppm. Igneous pyroxenes are usually reported in the range 50 to 300 ppm, and the metamorphic amphiboles examined show an average value of 27.5 ppm.

The affinity of Ni for ferromagnesian minerals in igneous rocks, especially early crystallizates, is well known. This is apparently because of its similarity to Mg, with which it has many chemical similarities (see Table V). There is little question that nickel replaces Mg and perhaps Fe^{+2} in the mineral structure. The paucity of Ni is, however, not so easily explained. Most sediments, except limestones and quartzites, contain at least 100 ppm Ni. The latter two types usually contain less than 10 ppm. There are, however, few other minerals in the marbles and skarns, save amphiboles and micas, that would afford a suitable site for nickel ions. It would seem that the availability of nickel in the Grenville rocks is low indeed.

Cobalt - Cobalt shows many similarities to Ni and Mg (see Table V). Its level of abundance is similar to Ni but its range of values is narrower - from 5 to 25 ppm - the mean value being close to 12 ppm.

It is somewhat more abundant in the metamorphic amphiboles (mean 22 ppm). The igneous rocks show an average value of 23 ppm (Rankama and Sahama, 1950) and shales carry about 18 ppm (Shaw, 1954). The minerals are somewhat poorer than igneous pyroxenes, in which most authorities find cobalt values of 30 to 100 ppm.

Sandell and Goldich (1943) showed that cobalt concentration varies linearly with magnesium over a wide range of and more than 500 ppm (which may be due to contamination) averages about 3 ppm. Very few exceed 5 ppm. This is very low in view of the fact that in pyroxenes from igneous rocks values up to 1,000 ppm are reported by Cornwall and Rose (1957) and Wager and Mitchell (1951).

Since even limestones and dolomites contain 10 to 20 ppm Cu, and pyroxenes are among the few silicate minerals in the rocks that can take any large amount of copper into their structure, it is a mystery where the copper went, unless the rocks were very low in copper at the outset.

Vanadium - The abundance of V in the crust is about 100 ppm (Shaw, 1954). Clays and shales contain about 120 ppm and carbonate rocks usually carry less than 10 ppm, according to Jost (1932). (See Rankama and Sahama, 1950, p.601).

In various metamorphic rocks its concentration has been found to vary from 5 to 75 ppm (Leutwein, 1939; Sahama, 1945). Leutwein believes V becomes partly mobilized during strong metamorphism.

Vanadium is one of the more abundant trace elements found in the pyroxenes. Its mean value is 31.2 ppm and its range is restricted from 9 to 63 ppm, again considerably less than in igneous pyroxenes where its abundance generally ranges from 25 to 300 ppm. Tröger (1934) reports instances as high as 1,000 ppm vanadium but does not give the source. Once again the mean for values obtained in the metamorphic amphiboles is significantly higher (57.1 ppm).

Vanadium exists in three valence states in nature; V^{+3}, V^{+4}, and V^{+5}. According to Goldschmidt (1954), in ferromagnesian minerals V^{+3} predominates, and as such would replace Fe^{+3}, whose size is similar. But Leutwein (1941) states that V^{+3} is a comparatively strong reducing agent, and would reduce the Fe^{+3} to Fe^{+2}. V^{+4}, on the other hand, is more plentiful in igneous rocks and readily replaces Ti^{+4}, Fe^{+3} and perhaps also Al^{+3}. It is probable that this also occurs in metamorphic minerals. Vanadium probably replaces iron, and to a lesser degree aluminium and magnesium in the lattice. Quinquevalent vanadium is largely restricted to the exogenic cycle, where stronger oxidation prevails.

Zirconium - Zirconium is an abundant trace element in the analysed pyroxenes, with values that range from 10 to 80 ppm, and averaging 37.7 ppm. The terrestrial abundance of Zr is 156 ppm, and Degenhardt reports the Zr content of metamorphic rocks is about equal to this figure.

The concentration of Zr in igneous pyroxenes is usually somewhat higher than in the metamorphic specimens examined by the writer: Cornwall and Rose (1957) report up to 700 ppm in pyroxenes from the Keweenawan lavas. The highest values are in aegirine: Tröger (1934), and Degenhardt (1957), report instances where Zr has approached 0.5%, i.e., 5,000 ppm in this variety.

Zr shows many similarities (radius, valence, Ip) to Ti, and according to Degenhardt a sympathetic variation can usually be shown. In the pyroxenes examined the ratio Ti:Zr is usually within the range 4:1 to 8:1, but when plotted against each other, these elements show no correlation. Ti is strongly attenuated in metamorphic pyroxenes compared to zirconium: the ratio Ti:Zr in igneous pyroxenes is as high as 100 to one (see Wager and Mitchell, 1951; Cornwall and Rose, 1957).

According to Degenhardt, among the main constituents of rocks, the pyroxenes and amphiboles are preferred hosts for Zr, presumably because they contain substantial amounts of Fe and Ti.

Manganese - Mangenese is present almost entirely in the bivalent state in natural silicates, and as such, replaces Fe^{+2}, Mg^{+2} and Ca^{+2}. According to Rankama and Sahama (1950), the replacement of Fe^{+2} is the most important of these. Mn^{+2} has an ionic radius such that it is on the borderline between the eight-fold co-ordinated and six-fold co-ordinated groups with respect to oxygen.

As a rule, igneous pyroxenes contain far more manganese than the metamorphic pyroxenes investigated, the latter averaging 1350 ppm. (See Table VIII) and having a range from 600 to 2,500 ppm approximately. The amphiboles examined show similar values, their mean value being 1,280 ppm. Igneous pyroxenes from the Keweenawan lavas contain up to 3,000 ppm Mn (Cornwall and Rose, 1957) and those from the Skaergaard intrusion up to 6,000 ppm, (according to Wager and Mitchell, 1951).

The darker-coloured pyroxenes are highest in Mn, and there is a regular diminution of Mn towards the lighter-coloured members. On the basis of the six chemical analyses made (see below) it is the darker samples that are highest in Fe. This would seem to indicate that Mn is replacing Fe in the mineral in a somewhat regular manner.

No.	Q-3	Q-87	ON-6	Q-19D-S13	Q-31A	Q19D.S14
Colour	Black	dark green	dark green	green	green	light green
Fe O%	14.51	8.49	4.36	3.89	2.66	1.51
Fe_2O_3%	3.64	1.72	2.17	.80	.88	.41
Total Fe Oxides %	18.15	10.21	6.53	4.69	3.54	1.92
Mn.ppm	2810	1015	1530	943	785	605

The analyses are listed in order of colour.

Scandium - The crustal abundance of Sc is 23 ppm. Mean concentration of Sc in the pyroxenes analysed was 8.8 ppm and approximately 12.5 ppm in the metamorphic amphiboles.

According to Oftedahl (1943) and Goldschmidt and Peters (1931) most of the scandium in the upper lithosphere is concealed in pyroxenes, amphiboles, and biotite. Oftedahl found a maximum of 150 ppm in a pyroxene from a basic igneous rock, and Cornwall and Rose (1957) report even higher values, up to 300 ppm in the Keweenawan lavas studied by them. The radius of Sc^{+3} permits its capture by Mg^{+2}, and Fe^{+2}. This, however, involves a coupled replacement, so the replacement is limited. The abundance of Sc in the exogenic cycle is considerably less than in the major cycle (see Table XI) which may also help explain its low level in the Grenville pyroxenes.

