MINOR ELEMENT DISTRIBUTION IN SOME METAMORPHIC PYROXENES

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ABSTRACT

Thirty-eight samples of pyroxene and five of amphiboles were obtained from a suite of skarn rocks, pyroxenites and hybrid rocks collected from various localities of the Grenville of Western Quebec and Eastern Ontario, and analyzed spectrographically for minor and trace element content. The elements, and their ranges of values were as follows: boron, 7–90 ppm; beryllium, 0–9 ppm; gallium, 0–60 ppm; chromium, trace to 200 ppm; lithium, 0–150 ppm; titanium 200–1200 ppm; nickel, 1–50 ppm; molybdenum, none; cobalt, 5–45 ppm; copper, 0–50 ppm; vanadium, 8–86 ppm; zirconium, 12–117 ppm; manganese, 600–2800 ppm; scandium, trace–15 ppm; yttrium, trace–18 ppm; tin, none; strontium, 17–450 ppm; lead, trace to 300 ppm; and barium, 1–44 ppm.

The location of the minor elements is discussed in terms of the crystal chemistry of the pyroxenes, and in terms of the known behaviour patterns of the elements in rocks and minerals. It is concluded that most of the minor components are, generally, in structural sites in the mineral.

When compared with pyroxenes of igneous genesis, the minerals are conspicuously poorer in most elements except Be, Ga, Sr, and Ba, which are at about the same level as in igneous pyroxenes; boron, however, has a higher concentration. 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 reconstitution the composition is governed by the country rock.

Calculations show that the total minor element composition of the pyroxenes is less than that of igneous pyroxenes, judging from the literature, and less than that of amphiboles from the same rocks. The method of calculation was devised so that elements were weighted with respect to their natural abundance.

INTRODUCTION

In the past few years, methods of spectrographic analysis have improved in reproducibility, precision and sensitivity to such a degree that reliable quantitative analyses can be made for many elements even at very low concentrations. A considerable number of analyses can be found in the recent literature for igneous rocks and minerals, but very few analyses are reported for metamorphic materials.

Consequently, the geochemistry of many elements is understood in the igneous, but not in the metamorphic environment. This is true of the pyroxenes, where most analytical work has been on igneous suites. The

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present study was undertaken to provide information on the trace element composition of metamorphic pyroxenes, and to compare this with the composition of igneous pyroxenes. Discussion will be limited to clinopyroxenes, since only monoclinic members are found in the rocks studied.

The Pyroxenes—Their Crystal Chemistry

Warren & Biscoe (1931) suggested as a general formula for the pyroxenes, $X_m Y_{2-m} Z_2(O,OH,F)_6$, where m tends to be zero or unity. In this general expression, m is unity for the diopside-hedenbergite series, and zero, or approaching zero, for the orthorhombic pyroxenes and the non-calcic clinopyroxenes (e.g.—enstatite, clinoenstatite, $Mg_2Si_2O_6$). It should be recalled that even in the case of the formula $Y_2Z_2O_6$, many other small ions, including X-size ions, are present in small significant amounts. Therefore, the general formula is still applicable to both orthorhombic and monoclinic members of the group.

In the mineral structure, the chains of silicon-oxygen tetrahedra are linked by cations, each of which is surrounded by six "active" oxygens, i.e., oxygens with only one of their bonds attached to a silicon atom. Calcium, however, because of its greater size has as near neighbors two of the inactive oxygen atoms, i.e., those forming links in the Si-O chains, and is therefore in eight-fold co-ordination with respect to oxygen, while a similar cation, say Mg, is in six-fold co-ordination. The Z-sites are the four-fold intratetrahedral locations. This difference in co-ordination number with its concomitant difference in size requirement is, of course, the factor that separates the various co-ordination groups X, Y, and Z in the monoclinic pyroxenes.

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

Symbol	Coordination	Ionic Radius	Ions
Z	4	.35–.64Å	Si^4, Al^3, Ti^4.
Y	6	.65–.90Å	$Mg^2Fe^2Fe^3Al^3Li^1Ti^4$
X	8	.90–1.22Å	Ca^2, Na^1, Mn^2

The clino-pyroxenes show a considerable tolerance for minor and trace elements of wide variety. Those found in the present study include B, Be, Ba, Ga, Cr, Li, Ti, Co, Cu, V, Zr, Mn, Sc, Y, Sn, Sr, and Pb.

The X-sites, normally occupied by Ca and Na, would be the sites occupied by the larger ions, such as Y, Sn, Sr, Pb, and Ba.