Yttrium - Yttrium, one of the most abundant of the rare earths, has a crustal abundance of 40 ppm, according to Fleischer (1955). Small amounts are frequently found in olivines, pyroxenes, amphiboles and garnets (Goldschmidt and Peters, 1931). They found these minerals to contain up to 8 ppm Y. Yttrium shows a notable tendency to form independent minerals. However, yttrian apatites, sphenes and garnets are known.

Cornwall and Rose report 100-200 ppm in the augites in their study, and Howie reports 50 to 60 parts per million in the clinopyroxenes of the Madras charnockites. The pyroxenes examined average 9 ppm, ranging approximately from 5 to 20 ppm. The five amphiboles average 12 ppm.

Yttrium resembles bivalent calcium in coordination, and it probably enters calcium sites in the lattice. But because it replaces a large ion (Ca) and its trivalency requires a coupled replacement, its substitution is limited. Yttrium also shows an affinity for fluorine compounds; but there is no significant difference in the yttrium content of pyroxenes from fluorine-rich skarns.

Tin - Although sought, tin was not found at a measurable level in any of the samples examined. According to Ottemann (1941), there is a relationship between the amount of fluorine in a rock or mineral and the amount of tin, due to the introduction of tin as the volatile tetrafluoride, $Sn\ F_4$. This

This was not detected in the present study.

Strontium - Strontium accompanies calcium in rocks and minerals of igneous and sedimentary genesis, the size, charge and chemical properties being very similar. The Sr crustal abundance is 450 ppm, and in sedimentary rocks as a whole its abundance is a little less - 610 ppm in limestones and 245 ppm in shales, according to Turekian and Kulp (1956).

Wager and Mitchell (1951) report values from 10 to 100 ppm in the Skaergaard pyroxenes, and Cornwall and Rose found from 60 to 400 ppm in pyroxenes from Keweenawan lavas but Howie found very little - usually less than 10 ppm - in the clinopyroxenes of the Madras charnockites.

The strontium values obtained range, with a few exceptions, from 20 to 120 ppm, avezaging 80 ppm. The amphiboles analysed are of the same order, their mean being 95 ppm. The values generally are higher than those given for igneous pyroxenes except for Cornwall and Rose's results, which seem to be anomalously high. In view of the abundance of Sr in the exogenic cycle (see Table XI), the writer's figures appear to be of the expected order of magnitude.

Barium - Barium shows certain geochemical similarities to strontium (see Table V) with respect to Ip, Ek, radius and valency, but is generally less abundant in nature. Barium, however, cannot enter calcium sites in minerals with the facility of strontium, because of its much greater size. Therefore, its substitution in pyroxenes is much more limited. This is found to be the case in the present study. Ba values average 11 ppm in the pyroxenes and about the same (15 ppm) in the amphiboles studied. The crustal abundance of Ba is 250 ppm (Green, 1953).

Barium does not attain much higher values in igneous pyroxenes: Nockolds and Mitchell (1948), in the Caledonian plutonic rocks, find only up to 20 ppm, and in the Skaergaard it is less than 10 ppm, except for one analysis.

Lead - In the majority of cases, the abundance of lead is about the same as, or below, the measurable level of detection of the method used. It was found in only seven analyses. In analyses Q30 and Q-31A, values of 15 and 49.8 ppm respectively were obtained. In the area from which these samples were taken, molybdenite is known to occur, and hence there is a possibility that PbS is also present. Sample Q34 also may be contaminated by sulphides. It is from a pyroxenite containing pyrrhotite, pyrite and molybdenite. Q73J is from a pyroxenite known to carry small amounts of PbS. These four analyses contain most of the Pb found in the analyses. The remaining three samples that show lead - CA-30B, CA-45, and CA-105 are not taken from sulphide-bearing rocks; they are from skarns.

There are three possibilities for the lead concentrations. First, that the lead is present in the mineral sample as foreign grains of galena, though this does not seem to be the case (see Appendix III). Secondly, the lead was absorbed by the pyroxene during formation of the sulphide minerals. This is possible for the pyroxenite rocks, which often carry small amounts of sulphide minerals. Third, the lead may be a part of the crystal structure. This may be the case with the skarn minerals.

If the latter is the case, Pb is most likely to be occupying Ca positions, in view of its size and valence.

Comparison with Igneous Pyroxenes

Table VIII gives the trace element content for eight igneous pyroxenes selected from the literature as being representative. Columns 2 and 3 give the average of values determined in the pyroxenes and amphiboles examined by the writer. The Skaergaard pyroxenes A, D and F, are respectively from the lower, middle and upper parts of the Skaergaard layered intrusion of East Greenland, analysed by Wager and Mitchell (1951). The two augites from the Keweenawan lavas are among those reported by Cornwall and Rose (1957). The last three columns are three pyroxenes of the charnockite series of Madras, India, reported by Howie (1955).

The most obvious point of difference between the igneous and metamorphic pyroxenes is the low amount of foreign elements present in the metamorphic members. This is especially true of the elements Ti, Mn, Ni, Co, Cr and V. B and Pb figures are not commonly found in the literature.

In order to compare igneous and metamorphic pyroxenes with respect to total trace element content, a scheme was devised whereby each element was weighted equally. Then the mean of these weighted values was calculated for all the elements in a given sample, in the following way: the abundance of each element (Ki) was divided by the crustal abundance figure (k_i) (See table VII). The mean (R) of these ratios for all elements in a given pyroxene gives a figure that affords a measure, for comparative purposes, of total trace element content with respect to the crust. In this way the average minor element content of each sample was assessed in terms of an independent scale of values. The calculation for sample Q-3 is as follows.

Element	Conc. in Q-3 (K_i)	Conc. in Crust (k_i)	K_i/k_i
B	16 ppm	3 ppm	5.33
Be	3	2	1.50
Ga	14	20	.70
Cr	42	100	.42
Li	0	29	.00
Ti	209	4400	.048
Ni	34	80	.42
Mo	0	1	.00
Co	30	23	1.30
Cu	3.5	70	.05
V	38.5	100	.38
Zr	60	156	.40
Mn	2810	1000	2.81
Sc	9.2	15	.60
Y	8.2	40	.20
Sn	0	2	.00
Sr	70	450	.15
Pb	0	15	.00
Ba	5.0	250	.02
			14.328

$$R = \frac{\text{Sum } \frac{K}{k}}{\text{no. of elements}}$$

$$= \frac{14.328}{19}$$

$$= .7541$$

TABLE VIII - MINOR ELEMENTS IN EIGHT TYPICAL IGNEOUS PYROXENES

Element	Mean of 38 Meta. Pyroxenes	Mean of 5 Meta. Amphiboles	Skaergaard Intrusion			Keweenawan Lavas		Charnockite Series		
			Pyroxene "A"	Pyroxene "D"	Pyroxene "F"	Augite 4-149	Augite 3-89	Augite 3709	Augite 2941	Augite 115
B	17.7	23.7	----	----	----					
Be	3.5	4.8				----	----			
Ga	10.3	35.2	3	5	10	----	----	5	10	10
Cr	51.5	51	3000	----	----	300	570	100	300	10
Li	*	*	3	----	50	----	----	4	25	40
Ti	331	758	8700	7100	16,900	5400	4200	4100	4200	5100
Ni	13.5	27.8	200	----	----	95	160	650	70	10
Mo	----	----	----	----	10	----	----	----	3	----
Co	12	21.8	60	40	15	86	75	60	50	25
Cu	2.9 **	3.6	----	500	100	320	51	----	----	----
V	31.2	57.1	300	30	----	570	520	25	400	50
Zr	37.7	65	30	50	----	80	30	----	150	200
Mn	1348	1276	1500	1700	6000	2800	2900	600	1500	3700
Sc	8.5	8.0	80	150	80	200	100	----	100	200
Y	8.9	12.8	----	----	500	90	100	----	40	150
Sr	80.4	94.8	10	80	100	200	60	----	10	----
Ba	11.2	15.4	----	10	60	40	----	----	5	10

* - measurable in so few cases an average is meaningless

** - omitting two cases of anomalous values, probably due to contamination

TABLE IX - R Values

Pyroxenes				Amphiboles		Pyroxenes (Igneous)	
Sample	R	Sample	R	Sample	R	Specimen	R
Q-3	.754	CA30B	.782	Q-7	.808	Skaergaard	
Q-7	.540	CA-44	.675	CA-47	1.186	Pyroxene A	3.024
Q-11B	.490	CA-45	.746	CA-76	.830	Pyroxene D	1.255
Q-12B	.521	CA-46	.733	CA-92B	1.436	Pyroxene F	1.902
Q-13B	.315	CA-47	1.128	ON-3A	.817	Keweenawan	
Q-16B	.565	CA-49	.566			Augite 4-149	2.989
Q-16D	..759	CA-53	.575	Mean	1.012	Augite 3-89	2.084
Q-19D-S13	.441	CA-56	.503				
Q-19D-S14	.392	CA-63A	.789			Charnockites	
Q-24C	.770	CA-65	.743			Pyroxene 3709	.990
Q-25	.467	CA-74	.796			Pyroxene 2941	1.882
Q-27	.486	CA-76	.766			Pyroxene 115	1.975
Q-30	.435	CA-92B	.777				
Q-31A	.892	CA-105	.476			Mean	2.016
Q-31B	.893						
Q-31C	.742	ON3A	.621				
Q-34	1.862	ON6A	.615				
Q-64	.785						
Q-69	.749	Mean	.664				
Q-73J	1.479						
Q-85	.759						
Q-87	.542						

Table IX gives the R values for the pyroxenes, for the amphiboles and for the igneous pyroxenes from Table VIII.

It is seen that the general level of minor element content (R) in metamorphic pyroxenes is significantly lower than in amphiboles or igneous pyroxenes. In metamorphic pyroxenes the mean of all values of R is .664, whereas in the amphiboles of the same rocks it is somewhat higher ($R = 1.012$) for the same group of elements. Ih the igneous pyroxenes, minor element content is yet higher, the mean of R for these minerals being 2.016. The standard deviation of R was also calculated and is of the same order in all three cases, when expressed as a percentage of the respective means.

TABLE X - MEANS AND STANDARD DEVIATIONS OF R

	R mean	S.D.	%
Metamorphic pyroxenes	.664	.2812	42%
Igneous pyroxenes	2.016	.7202	35
Metamorphic amphiboles	1.012	.3307	32

As was pointed out in an earlier section, one does not expect the concentrations of minor elements to approach the crustal abundance figures, since the minor element composition of a mineral such as a pyroxene is governed by other factors more influential than the mere availability of elements in the lithosphere. The crustal abundance figures do, however, afford a yardstick that can be used for purposes of qualitative comparison and evaluation. Since in the igneous pyroxene analyses the data are taken from a variety of sources, analysed by different methods, further interpretations must be made with caution.

Minor Elements in Sedimentary Rocks

It should be recalled that the distribution of the minor elements in the sedimentary rocks, per se, is for some elements quite different from their concentrations in the crust. The abundances of the elements in the principal types of sediments is given in Table XI; the sources are given in the last column.

Any discussion involving figures for sediments is complicated by the widely varying concentrations in different kinds of sediments, and a figure for an "average sediment" becomes meaningless because of the wide variation of assemblages possible. However, the bulk composition of sediments is influenced to a large degree by the clays or shales, which make up 60 to 80% of all sediments, according to various estimates (Mason, 1952). Also, they generally contain more of a given minor element than the arenaceous or carbonate rocks.

Bearing these facts in mind, a comparison of Tables VII and XI shows that sedimentary rocks contain much more B than the average igneous rock. Barium is also somewhat more abundant. Copper and Mn have a lower concentration. For most other elements listed the concentration in the average igneous rock and sedimentary rocks is about the same, at least with respect to shales. Certain areas of the Grenville, however, are relatively high in carbonate sediments, and this is the case in Western Quebec, north of the Ottawa River. Such a sediment would, in bulk, have a lower concentration of most trace elements, save perhaps boron, which has an extremely high concentration in shales relative to other rock types.

Since the minor element content of the metamorphic pyroxenes is less than that in pyroxenes of igneous origin, for all elements except boron, it is proposed that their minor element content has been influenced by the bulk composition of the country rocks.

TABLE XI - ABUNDANCES OF SOME ELEMENTS IN SEDIMENTARY ROCKS

(in ppm)

Element	Shales	Sandstones	Carbonates	Source
B	310	9-30	3	Rankama and Sahama, 1950
Be	3	0	0	" " "
Ga	19	5	5	Shaw, 1954; Goldschmidt, 1954
Cr	110	---	2	Shaw, 1954; Rankama and Sahama
Li	66	17	0	Horstmann, 1957
Ti	4300	960	0	Rankama and Sahama
Ni	64	2-8	0	Shaw, 1954; Rankama and Sahama
Mo	1	0	0.5	Kuroda and Sandell, 1954
Co	18	0	0	Shaw, 1954; Rankama and Sahama.
Cu	18	---	10-20	Shaw, 1954; Rankama and Sahama
V	120	20	10	Rankama and Sahama.
Zr	170	200 +	20±	Degenhardt, 1957
Mn	620	tr	385	Rankama and Sahama
Sc	13	1	0	Shaw, 1954; Rankama and Sahama
Y	44	1.6	0	Shaw, 1954; Rankama and Sahama
Sn	11	---	---	Onishi and Sandell, 1957
Sr	245	20	610	Turekian and Kulp, 1956
Pb	20±	6	9	Wedepohl, 1956
Ba	460	170	120	Rankama and Sahama

Element Trends

Three possible relations between properties and compositions were investigated. These were:

i) variation of minor element content with colour,

ii) variation of minor element content with rock type,

iii) variations between different pairs of elements.

Colour - In the pyroxene family, colour varies considerably with proportions of major constituents. Diopside is usually pale green to white, but with increasing amounts of iron and aluminium, the composition changes to augite or salite, and the colour changes to a dark green or black in hand specimen. The colour of grains under the binocular varies from colourless through green to dark green.

When arranged in order of colour some interesting changes in minor element content are observed. With decreasing colour (i.e. lighter colour) some elements are seen to show a decreasing abundance. Be, Mn, Ga, Ni, Co, Sc, V, Zr, and Ti all show a decrease. Of these, those showing the most regular diminution are Mn, Ni, Co, V, and Ga.

Chemical analyses were available for only six of the samples. These samples showed a range of colour from pale green to almost black. As was expected, they showed an increasing Fe (total oxides) content from 1.92 to 18.15% with deepening of colour. It seems then to be a reasonable, but unproved assumption to say that Fe is the major colour control of the mineral, and to conclude that the ferride elements that show an increase in concentration in darker samples are accompanied by a concomitant increase in Fe content.

Whether the decrease in Ca content is associated with a decrease in Fe or Al is difficult to decide on the basis of the six chemical analyses available. Al also shows a variation with colour, but the range of Al values is much narrower. This has been discussed on an earlier page (see section on gallium).

Other elements (B, Y, Sr, Ba, Cu, and Cr) show no clear trend. Y, Sr, and Ba, show some sympathetic variation with Ca in many minerals, but the amount of Ca present does not vary as much as Fe in these specimens; therefore, one would not expect the values of Y, Sr, and Ba to show as great a variation. Similarly B, which follows Si in some minerals, shows no change with darkness of colour.