The *Y*-sites, commonly occupied by Mg, Fe^2, Fe^3, Al and, in spodumene, by Li, covers the range of ionic radius from .65 to .90 Å, and is suitable to the larger number of the transition group of elements. Hence, it is the *Y*-sites that afford the greatest opportunity for accommodation of foreign elements. From consideration of their radii, we could expect Ga, Cr, Li, Ni, Ti, Mo, Co, Cu, V, Zr, Mn, Sc, Y, and Sn to be suitable in this group.

The intratetrahedral (*Z*) sites are occupied by Si and Al in the main. Only a few elements are qualified 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 other factors appear to be operative. Among these, the ionization potential, the electronegativity, and the degree of polymerization of the silicon-oxygen bonds, are probably contributive in the selection of ions by the structure. These mechanisms have all been considered by investigators interested in the crystallization of minerals from a rock melt (see Ahrens, 1952; Fyfe, 1951; Doerffel, 1953) who have explained selection of ions in these terms. 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 of growth; these explanations postulate free movement of ions in the magma solution, allowing a high degree of selectivity to operate, 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 of materials takes place, indeed, must, if only on the intragranular scale, the migration of ions is greatly impeded in the metamorphic situation. 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 that the case is different from that of crystallization from a practically homogeneous magmatic solution. It is the purpose of this paper to demonstrate the effect of this factor upon trace and minor element distribution in the pyroxenes.

THE SPECIMENS

The specimens used in this study were collected from the Grenville province of Southern Quebec and Ontario (only two are from Ontario). Many were collected from an area very typical of the Grenville, the region immediately north of the Ottawa River in the counties of Pontiac and Gatineau. The Grenville province is characterized by a distinctive group of metamorphosed sedimentary rocks—crystalline limestones, quartzites, and sillimanite gneisses—any one of which may predominate at a given locality. That the rocks in different areas are contemporaneous is not yet established, so the name applies merely as a descriptive term to cover a group of lithologically similar rocks. Of the intrusive rocks, anorthosites and associated rock types are distinctive (the Buckingham Series, Wilson, 1924); younger than these are the intrusive masses of granite and syenite and their gneissic equivalents. In the area north of the Ottawa River, four main lithological groups may be recognized, according to Dresser & Denis (1944). These are, first, a series of 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 interrelated; third, batholithic masses of granite and syenite; and fourth, masses consisting of diopside, scapolite and other lime-silicate minerals formed at the contacts of the various intrusive rocks with the crystalline limestones.

The Skarns

Most of the specimens studied in this investigation were taken from this last group, called the Skarn Series by Shaw (1958). Shaw has subdivided the Skarn Series into five members, (1) hybrid rocks such as pyroxene granite and diorites; (2) fluorite-type skarns; (3) scapolite-augite skarns; (4) pyroxenite skarn rock; and (5) pink calcite-marble type skarns.

The Skarn Series represents equilibrium assemblages of minerals derived during metamorphism by means of exchanges or transfer of materials; according to Shaw, it does not seem necessary to postulate introduction of material from outside the skarn zone system to account for the mineral assemblages observed, so the group may be said to represent a chemical adjustment *in situ.*

Pyroxene, usually augite or diopside, occurs in all five of the different skarn types, in the marbles and amphibolites of the series and in the hybrid igneous rocks. The pyroxenes are thus of fairly common occurrence in the rocks of the Grenville.

Specimens

The pyroxenes were extracted from members of a suite of samples collected by D. M. Shaw while mapping and examining radioactive skarn deposits in southwestern Quebec for the Quebec Department of Mines.

Twenty-three of the pyroxene specimens were taken from scapolite-augite skarn rocks; six are from the metamorphic pyroxenite rocks; nine pyroxene specimens were separated from the hybrid intrusive rocks, and five specimens of amphibole (hornblende) were extracted from the pyroxene-bearing rocks and analyzed for purposes of comparison (see Appendix I—Sample localities). All specimens are believed to be of the amphibolite facies of metamorphism.

A brief description of the pyroxenes from the main rock types sampled follows (Shaw, 1958):

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

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

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

Pink calcite skarn rocks. These rocks contain a pale green sugary aggregate of diopside that makes up 20 per cent or less of the rock. Anhedral crystals of diopside up to two cm. in diameter are often seen. The rock may show a coarse banding of calcite, diopside and mica.

Scapolite-pyroxene rocks. The pyroxene in these rocks varies from green to black. Pleochroism is weak and its color 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, constituting more than 60 per cent of the rock. It occurs as a sugary mass of rounded grains, or as aggregates of interlocking prismatic crystals.

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

SEPARATION AND ANALYSIS

The rock samples were crushed in a steel mortar, and screened, the 100–200 mesh portion being retained for separation of the pyroxene fraction. This was accomplished by use of the Frantz electromagnetic separator and heavy liquids. In many cases magnetic separation was all that was necessary to produce a high-purity pyroxene fraction from the rock.