Cu is generally present at a low level and no significant trend can be observed.

Cr values show very random distribution with respect to colour change.

<u>Rock type</u> - The minerals were subdivided according to the rocks from which they were taken, in order to determine if there were any significant changes in their minor element content with respect to environment. Four divisions were made:

i) Pyroxenes from hybrid igneous rocks.
ii) " " scapolite-rich skarns.
iii) " " scapolite-poor skarns.
iv) " " pyroxenite rocks.

In only two cases was a significant difference noted in element distributions in different environments. Only two are worthy of note: (i) boron attains its highest values in pyroxenes from scapolite rich skarns; (ii) pyroxenes in the hybrid igneous rocks, as a whole, carry more manganese than the skarn pyroxenes. Their range is from 1,800 to 3,000 ppm, while other pyroxenes rarely exceed 2,000 ppm.

These two facts may indicate that, first, the highly mobile boron had its origin in the skarns with the Cl and CO_2 and other volatiles, which most likely originate in the sediments at hand, as also may the boron; second, manganese is more abundant in the igneous rocks than in the sedimentary rocks of the area.

Inter-element trends - Concentrations of several pairs of elements that show similar properties to each other were plotted to see if correlations could be shown. The pairs examined this way were:

Ti	vs	V	*	V	vs	Ni	**	Ni	vs	Co	***
Ti		Zr	o	V		Co	**	Ni		Cr	o
Ti		Mn	o	V		Cr	o	Co		Cr	o
V		Zr	*	Zr		Mn	**	Sr		Ba	o
V		Mn	*	Y		Sc	O				

Good	correlation	***
Fair	"	**
Some	"	*
None		o

The relationships between V, Ni and Co are quite good, as is the Zr-Mn plot. Chromium shows an erratic distribution with respect to other elements.

As an example the plot of Ni vs Ni/Co is shown in

Fig. 2. It is interesting to note that as the amount of Ni increases, the ratio of Ni/Co, less than one at low concentrations, approaches and passes unity. This is the same relationship as is noted in igneous rocks. In the basic rocks, where Ni concentrations are highest, Ni exceeds Co. In the granitic rocks on the other hand, where total Ni and Co is much lower, Co exceeds Ni.

Some General Considerations

The pre-eminent fact about the present study is the low general level of minor elements in the pyroxenes of the Grenville rocks. This is true not only with respect to the eight igneous pyroxenes quoted in Table VIII, but also of most others in the literature.

Four possibilities to explain this anomaly are examined:

i) Lower temperature of formation for the minerals compared to igneous pyroxenes.

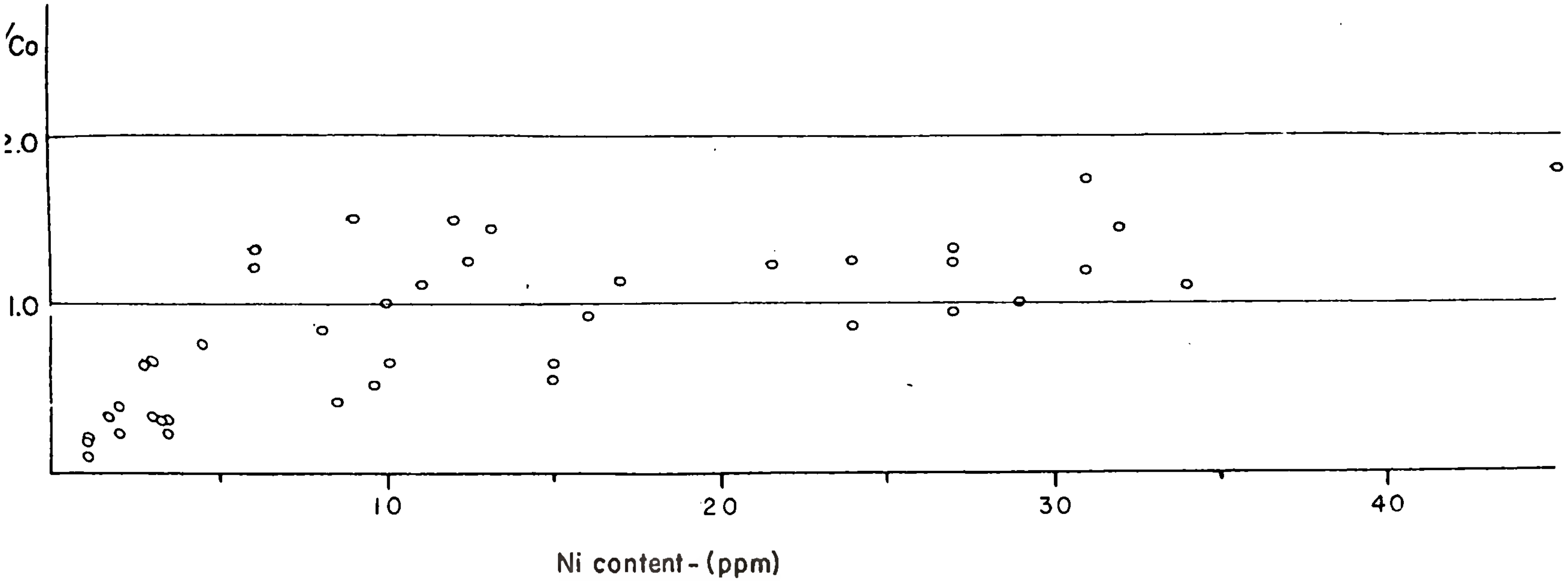
ii) Formation under conditions affording low mobilization of substances, e.g., lack of intergranular fluids.

iii) The contemporaneous formation of minerals more suitable as hosts for some elements, e.g., titanium in sphene and zirconium in zircon.

iv) A paucity of minor elements in the sediments of the Trenville at the outset, coupled with a low degree of material transfer during metamorphism.

First, the temperature of formation of the skarn zones and of the hybrid rocks cannot have been very much lower than

Fig.2 – NICKEL-COBALT RATIOS IN THE PYROXENES.



the temperature of igneous conditions, if at all. An intrusive mass generally would not be superheated, but the temperature must have been quite high during its emplacement. It has been recognized for a long time that minerals will tolerate foreign substances at elevated temperatures that they will not accept at lower temperatures, where the structure is less elastic - this is demonstrated by exsolution phenomena. It is difficult to make a case of this sort for the metamorphic pyroxenes - their temperature of formation must have been close to igneous temperatures.

Secondly, the possibility exists that the minerals formed under conditions that afforded a low degree of mobilization. Presumably in the skarn zones, (though not in the hybrid rocks), some mineral transformations took place in the solid state. According to Buerger (1948) the activation energy of metals in crystal growth is about twice the energy required to diffuse them through the crystal structure. Therefore, when a crystal grows there is already a high level of diffusive energy present. Now if this diffusive power is present, combined with the presence of an intergranular vapour or fluid, the mobility of elements, though still varying according to their individual capacity for mobilization, (the E-value of Wickman (1943)), will be quite high. The presence of such substances as F, Cl, and CO_2 in the skarn minerals would seem to indicate that an intergranular phase of some kind would have been present. From these two considerations it appears that temperature and chemical conditions afforded adequate opportunity for elements to locate in the newly-forming crystals.