Two methods of spectrographic analysis were employed. For the majority of the elements sought, a method employing graphite with palladium as internal standard was satisfactory. Each sample was diluted with an equal weight of graphite containing 0.1 per cent Pd and exposures were made using an air-jet. Elements determined were Ba, Be, B, Co, Cr, Cu, Ga, Mo, Mn, Ni, Sc, Sr, Ti, V, Y, and Zr. This method has been outlined by Shaw (1960).

A second method for determining a few more elements, developed later by Shaw, Wickremasinghe & Yip (1958), yielded plates free of cyanogen bands and of very low background darkness. Elements sought using this method were Li, Pb, and Sn. Ga and Cu were also rechecked. The technique, employing an atmosphere of argon and oxygen, and using indium as internal standard, seems to have adequate reproducibility. It has been outlined at some length in the above paper.

Listed in Table 1 are the relative error "*E*" for each spectral analysis line, and the range of sensitivity of the line for the graphite matrix method. The sensitivity of each line is, in all cases, the lower limit of the range. The method of calculating the precision is that described in Mood

TABLE 1. SPECTRAL LINES, RANGE AND RELATIVE ERROR FOR GRAPHITE-MATRIX METHOD

Spectral Line		Relative Error "*E*" for Triplicate Analysis	Range of Line
B	2497.733 Å	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	12.7	1–1000
Pd	3258.780	Standard Lines	
Pd	2476.718		

Working curves calculated by regression analysis method.
Wave-lengths are those given by Harrison, *et al.* (1939).

TABLE 2. 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
Pb	A	3683.471	10–300
Pb	B	4057.820	10–300
In		3256.090	Standard Line

Working curves not calculated by regression analysis.

(1950, p. 300), given as relative error "*E*" expressed as a percentage. The precision has not been calculated for lines using the argon-oxygen method. According to Shaw, Wickremasinghe & Yip (1958), the reproducibility and sensitivity are adequate, as shown by their analyses of standard granite G-1 and standard diabase W-1. The lines used and their ranges are given in Table 2.

EXPERIMENTAL RESULTS

The analyses are listed in Table 3, accompanied by explanatory footnotes. Although lines used in the determination of Sn and Mo were quite sensitive (sensitivities 3 and 1 ppm, respectively), they were not found at a measurable level in any analysis. In a few cases they were faintly visible. Lithium is rather insensitive with the method employed (sensi-

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NOTES ON TABLE 3

All values are given in parts per million (ppm).

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

Where possible, values are given to three significant figures.

An asterisk (*) denotes that the element was sought and found not present.

Trace amounts, symbolized "tr," means the element was present, 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 spectral line used.

"Less than" (<) is used where concentration in one or two of the three replicate analyses was below a measurable level.

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

Sensitivity (*S*) is that given in Tables 1 and 2.

[1] This high copper value probably due to sample contamination.

TABLE 3. PYROXENES, SPECTROGRAPHIC ANALYSES

	B^3	Be^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

tivity 30 ppm). Although it attains measurable values in only four analyses, it may also be present in other cases.

Ti and Mn are seen to be the most abundant minor elements present. These elements were both measured on more than one line and the mean value listed in Table 3. The mean was adjudged, from considerations of relative error, to be a statistically sound approximation in both these cases.

Purity of Samples. In spite of reasonable precautions, it was impossible to separate completely all foreign grains from pyroxene in some samples. This is especially true in the case of minerals with similar magnetic susceptibility and specific gravity, such as amphiboles, zircon, and allanite. In a heavy liquid separation small numbers of foreign grains may remain in a suspended fraction despite agitation. These could affect the results; for instance included sphene and zircon will affect the Ti and Zr values significantly.

As a check on whether the minor element values of the pyroxenes were influenced either by the presence of foreign grains, or by inclusion or intergrowth within the grains, the separated fractions were examined under a binocular microscope, equipped with a counting graticule.

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 it is less than one grain in every five hundred. For most elements this will not make a measurable difference upon the analytical results. For elements such as Ti and Y a different situation obtains, however. The content of titanium in sphene is 25% by weight, approximately. If one grain in every thousand, or .1% of a sample, is sphene, the sample will contain 250 ppm, a considerable figure in view of the titanium figures shown in the analyses (Table 3). 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 results, although it might be argued that the results have less significance in these cases.

Intergrowths were observed in only three cases, where they occurred in one or two of the grains. The foreign mineral (usually biotite) constituted only about 10% of a grain, and so constituted a very 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 only a small proportion of the grains was affected in these cases.

Of the four sources of contamination, i.e., foreign grains, intergrowths, staining by solutions, and the effect of altered grains, that most likely to affect the results appears to be the inclusion of small amounts of foreign grains. Careful examination of the samples, however, seems to indicate that this has had little effect on results on the whole.

LOCATION OF MINOR ELEMENTS

There are, in all, five possible locations for the minor constituents. These are (1) in foreign grains, (2) in inclusions and intergrowths in the mineral grains, (3) in voids in the lattice structure, (4) in an absorbed or adsorbed phase, developed during crystal growth, and (5) within the crystal structure.

The first two have already been discussed and it was shown that foreign grains may give anomalous results in some cases.

With respect to location in lattice voids, it is pertinent that in the specimens analysed, the amphiboles all have a higher minor element content than the pyroxenes; yet by applying Fairbairn's packing index it can be shown that the percentage of empty space in the unit cell is about the same in both pyroxenes and amphiboles. If the minor elements were occupying lattice voids, then, one would expect them to be about equally distributed in the two mineral groups. That they are not seems to rule out lattice voids as a possible location.

The possibility of absorbed or adsorbed phases is difficult to assess and has not been investigated.

Two factors suggest that the foreign elements are occupying lattice sites. First, the small amounts present; the stability of an element in a mineral governs to a large extent the concentration that the element can achieve at a given energy level, without a structural breakdown in the mineral. In other pyroxenes recorded in the literature, concentrations of most elements are twice to twenty times as great as those examined by the writer. If these amounts do not exceed the stability limit, presumably the amounts found in this study are well below the tolerance limits of the structure, and could be accommodated in the structure.

Also, the concentrations of various elements vary as their suitability as lattice-builders. 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, presumably because it is much less suitable in terms of replacing calcium in a lattice due to its excessively large size.

DISCUSSION OF THE ELEMENTS PRESENT

Boron. Boron figures are subject to greater error than most others; accuracy and reproducibility are not as satisfactory. The mean boron concentration in the metamorphic pyroxenes is 17.7 ppm, the range lying from 5 to 50 ppm. The small diameter of boron requires a low co-ordination number, so it may replace silicon in the silicon-oxygen tetrahedron. The degree of substitution remains small, however, because of the difference in size of 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. The element is concentrated in the samples examined by an average factor of 5.9 over its crustal abundance.

Beryllium. Beryllium is a rare element; Sandell (1952) gives its terrestrial abundance as about 2 ppm; its concentration in sedimentary rocks is of the same order, and igneous pyroxenes show an abundance of 2 to 10 ppm. Nepheline-bearing rocks are often higher in Be than others: Goldschmidt reports 360 ppm in an aegerine from a nepheline syenite pegmatite.

The mean in the pyroxenes examined is 3.5 ppm and in the amphiboles it is slightly higher: 4.8 ppm. Because of its ionic radius, Be readily replaces Si in the Si-O group, in fact, some beryllate compounds have structures analogous to silicates (Goldschmidt, 1954).

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 the crustal abundance figure of 20 ppm given by Fleischer (1955). Gallium has long been known to show a close association with aluminum, with which is shares many physical and chemical properties. The amphiboles, all a dark variety of hornblende containing more Al than the pyroxenes, show a greater Ga content. This would seem to demonstrate that Ga replaces a major constituent in the crystal structure.

Chromium. Chromium may attain a high level in pyroxenes; chromium diopsides (endiopside) contain up to 2% Cr. Igneous pyroxenes are reported to contain 200 to 2000 ppm. The present results indicate values from zero to 50 ppm, with occasional values as high as 200 ppm, but, on the whole, much less than in igneous members. The low general level of Cr suggests that little was available during metamorphic readjusment.

Lithium. Lithium was found at a measurable level in only two pyroxenes and two amphiboles, since the sensitivity of the lithium line was rather poor.

Titanium. Titanium is, next to manganese, the most abundant of the minor constituents; the average value is 330 ppm and its range is from 150 to 1000 ppm, lower than in the amphiboles and considerably lower than the values usually encountered in igneous pyroxenes, where values are usually of the order of 1000 to 16,000 ppm. Titanium can become a major constituent in pyroxenes: Lebedev & Lebedev (Rankama & Sahama, 1952, p. 560) report a titanaugite bearing 8.97% TiO_2.

In the samples studied, titanium probably replaces iron, magnesium, and possibly aluminum in augitic specimens. It seems reasonable to assume that titanium occupies lattice sites; if augites bearing several per cent of TiO_2 show only one phase present, concentrations of the order found can be readily accommodated in the structure.