A third question that arises in the case of two elements in particular (Ti and Y) is that of contemporaneous formation of minerals more suitable as hosts for these elements, namely sphene, and to a lesser degree, allanite. In some skarn zones, sphene is very abundant, but the Ti content of the pyroxenes is still far below that of igneous pyroxenes. Usually one considers that a mineral of a particular element will form when other minerals are saturated with respect to it. On the other hand, if energy conditions are suitable, an element will seek one mineral phase to the exclusion of all others. Such considerations, however, involve the question of phase equilibria of multiple-component systems, a matter beyond the scope of the present study. This question only concerns the element Ti, and possibly Y and Zr in a few cases, so does not apply to the problem as a whole.

If the power of mobilization existed, as has been discussed above, and if, as has been shown, the pyroxenes were capable of absorbing more foreign substances, and if in the majority of cases, the elements have not located in other minerals to a significant degree, the answer to the problem of why the minerals do not carry higher concentrations of minor elements must lie in the fact that the elements were not present in sufficient quantity when the minerals formed. What was the source of the minor elements that are present? There are two possibilities: the Grenville sediments or the intrusive bodies. Igneous rocks, on the whole, bear more of the elements under discussion, save boron, than sedimentary rocks, and their pyroxenes are accordingly higher in minor element content. Thus one concludes that the sources must have lain in the original sedimentary rocks and not much introduction of material from the igneous rocks has taken place. In other words, there was no source rich enough to provide the elements in the abundances encountered in the pyroxenes of igneous rocks.

The abundance of boron found in the minerals is noteworthy. It may originate as emanations from the intrusive rocks or may have been present in the original sediment. In view of the abundances of boron given by various writers for igneous rocks of all types (1 to 5 ppm) and in view of the abundances it attains in sedimentary rocks (see Table XI), it seems likely that the boron, a small easily mobilized ion, had its origin in the sediments. That boron may arise from magmatic emanations has long been recognized, and is indeed possible in the present case. However, considering Goldschmidt's evidence of intrusive rocks which have been enriched in boron by their host rocks, it seems very likely that boron originated in the sediments.

From the small amount of work done on establishing trends between minor and major elements, the minor elements seem to follow the same major elements in the metamorphic minerals as they do in igneous minerals. This would seem to be entirely reasonable, but is not a safe general conclusion from the evidence seen.

VII. CONCLUSIONS

The minor and trace elements present appear to be in the lattice structure of the minerals. The possibility that they are present in the lattice voids was examined in the light of Fairbairn's "packing index" concept and the work of Pearson (1955) and found not to account satisfactorily for their concentrations. Sample impurities do not account for the concentrations measured.

In accordance with the views of most workers, it appears that the proportions of the minor elements in the minerals studied vary not only according to their availability but also according to their suitability as lattice building components.

Several elements show a diminution with lighter colour, and from the chemical analyses it is seen that iron content is an important colour control. Hence there is some evidence that minor element content is dependent upon major element composition, insofar as Fe is concerned. This is not a well-defined conclusion, since it is based on only six chemical analyses.

A few pairs of elements show sympathetic relationships in their concentrations: these include V-Ni, Ni-Co, Co-V, and Zr-Mn. No inverse relationships were noted between pairs of elements.

The metamorphic pyroxenes have a considerably lower minor element content than their igneous counterparts; it is concluded that this is because their composition has been governed to a large degree by the availability of elements in the

Grenville sediments.

There is little difference between the pyroxenes from the different rock-types sampled. The hybrid rocks, the scapolite-rich skarns, the scapolite-poor skarns, and the pyroxenite rocks all show about the same level of element content in their pyroxenes, with two exceptions: boron attains a higher concentration in scapolite-rich skarns than in other rocks, and manganese is somewhat higher in hybrid rocks than in other types. These two facts have been discussed.

The pyroxenes examined show less minor element content than the amphiboles of the same rocks, on comparison with the analyses of five amphiboles. It is concluded that the amphiboles, due to their more complex bonding relationships, and consequently less rigid structure, show a greater tolerance for foreign components, under similar conditions of formation. This is in accordance with the views of Goldschmidt, Ramberg, and others.

APPENDIX I - SAMPLE LOCATIONS

Sample	Township	Con.	Lot	Geology of Sample Location
Q-3	Grand Calumet	VII	28	Pyroxene granodiorite rock.
Q-7	Huddersfield	V	19	Calcite-sphene-amphibole skarn.
Q-11	"	IV	20	Scapolite-augite-sphene skarn.
Q-12B	"	V	19-20	" " " " .
Q-13	"	IV	20	" " " " .
Q-16B	"	V	16-17	" " -calcite skarn.
Q-16D-5	"	V	"	" " -sphene skarn.
Q-19D-S13	"	V	22	" " -calcite " .
Q-19D-S14	"	V	"	Pyroxenite (diopside)- transitional to diopside-phlogopite marble.
Q-24C	Clapham	II	38	Quartz-scapolite-microcline-augite skarn.
Q-25B	Leslie	IV	48-49	
Q-27	Huddersfield	V	29	Scapolite-augite skarn.
Q-30	Clarendon	XIII	3	" " " . Molybdenite occurs on this property.
Q-31A	"	"	3	Pyroxenite-with some calcite.
Q-31B	"	"	"	Scapolite-microcline-epidote skarn.
Q-31C	"	"	"	Scapolite-augite-sphene skarn.
Q-34	Masham	X	55	Pyroxenite (diopsidic)- some sulphides-pyrite, molybdenite, occur on property.

Sample	Township	Con.	Lot	Geology of Sample Location
Q-64A	Sicotte	I	27	Pyroxene tonalite.
Q-69	Mitchell	On Gatineau R.		Pyroxene syenite.
Q-73J	Baskatong	II	29	Pyroxenite (diopside) - A conformable sequence of metasediments. Rock locally carries disseminated galena and spahlerite.
Q-85	Huddersfield	IV	26	Scapolite-augite skarn.
Q-87	"	V	16-17	" " -calcite skarn.
CA-30	Grand Calumet	VII	25	Scapolite-augite skarn - near a gabbro contact.
CA-44	" "	"	28	Pyroxene-syenite rock.
CA-45	" "	"	"	Pyroxene syenite rock.
CA-46	" "	"	"	Vug crystals of pyroxene from a pegmatite.
CA-47	" "	"	"	Pyroxene granodiorite rock.
CA-49	" "	"	30	" syenite rock.
CA-53	" "	"	32	Pyroxene granite rock.
CA-56	" "	North Range	13	Scapolite-pyroxene skarn.
CA-63A	" "	VI	31	Scapolite-augite skarn.
CA-65	" "	VI	33	Sphene-scapolite-augite skarn. Rock is 60% sphene.
CA-74B	" "	VIII	32	Scapolite-augite skarn. Also some sphene.

Sample	Township	Con.	Lot	Geology of Sample Location
CA-76	Grand Calumet	VIII	33	Skarn-Sphene-Pyroxene-quartz-plagioclase.
CA-92B	" "	VI	29-30	Pyroxene-hornblende rock.
CA-105	" "	V	22	Diopside-phlogopite-calcite skarn.
ON-6A	Monmouth, Ont.	16	13	Scapolite-augite skarn.
ON-3	Lyndock, Ont.	16	13	Froma scapolite skarn in nepheline syenite.