Nickel. The nickel figures obtained lie within a limited range of 5 to 40 ppm. This is considerably less than in igneous pyroxenes, where values in the range of 50 to 300 ppm are more common. The affinity of Ni for ferromagnesian minerals is well-known, and the paucity in the present case is not easily explained, since most sediments, except limestones and quartzites, contain of the order of 100 ppm. It would seem that the availability of nickel in the Grenville rocks is low indeed.

Cobalt. The level of abundance of cobalt in the minerals is of the same order as nickel but its range of values is somewhat narrower—from 5 to 25 ppm. The concentrations are lower than for igneous pyroxenes in which most authors find cobalt values of 30 to 100 ppm. Sandell & Goldich (1943) showed that cobalt concentration varies linearly with magnesium over a wide range of values, which seems to indicate that it does replace magnesium in minerals.

Molybdenum. This element, though sought, was not found. Molybdenum's low terrestrial abundance, combined with its strong affinity for sulphur, seem to preclude its occurring at a significant level in silicates.

Copper. The copper content was generally very low; leaving aside two relatively high values, it averages about three ppm, again considerably lower than most pyroxenes of igneous genesis, where values up to 1000 ppm are reported (Cornwall & Rose, 1957). Unless the rocks were very low in copper at the outset, it is a mystery where the copper is, for the pyroxenes are among the few silicate minerals in the rocks that can take any large amount of copper into their structure.

Vanadium. Vanadium is one of the more abundant elements. Its mean value is 31.2 ppm, much less than in igneous pyroxenes. Once again, the average value obtained in the metamorphic amphiboles is significantly higher (57.1 ppm). On the basis of its chemistry, vanadium probably replaces iron, and to a lesser degree aluminum and magnesium.

Zirconium. Zirconium values range from 10 to 80 ppm, the mean being 37.7 ppm. Its concentration in igneous pyroxenes is somewhat higher: Cornwall & Rose (1957) report up to 700 ppm and Degenhardt (1957) reports cases where Zr has approached .5% in aegerine. Zirconium shows many similarities to titanium (radius, valence, *Ip*); however, no relationship seems to exist between Zr and Ti values in these minerals.

Manganese. Manganese 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 & Sahama (1952), the replacement of Fe^2 is the most important of these. Igneous pyroxenes, as a rule, have a much higher content than those studied, which average 1350 ppm. The former are reported as containing up to 6000 ppm (Cornwall & Rose, 1957; Wager & Mitchell, 1951). The darker colored pyroxenes, i.e., the most iron-rich, contain the most manganese and there is a regular diminution towards the lighter colored members.

Scandium. The mean concentration of Sc is 8.8 ppm, and is 12.5 ppm in the amphiboles. Oftedahl (1943) found 150 ppm in a pyroxene from a basic rock, and Cornwall & Rose (1957) report even higher values, up to 300 ppm, in the Keweenawan lavas they studied. The radius of Sc^3 permits its capture by Mg^2 and Fe^2; this involves a coupled replacement, however, so replacement is limited.

Yttrium. Yttrium resembles bivalent calcium in co-ordination, and it probably enters calcium sites in the structure. Values range from 5 to 20 ppm, less than most igneous pyroxenes in the literature. Yttrium shows a notable tendency to form independent minerals.

TABLE 4. CRUSTAL ABUNDANCES OF THE ELEMENTS (in ppm)

Element	Crustal Abundance (Average Igneous Rock)	Source of Figures
B	3	Goldschmidt & Peters (1932)
Be	2	Sandell (1952)
Ga	20	Fleischer (1955)
Cr	100	Shaw (1954)
Li	29	Horstman (1952)
Ti	4400	Green (1953)
Ni	80	Sandell & Goldich (1943)
Mo	1	Kuroda & Sandell (1954)
Co	23	Sandell & Goldich (1943)
Cu	70	Sandell & Goldich (1943)
V	100	Shaw (1954)
Zr	156	Degenhardt (1957)
Mn	1000	Green (1953)
Sc	15	Shaw (1954)
Y	40	Fleischer (1955)
Sn	2	Onishi & Sandell (1957)
Sr	450	Turekian & Kulp (1956)
Pb	15	Wedepohl (1956)
Ba	250	Green (1953)

Tin. This element was not found at a measurable level in any of the samples examined.

Strontium. The strontium values range, with a few exceptions, from 20 to 120 ppm, averaging 80 ppm. Wager & Mitchell (1951) report values of this order in the Skaergaard Intrusion, and values in the pyroxenes from the Keweenawan lavas lie in the range 60 to 400 ppm. Strontium values more nearly approach the values noted in igneous pyroxenes than most other elements.

Barium. Barium shows certain geochemical similarities to strontium with respect to ionization potential, electronegativity, radius and valency, but it is generally less abundant in nature. Because of its greater size, it cannot enter calcium sites with the facility of strontium, and hence its substitution is much more limited. This seems to be borne out in the present study.

Lead. In the majority of cases, lead if present, was below the level of detection; it was found in only seven analyses. If the lead is part of the crystal structure, it is more likely to occupy Ca positions, in view of its size and valency.

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

TABLE 5. ABUNDANCES OF SOME ELEMENTS IN SEDIMENTARY ROCKS (in ppm)

Element	Shales	Sandstones	Carbonates	Source
B	310	9–30	3	Rankama & Sahama (1952)
Be	3	0	0	Rankama & Sahama (1952)
Ga	19	5	5	Shaw (1954); Goldschmidt (1954)
Cr	110	—	2	Shaw (1954); Rankama & Sahama
Li	66	17	0	Horstman (1957)
Ti	4300	960	0	Rankama & Sahama
Ni	64	2–8	0	Shaw (1954); Rankama & Sahama
Mo	1	0	0.5	Kuroda & Sandell (1954)
Co	18	0	0	Shaw (1954); Rankama & Sahama
Cu	18	—	10–20	Shaw (1954); Rankama & Sahama
V	120	20	10	Rankama & Sahama
Zr	170	200+	20±	Degenhardt (1957)
Mn	620	tr	385	Rankama & Sahama
Sc	13	1	0	Shaw (1954); Rankama & Sahama
Y	44	1.6	0	Shaw (1954); Rankama & Sahama
Sn	11	—	—	Onishi & Sandell (1957)
Sr	245	20	610	Turekian & Kulp (1956)
Pb	20±	6	9	Wedepohl (1956)
Ba	460	170	120	Rankama & Sahama

concentration in the crust. The abundances of the elements in the principal types of sediments is given in Table 5.

Any discussion involving figures for sediments is complicated by the widely varying concentrations of various elements in different kinds of sediments, and figures for an "average sediment" become meaningless because of the wide variation of sedimentary 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 per cent of all sediments, according to various estimates (Mason, 1952). Also, they usually contain more of a given minor element than the arenaceous or carbonate rocks.

Bearing these facts in mind, a comparison of Tables 4 and 5 shows that sedimentary rocks contain much more boron than the average igneous rock. Barium is also somewhat more abundant. Copper and manganese have a lower concentration. For most other elements, the concentration in the average crust and in sediments is of the same order, at least with respect to shales. In certain areas of the Grenville, however, carbonate sediments are abundant, 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 elements, save boron and strontium, than the so-called average igneous rock.

Since the minor element content of the metamorphic pyroxenes is less than that of pyroxenes of igneous origin, for all elements except boron and strontium, there seems to be a strong indication that their minor element content has been influenced by the bulk composition of the country rocks.

COMPARISON WITH IGNEOUS PYROXENES

Table 6 gives the trace element content for eight pyroxenes of igneous origin selected from the literature as being representative. Columns 2 and 3 give the averages of values obtained 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, analyzed by Wager & Mitchell (1951). The two augites from the Keweenawan Lavas are among those reported by Cornwall & Rose (1957). The last three columns are three pyroxenes from the Charnockite Series of Madras, India, reported by Howie (1955).

The most obvious point of difference is the low amount of minor elements in the metamorphic members. This is also true with respect to other igneous pyroxenes 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 means of these weighted values were calculated for all the elements in a given sample in the following way: the abundance of each element (K_i) was divided by its crustal abundance figure (k_i); the mean (R) of these 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 crustal abundance; in this way the minor element content of each sample was assessed in terms of an independent scale of values.

Table 7 gives the R values for the pyroxenes, for the amphiboles and for the igneous pyroxenes from Table 6. It is seen that the general level of minor element content (R) in metamorphic pyroxenes is significantly lower than in the amphiboles or igneous pyroxenes. In the 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) and in the igneous pyroxenes, the mean of all values is yet higher (2.016). Other igneous pyroxenes in the literature give higher values than these, with R approaching 3.0 (Wilkinson, 1959; Snyder, 1959).

As was pointed out in an earlier section, one does not expect the concentrations to be in line with crustal abundance figures, but the latter do afford a convenient 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

TABLE 6. MINOR ELEMENTS IN EIGHT TYPICAL IGNEOUS PYROXENES

Element	Mean of 38 Meta. Pyroxenes	Mean of 5 Meta. Amphiboles	Skaergaard Intrusion			Keweenawan Lavas		Charnockites		
			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	31.3	31	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	—	—	93	160	650	70	10
Mo	—	—	—	—	10	—	—	—	3	—
Co	12	21.8	60	40	15	88	75	60	50	25
Cu	2.9**	3.6	—	300	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, probablv due to contamination.

of sources, obtained by different methods, further interpretations must be made with caution.