APPENDIX II - IMPURITIES IN SAMPLES

Sample	Foreign Grains	Intergrowth and Staining	Alteration
Q-3	none detected	none detected	fresh
Q-7	" "	" "	"
Q-11B	" "	" "	"
Q-12B	sphene and amphibole less than .2%	" "	"
Q-13	none detected	" "	"
Q-16B	" "	some graines Fe-stained (5%)	"
Q-16D	sphene grains, <.1%	none detected	"
Q19D-S13	none detected	" "	"
Q19D-S14	very rare grains of allanite	" "	"
Q-24C	quartz and occ. sphene, <.2%	" "	"
Q-25B	none detected	" "	"
Q-27	" "	Fe stains on 3-5% of grains	"
Q-30	allanite and biotite less than .1%	none detected	"
Q-31A	rare foreign grains less than .1%	" "	"
Q-31B	flakes of phlogopite (.1%)	" "	"
Q-31C	" " "	" "	"
Q-34	hornblende, epidote uralite? <1%	1% show intergrowths of biotite and hornblende 5% Fe-stained	"
Q-64A	1/2 - 1% sphene	none detected	"
Q-69	Rare grains of quartz	" "	1% altered

Sample	Foreign Grains	Intergrowth and Staining	Alteration
Q-73J	Sphene grains - <.1%	1-2% of grains show fine impurities	fresh
Q-85	" " - app. .2%	none detected	"
Q-37B	Allanite and sphene - 1% or less	5% of grains show Fe staining	some grains slightly altered
CA-30	muscovite flakes .1% app. rare calcite grain	1% Fe-stained	fresh
CA-44	sphene, garnet 2%	2% show intergrowths of quartz. 3-5% Fe-stained	10% of grains show slight alt.
CA-45	none detected	5-10% show Fe staining	5-10% show slight alt.
CA-46	" "	none detected	5% show alt. on edges.
CA-47	" "	" "	fresh
	Very dark - perhaps some allanite or sphene not visible.		
CA-49	Rare allanite and quartz. <.2%	2% show Fe stains	fresh
CA-53	none detected	none detected	"
CA-56	" "	10% Fe-stained	"
CA-63A	allanite <1%	3-5% Fe-stained	"
CA-65	biotite flakes - 3%. Rare zircon grains	10% Fe-stained	5% slightly alt.
CA-74B	Sphene and other dark grains. Many are probably dark pyroxene grains. Less than .5%	none detected	fresh
CA-76	biotite flakes, allanite (?) Less than .2%	" "	"

APPENDIX II - continued

Sample	Foreign Grains	Intergrowth and Staining	Alteration
CA-92B	none detected	rare red staining	fresh
CA-105	" "	none detected	"
ON-3A	biotite flakes, and rarely allanite. .5-1%	" "	"
ON-6A	rare foreign grain	" "	"
Amphiboles			
Q-7	none detected	none detected	fresh
CA-47	" " (Very dark- perhaps some pyroxene not visible)	" "	"
CA-76	none detected	none detected	"
CA92-B	occasional grain of augite	" "	"
ON-3A	biotite flakes - less than 1%	" "	"

APPENDIX III - MULTIPLE ANALYSES, WITH ACCEPTED VALUES

	Be^2			Ga^3				Ti^4				Mn^2			Pb^2		
R	.35			.62				.68				.80			1.20		
Sample	A	B	Accepted	A	C	B	Accepted	B	C	D	Accepted	D	C	Accepted	A	B	Accepted
Q-3	tr	5	5	1.0	4.60	14	14	236	<200	215	208.7	3520	2100	2810	ND	ND	ND
Q-7 pyr.	<1.0	1.5	1.5	2.0	5.9	6.2	6.2	710	605	520	612	910	545	728	tr	tr	tr
Q-11B	tr	1.8	1.8	< 1	5.8	6.4	6.4	285	<200	241	234	1210	700	955	3.0	2.0	2.5
Q-12B	tr	1.5	1.5	<1.5	6.5	8.8	8.8	540	370	400	457	1240	795	1018	18	23	20.5
Q-15B	tr	1.5	1.5	2.0	3.8	5.6	5.6	345	220	336	300	990	900	945	tr	tr	tr
Q-16B	tr	1.5	1.5	4.1	11.8	10.0	10.0	190	<150	177	164	1850	1170	1500	<10	tr	tr
Q-16D	tr	1.6	1.6	3.2	16.5	9.6	9.6	250	200	220	223	1890	1200	1545	ND	ND	ND
Q-19D-S13	tr	tr	tr	ND	2.51	11.5	11.5	190	150	180	165	1130	765	945	ND	ND	ND
Q-19D-S14	tr	ND	tr	ND	ND	ND	ND	230	200	220	235	740	470	605	ND	ND	ND
Q-24C	3.5	8.9	8.9	6.4	14.5	12.5	12.5	370	264	310	315	2390	1680	2185	ND	ND	ND
Q-25B	tr	1.1	1.1	1-	7.4	10.8	10.8	257	<200	209	214	1150	710	930	<10	tr	tr
Q-27	1.0	2.65	2.65	1.8	tr	5.6	5.6	190	<150	220	178	1150	700	915	tr	tr	tr
Q-30	tr	<7	< 7	5.5	16.5	10.5	10.5	175	<200	100	150	910	545	728	9.0	21.0	15.0
Q-31A	tr	tr	tr	tr	2.50	11.5	11.5	290	225	209	241	960	650	785	52.5	47.0	49.8
Q-31B	ND	tr	tr	<1.5	5.6	9.0	9.0	285	<200	241	234	950	615	875	72	78	75
Q-31C	ND	1.5	1.5	2.5	6.7	13.5	13.5	740	990	860	865	945	680	815	32	30	31

APPENDIX III - continued

R	Be^{2} .35			Ca^{3} .62				Ti^{4} .68				Mn^{2} .80			Pb^{2} 1.20		
Sample	A	B	Accepted	A	C	B	Accepted	B	C	D	Accepted	D	C	Accepted	A	B	Accepted
Q-34	2.2	2.0	2.0	ND	3.51	5.6	5.6	195	150	176	165	935	625	780	375	310	345
Q-64A	1.3	4.5	4.5	2.9	5.9	6.7	6.7	435	410	418	421	1830	1250	1540	tr	ND	tr
Q-69B	3.05	6.5	6.5	8.2	15.5	11.7	11.7	208	410	320	313	2900	1620	2260	tr	tr	tr
Q-75J	6.7	11.5	11.5	ND	ND	ND	ND	250	320	282	284	2030	1870	1895	221	210	215.5
Q-85	ND	tr	tr	12	21.5	26.6	26.6	440	320	300	353	720	450	585	ND	ND	ND
Q-87B	tr	tr	tr	2	15	10.5	10.5	153	<150	180	168	1170	860	1015	10	tr	tr
CA-30B	tr	1.75	1.75	45.0	6.6	7.3	7.3	227	390	342	320	1100	690	895	62.3	55.0	59.1
CA-44	1.38	3.6	3.60	4.5	9.0	8.0	8.0	226	<200	172	191	2100	1150	1625	19.5	11.0	15.5
CA-45	6.1	3.85	3.85	6.4	10.2	9.4	9.4	175	<150	193	164	2925	1690	2308	<3	<3	<3tr
CA-46	1.9	9.1	9.1	6.4	25	17.5	17.5	295	<300	237	236	2230	1265	1785	tr	tr	tr
CA-47	12.4	19.0	19.0	14.0	21.5	20.0	20.0	175	<150	195	165	3620	2050	2835		15.0	15.0
CA-49	1.50	5.42	5.42	1.50	5.9	6.4	6.4	253	<150	275	219	1600	1400	1500	7.5	11.0	9.0
CA-55	1.8	4.3	4.3	5.0	9.3	8.0	8.0	253	<200	175	203	2320	1370	1845	tr	tr	tr
CA-56	tr	tr	tr	tr	8.0	22.5	22.5	204	665	562	477	1295	840	1068	ND	ND	ND
CA-65A	<1.0	2.0	2.0	tr	12.8	15.7	15.7	250	220	225	232	1710	1075	1390	tr	ND	tr
CA-65	1.70	4.30	4.3	6.8	11.8	12.2	12.2	375	270	295	315	1800	1110	1455	tr	tr	tr

APPENDIX III - continued

	Be[2]			Ca[3]				Ti[4]				Mn[2]			Pb[2]		
R	.35			.62				.68				.80			1.20		
Sample	A	B	Accepted	A	C	B	Accepted	B	C	D	Accepted	D	C	Accepted	A	B	Accepted
CA-74B	tr	tr	tr	1.0	21.7	16.3	16.3	250	485	430	588	1980	1080	1500	ND	ND	ND
CA-76	tr	5.9	5.9	15.0	46	26.0	26.0	<1000	1100	950	955	1210	700	955	ND	ND	ND
CA-92B	2.0	9.1	9.1	2.0	5.3	7.4	7.4	370	260	242	291	2320	1440	1880	tr	ND	tr
CA-105	tr	1.5	1.5	ND	ND	ND	ND	125	<150	180	165	1710	860	1285	25.5	34.0	29.7
ON-3A	1	1.0	1.0	4.0	14.5	18.7	18.7	>1000	735	640	703	1190	845	1018	tr	tr	tr
ON-6A	5.0	9.0	9.0	3.5	20.4	18.7	18.7	290	245	237	257	1600	1260	1550	3*	tr	tr
Amphiboles																	
Q-7	tr	tr	tr	<2.0	5.9	32	32	>1000	650	555	645	870	570	720	ND	ND	ND
CA-47	2.60	6.0	6.0	14	21.5	47	47	>1000	755	648	711	2740	1600	2170	tr	4.0	tr
CA-76	tr	tr	tr	15	46.0	62	62	>1000	1950	860	1167	895	520	708	ND	ND	ND
CA-92B	<1.0	13.5	13.5	13.5	62.5	24.2	24.2	>700	620	535	585	2210	1370	1790	ND	ND	ND
ON-5A	<1	4.5	4.5	4	14.5	21	21	>1000	650	530	660	1150	340	995	ND	ND	ND

See notes on following page.

Notes on Appendix III - Multiple Analyses, with the Accepted Values.

Notes: Letters A, B, etc., refer to the respective lines of the elements as listed in Tables 3 and 4.

Beryllium "B" line was found to be more sensitive line, and yielded a more statistically reliable working curve; for this reason it was accepted.

Gallium "B" line, using indium as internal standard and argon-oxygen atmosphere, yielded a much more reliable line than "A" or "C", and it was useful over a wide range of values. This line was developed after the other two were used, and proved more acceptable.

Titanium in some cases shows considerable differences on its lines, although the working curves show about the same degree of error. While the "B" line has a slightly higher relative error "E", lines "C" and "D" are less sensitive at lower values where "B" is useful. It was decided that the mean of the three values was a sound approximation.

Manganese was measured on two lines, "C" and "D". Since both lines show the same error and sensitivity, values were averaged to produce the accepted value.

Lead has two lines, "A" and "B" of equal usefulness. The two lines, A and B, behave in a parallel manner, usually showing similar dy values. For these reasons, values were averaged to produce the accepted value.

BIBLIOGRAPHY

1. Ahrens, L.H., (1950). Spectrochemical analysis; Addison-Wesley Publishing Co., Inc., Cambridge, Mass.
2. ____________, (1952). The use of ionisation potentials, Part I. Geochim et Cosmochim. Acta, Vol.2, pp. 155-169.
3. ____________, (1953). The use of ionisation potentials. Part II. Geochim et Cosmochim. Acta. Vol.3, pp. 1-29.
4. ____________, (1954). Quantitative spectrochemical analysis of silicates. Pergamon Press, London.
5. Barth, T.F.W., (1931). Pyroxen von Hiva Oa, Marquesas Inseln und die Formel titanhaltiger Augit. Neues Jahrb. Min., Abt A, Bl.-Bd. 64, pp. 217-224.
6. Berman, H., (1937). Constitution and Classification of Natural Silicates. Am. Min., v. 22, pp.333-415.
7. Bragg, W.L., (1937). The Atomic Structure of Minerals. Cornell University Press, Ithaca, N.Y.
8. Brown, G.M., (1957). Pyroxenes from the middle and early stages of fractionation of the Skaergaard intrusion, East Greenland. Mineral. Mag., v.31, pp. 511-543.

9. Cornwall, H.R., and Rose, H.J., (1957). Minor elements in Keweenawan Lavas, Michigan. Geochim. et Cosmochim. Acta, v.12, pp. 209-224.

10. Degenhardt, H., (1957). Untersuchungen zur geochemischen Verteilung des Zirkoniums in der Lithosphäre. Geochim. et Cosmochim. Acta, v.11, pp.279-309.

11. DeVore, G.W., (1955). The role of adsorption in the fractionation and distribution of elements. Jour. Geol., v.63, pp. 159-190.

12. Dittler, E., (1929). Zur Frage der Oxydationsstufe des Titans in den Silikaten (abstract). Min. Abstracts, v.4, pp. 308-309.

13. Dixon, B.E., and Kennedy, W.Q., (1933). Optically uniaxial titanaugite from Aberdeenshire. Zeits. Krist., v.36, pp. 112-120.

14. Dixon, W.J. and Massey, F.J., (1951). Introduction to Statistical Analysis. McGraw-Hill Book Co., Inc., Toronto.

15. Doerffel, K., (1953). Die Bedeutung der Gitterenergie für die Mineralogie. Freiburger Forschungshefte, Hefte 5, pp. 68-72.

16. Dresser, J.A. and Denis, T.C., (1944). Geology of Quebec, v.2. Quebec Dept. Mines, Geol. Rept. 20.

17. Fairbairn, H.W., (1943). Packing in Ionic Minerals. Geol. Soc. America, Bull., v.54, pp.1305-1374.

18. Faust, G.J., (1936). The fusion relations of iron-orthoclase. Am. Min., v.21, pp. 735-763.

19. Fleischer, M., (1955). Estimates of the abundances of some chemical elements and their reliability. Geol. Soc. America, Spec. Paper 62, (Crust of the Earth), pp. 145-54.

20. Ford, W.E., (1932). Dana's Textbook of Mineralogy, 4th Ed.: John Wiley and Sons, Inc., New York.

21. Fyfe, W.S., (1951). Isomorphism and bond type. Am. Min., v. 36, pp. 744-757.

22. Goldschmidt, V.M., (1954). Geochemistry: Clarendon Press, Oxford.

23. ____________, and Peters, Cl., (1931). Zur Geochemie des Scandiums. Ges. Wiss. Göttingen, Nachr., Math.-Phys. Kl., p.257.

24. ____________________________, (1932). Zur Geochemie des Berylliums. Ges. Wiss. Göttingen, Nachr., Math.-Phys. Kl., pp. 360-376.

25. Green, Jack, (1953). Geochemical table of the elements for 1953. Geol. Soc. America, Bull., v.64, pp. 1001-1012.

26. Harrison, G.R., (1939). M.I.T. Wavelength Tables; John Wiley and Sons, New York.

27. ____________, (1949). Chemical Composition and optical properties of common clinopyroxenes, Part I. Am. Min., v.34, pp. 621-666.

28. ______________, (1952). Orthopyroxenes of the Bushveld type, ion substitutions and changes in unit-cell dimensions. Am. Jour. Sci., Bowen Volume, pp. 173-187.