ELEMENT TRENDS

Three possible relationships between properties and compositions were investigated. These were: (i) variation of minor element content with color, (ii) variation of minor element content with rock type, (iii) variation between different pairs of elements.

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

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

TABLE 7. TRACE ELEMENTS IN PYROXENE, *R* VALUES

	Pyroxenes			*Amphiboles*		*Pyroxenes (Igneous)*	
Sample	*R*	Sample	*R*	Sample	*R*	Specimen	*R*
Q-3	0.754	Q-85	0.759	Q-7	0.808	Skaergaard	
Q-7	.540	Q-87	.542	CA-47	1.186	Pyroxene A	3.024
Q-11B	.490	CA30B	.782	CA-76	.830	Pyroxene D	1.255
Q-12B	.521	CA-44	.675	CA-92B	1.436	Pyroxene F	1.902
Q-13B	.315	CA-45	.746	ON-3A	.817	Keweenawan	
Q-16B	.565	CA-46	.733			Augite 4-149	2.989
Q-16D	.759	CA-47	1.128			Augite 3-89	2.084
Q-19D-S13	.441	CA-49	.566				
Q-19D-S14	.392	CA-53	.575			Charnockites	
Q-24C	.770	CA-56	.503			Pyroxene 3709	.990
Q-25	.467	CA-63A	.789			Pyroxene 2941	1.882
Q-27	.486	CA-65	.743			Pyroxene 115	1.975
Q-30	.435	CA-74	.796				
Q-31A	.892	CA-76	.766				
Q-31B	.893	CA-92B	.777				
Q-31C	.742	CA-105	.476				
Q-34	1.862						
Q-64	.785	ON3A	.621				
Q-69	.749	ON6A	.615				
Q-73J	1.479						
		Mean	.664	Mean	1.012	Mean	2.016

Chemical analyses were available for only six of the samples. These samples showed a range of color 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 color. It seems to be a reasonable assumption that iron is the major color control in the mineral, and that, in turn, the ferride elements that show an increase in concentration in darker samples are accompanied by a concomitant increase in iron content.

Other elements (B, Y, Sr, Ba, Cu, and Cr) show no clear trend. Cr values show very random variation with respect to color change.

Rock type. 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) pyroxenes from scapolite-rich skarns, (iii) pyroxenes from scapolite-poor skarns, (iv) pyroxenes from pyroxenite rocks.

In only two cases was a significant difference noted in element distribution in different environments: (1) boron attains its highest values in pyroxenes from scapolite rich skarns; (2) pyroxenes in the hybrid igneous rocks carry more manganese than the skarn pyroxenes. The former carry 1800 to 3000 ppm, while other pyroxenes rarely exceed 2000 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 may boron; second, manganese is more abundant in the igneous rocks than in the sedimentary rocks of the area.

Inter-element trends. Concentrations of various pairs of elements that show similar properties were plotted to see if correlations could be shown. The pairs examined in 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			

Key—Good correlation ***
Fair correlation **
Some correlation *
No correlation o

The relationships between V, Ni, and Co and between Zr-Mn are quite good. Chromium shows an erratic distribution with respect to other elements. 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 that has been noted in igneous rocks. In the basic rocks where Ni concentrations are the highest, Ni exceeds Co, whereas in the granitic rocks where total Ni and Co is much lower, Co commonly exceeds Ni.

SOME GENERAL CONSIDERATIONS

The outstanding fact resulting from 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 igneous pyroxenes quoted in Table 6, but also to most others in the literature.

Four possibilities come to mind to explain this anomaly:

(i) Lower temperature of formation for these 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 Grenville at the outset, coupled with a low degree of material transfer during metamorphism.

First, the temperature of the skarn zones and of the hybrid rocks cannot have been very much lower than the temperature of igneous conditions, if at all. An intrusive mass generally would not be superheated, but the temperature must have been high during its emplacement. It has been long recognized that minerals will tolerate foreign substances at elevated temperatures which 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 vapor 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 seems to indicate that an intergranular phase of some kind was 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 (titanium and yttrium) is that of contemporaneous formation of minerals more suitable as hosts to these elements, namely sphene, and to a lesser degree, allanite. In some skarn zones, sphene is very abundant, but the Ti content 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 multi-component systems, a matter beyond the scope of the present study. This question only concerns titanium, and possibly yttrium and zirconium 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, and the minor element content was thus influenced by the nature of the country rocks in which they were developed.