29. Hawley, J.E., and MacDonald, G., (1956). Quantitative spectrochemical analysis of some silicate rocks and iron-ores with the Stallwood air-jet. Geochim. et Cosmochim. Acta., v.10, pp. 197-223.

30. Hess, H.H., (1941). Pyroxenes of common mafic magmas. Am. Min., v.26, pp. 515-535 and 573-594.

31. Honerjäger-Sohm, M, and Kaiser, H, (1944) Berucksichtigung des Untergrundes bei der Messung von Intensitatsverhaltnissen. Spectrochim. Acta., v.2, pp. 396-416.

32. Horstman, E.L., (1957). The distribution of lithium, rubidium and caesium in igneous and sedimentary rocks. Geochim. et Cosmochim. Acta., v.12, pp. 1-28.

33. Howie, R.A., (1955). The geochemistry of the charnockite series of Madras, India. Trans. Royal. Soc. Edinburgh, v.62, pt.III, no.18.

34. Jost, K., (1932). Uber den Vanadiumgehalt der Sedimentgesteine und sedimentären Lagerstätten. Chemie der Erde, v.7, pp. 177-290.

35. Kunitz, W., (1936). Beitrag zur Kenntniss der magmatischen Assoziationen, III. Die Rolle des Titans und Zirkoniums in den gesteinsbildenden Silikaten. Neues Jahrb. Min. Geol., Bl.-Bd. 70, Abt.A, p.385.

36. Kuno, H., (1954). A study of orthopyroxenes from volcanic rocks. Am. Min., v.39, pp. 30-46.

37. ____________, (1955). Ion substitution in the diopside-ferropigeonite series. Am. Min., v.40, pp.70-93.

38. Kuroda, P.K., and Sandell, E.B., (1954). Geochemistry of molybdenum. Geochim. et Cosmochim. Acta, v.6, pp. 36-63.

39. Larsen, E.S., and Berman, H., (1934). Microscopic Determination of the Non-opaque Minerals. U.S. Geol. Surv., Bull. 848.

40. Mason, B., (1952). Principles of Geochemistry. John Wiley and Sons, Inc., New York.

41. Mood, A.M., (1950). Introduction to the Theory of Statistics. McGraw-Hill Book Co., Inc., Toronto.

42. Muir, I.D. (1950). The clinopyroxenes of the Skaergaard Intrusion, eastern Greenland. Mineral. Mag., v.29, pp. 690-714.

43. Nockolds, S.R., and Mitchell, R.L., (1948). The geochemistry of some Caledonian plutonic rocks. Trans. Roy. Soc. Edinburgh, v.61, pp.563.

44. Oftedahl, I., (1943). Scandium in biotite as a geological thermometer. Norsk. Geol. Vids, v.23, p.202.

45. Onishi, H., and Sandell, E.B., (1957). Meteoritic and Terrestrial Abundance of Tin. Geochim. et Cosmochim. Acta, v.12, pp. 262-270.

46. Osborne, F. Fitz, (1944). Calumet Island Area. Dept. Mines Quebec, Geological Rept. 18.

47. Ottemann, J., (1941). Untersuchungen zur Verteilung von Spurenelementen, insbesondere Zinn, in gesteinsbildenden Mineralien des Harzes. Zeit. angerv. Mineralien, v.3, p. 142.

48. Pearson, G.R., (1955). A geochemical study of sillimanite, andalusite and kyanite. Unpublished M.Sc. thesis, McMaster University, pp. 53.

49. Ramberg, H., (1952). Chemical bonds and the distribution of cations in silicates. Jour. Geol., v.60, pp. 331-355.

50. Rankama, K., and Sahama, Th.G., Geochemistry: University of Chicago Press, Chicago, Ill. 912 pp.

51. Ringwood, A.E., (1955). The principles governing trace element distribution during magmatic crystallization. Geochim. et Cosmochim. Acta, v.7, pp. 189-202 and 242-254.

52. Rosenquist, I., (1951). Investigations in the crystal chemistry of silicates. (see Kuno, 1955).

53. Sabine, P.A., (1950). The optical properties and composition of the acmitic pyroxenes. Mineral. Mag., v.29, pp. 113-125.

54. Sahama, Th., (1945). Spurenelemente der Gesteine im Südlichen Finnisch-Lappland. Bull. Comm. geol. Finlande 138, p.88.

55. Sandell, E.B., (1952). The beryllium content of igneous rocks. Geochim. et Cosmochim. Acta, v.2, pp. 211-216.

56. ____________, and Goldich, S.S., (1943). Rarer metals in American rocks and minerals. Jour. Geol., v.51, pp. 99-115 and 167-189.

57. Segnit, E.R., (1953). Some data on synthetic aluminous and other pyroxenes. Min. Mag., v.30, pp. 218-226.

58. Shaw, D.M., (1953). The camouflage principle and trace-element distribution in magmatic rocks. Jour. Geol., v.61, pp. 142-151.

59. ____________, (1954). Trace Elements in Pelitic Rocks, Parts I and II. Geol. Soc. America, Bull, v.66, pp. 1151-1182.

60. ____________, (1956). Geology of Some Skarn-deposits of Western Quebec. Unpublished report.

61. ____________, (1958). D.C. Spectrochemical Analysis of Silicates using the Stallwood jet. Unpublished paper.

62. ____________, and Bankier, J.D., (1953) - Statistical Methods Applied to Geochemistry. Geochim. et Cosmochim. Acta., v.5, pp. 111-123.

63. ____________, Wickremasinghe, O.C., and Yip, C., (1958). A simple device for the spectrochemical analysis of minerals in an inert atmosphere using the Stallwood Jet. Unpublished paper. In press, 1958.

64. Strock, L.W., (1936). Zur Geochemie des Lithiums. Ges Wiss Göttingen, Nachr. 4, v.1, no.15, p. 171.

65. Tröger, E., (1934). Der Gehalt an selteren Elementen bei Eruptivgesteinen - Chemie der Erde, v.9, pp. 286-310.

66. Turekian, K.K., and Kulp, J.L., (1956). The geochemistry of strontium. Geochim. et Cosmochim. Acta, v.10, pp. 245-296.

67. Wager, L.R., and Deer, W.A., (1938). Two new pyroxenes included in the system clinoenstatite, clinoferrosilite, diopside and hedenbergite. Min. Mag., v.25, pp. 15-22.

68. ____________, and Mitchell, R.L., (1951). The distribution of trace elements during strong fractionation of a basic magma. Geochim. et Cosmochim. Acta, v.1, pp. 129-208.

69. Walker, F., and Poldervaart, A., (1949). Karroo Dolerites of the Union of South Africa. Geol. Soc. Amer., Bull., v.60, pp. 591-706.

70. Warren, B.E., (1930). Structure of the amphiboles. Zeits. für Krist., v.72, p.493.

71. ______________, and Biscoe, J., (1931). The crystal structure of the monoclinic pyroxenes. Zeits. für Krist, v.80, p. 391.

72. Wasserstein, B., (1951). South African granites and their boron content. Geochim. et Cosmochim. Acta, v.1, p. 329-338.

73. Wedepohl, K.H., (1956). Untersuchungen zur Geochemie des Bleis. Geochim. et Cosmochim. Acta, v.10, pp. 69-148.

74. Wilson, M.E., (1924). Arnprior-Quyon and Maniwaki Areas, Ontario and Quebec. Geol. Surv., Canada, Mem. 136.

75. Winchell, A.N., and Winchell, H., (1951). Elements of Optical Mineralogy, pt.II: Descriptions of Minerals. John Wiley and Sons, Inc., New York. 551 pp.