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 5), it seems likely that boron, a small easily mobilized ion, had its origin in the sedimentary rocks. That boron may arise from magmatic emanations has long been recognized, and is indeed possible in the present case. However, bearing in mind Goldschmidt's evidence of intrusive rocks which have been enriched in boron by their host rocks, it seems very possible that the 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 it is not a safe general conclusion from the evidence available.

CONCLUSIONS

Evidence indicates that the minor and trace elements present are in the structure of the minerals. The possibility that they are present in the lattice voids was examined in the light of the "packing index" concept and other considerations 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 color, and from the chemical analyses it is seen that iron-content is an important color control. Hence there is some evidence that minor element content is dependent upon major element composition, insofar as iron 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 minor element composition has been governed to a large degree by the availability of elements in the Grenville sedimentary rocks.

There is little difference in the pyroxenes from the various rock-types sampled with respect to minor elements, with two exceptions: boron attains higher concentrations in the 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. 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.

ACKNOWLEDGMENTS

The writer wishes to express his sincere thanks and gratitude to Dr. D. M. Shaw of McMaster University for his kind assistance and direction throughout the course of this study. It was he also who provided the specimens used. I am also indebted to Messrs. C. Yip and O. C. Wickremasinghe for their assistance in the analytical work. To all others, faculty and fellow students, who aided the writer through their helpful discussions and suggestions, I would like to express my appreciation.

The descriptions of rocks and minerals, and the mineral analyses appear with the permission of the Quebec Department of Mines. Financial aid was given to this study through funds made available by the Geological Survey of Canada and the National Research Council of Canada.

The writer would also like to extend his gratitude to the Walker Mineralogical Club of the University of Toronto for their interest, and for their kindness in awarding me the annual Peacock Memorial Prize in Mineralogy.

APPENDIX

SAMPLE LOCATIONS

Sample	Township	Con.	Lot	Geology of Sample Location
Q-3	Grand Calumet	VII	28	Pyroxene granodiorite.
Q-7	Huddersfield	V	19	Calcite-sphene-amphibole skarn.
Q-11	Huddersfield	IV	20	Scapolite-augite-sphene skarn.
Q-12B	Huddersfield	V	19–20	Scapolite-augite-sphene skarn.
Q-13	Huddersfield	IV	20	Scapolite-augite-sphene skarn.
Q-16B	Huddersfield	V	16–17	Scapolite-augite-calcite skarn.
Q-16D-5	Huddersfield	V	16–17	Scapolite-augite-sphene skarn.
Q-19D-S13	Huddersfield	V	22	Scapolite-augite-calcite-skarn.
Q-19D-S14	Huddersfield	V	22	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	Scapolite-augite skarn. Molybdenite occurs on this property.

Q-31A	Clarendon	XIII	3	Pyroxenite-with some calcite.
Q-31B	Clarendon	XIII	3	Scapolite-microcline-epidote skarn.
Q-31C	Clarendon	XIII	3	Scapolite-augite-sphene skarn.
Q-34	Masham	X	55	Pyroxenite (diopside)-some sulphides-pyrite, molybdenite, occur on this property.
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 meta-sediments. Rock locally carries disseminated galena and sphalerite.
Q-85	Huddersfield	IV	26	Scapolite-augite skarn.
Q-87	Huddersfield	V	16–27	Scapolite-augite-calcite skarn.
CA-30	Grand Calumet	VII	25	Scapolite-augite skarn—near a gabbro contact.
CA-44	Grand Calumet	VII	28	Pyroxene syenite.
CA-45	Grand Calumet	VII	28	Pyroxene syenite.
CA-46	Grand Calumet	VII	28	Vug crystals of pyroxene from a pegmatite.
CA-47	Grand Calumet	VII	28	Pyroxene grandiorite.
CA-49	Grand Calumet	VII	30	Pyroxene syenite.
CA-53	Grand Calumet	VII	32	Pyroxene granite.
CA-56	Grand Calumet	North Range	13	Scapolite-pyroxene skarn.
CA-63A	Grand Calumet	VI	31	Scapolite-augite skarn.
CA-65	Grand Calumet	VI	33	Sphene-scapolite-augite skarn. Rock is 60% sphene.
CA-74B	Grand Calumet	VIII	32	Scapolite-augite skarn. Also some sphene.
CA-76	Grand Calumet	VIII	33	Skarn-sphene-pyroxene-quartz-plagioclase.
CA-92B	Grand Calumet	VI	29–30	Pyroxene-hornblende rock.
CA-105	Grand Calumet	V	22	Diopside-phlogopite-calcite skarn.
ON-6A	Monmouth, Ont.	16	13	Scapolite-augite skarn.
ON-3	Lyndoch, Ont.	16	13	From a scapolite skarn in nepheline syenite.

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