THE PETROLOGY AND GEOCHEMISTRY OF SOME GRENVILLE SKARNS

PART II: GEOCHEMISTRY[1]

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GEOCHEMISTRY OF THE MINERAL SERIES

Samples Analysed

All the samples studied were collected by the senior author, with the exception of those prefixed by "M" and ON27 which came from university collections, those prefixed by "A" which were donated by H. S. Armstrong and ON53, which was given by J. Gittins. In several cases more than one sample was taken from the same or nearby locality. Thus CA44, 46, 47 and Q3 came from nearby outcrops on the CUM property; Q7, 11, 12, 13 came from the Camp showing and Q16, 87 came from the Matte showing of the YUM property; Q19 and CA105 came from the main HUM showings; Q67, 69 came from the DOM deposit; ON6, 20 came from the same road-cut on Highway 121 near Tory Hill; ON26 and A2 came from pits in the Essonville granite north of Tory Hill; ON31, 37 and A5 came from an area of extensive blasting for the rerouting of Highway 500, west of the village of Gooderham, which exposed a fine granite-marble reaction complex (now largely concealed).

Sample localities are summarized in Table 2, which includes brief descriptions of the rocks, the abbreviated property symbol (where appropriate), the Skarn Series symbol from the last section, and also indicates what minerals were extracted and analysed from each. Altogether there were 76 samples (additional ones were partially separated and rejected), from which 40 scapolites, 38 pyroxenes, 19 calcites, 5 amphiboles and 2 feldspars were analysed. Among these there were 16 scapolite-pyroxene pairs, 3 pyroxene-amphibole pairs, 1 calcite-pyroxene pair, 2 scapolite-pyroxene-amphibole trios and 1 scapolite-pyroxene-calcite trio. It is unfortunate that more scapolite-calcite pairs were not available, but the reason lies in the difficulty of separation.

[1]Part I: Geology and Petrography, with an abstract of the whole paper, is printed in part 3 of this volume, pp. 420–442.

In preparation of the samples for analysis scapolite and pyroxene were extracted at the same time, after preliminary crushing and sieving to obtain a fraction held between the 100- and 200-mesh sieves. Separation was accomplished using the Frantz Isodynamic Separator and with heavy liquids: details may be found in the theses quoted previously. Calcite was obtained after crushing and handpicking, followed by the same separation methods. For each mineral the final samples were examined under the binocular and/or petrographic microscope to identify and count foreign and impure grains. Samples containing more than 1 per cent of impurities were rejected.

Examination of scapolite showed a few grains of feldspar or quartz to be present in some samples, but calcite was excluded by leaching with dilute formic acid. Alteration was usually absent and most of the samples were very clean. In the case of the pyroxenes, a few grains of sphene, mica, fluorite, zircon and allanite were commonly present: in four cases these amounted to 0.5–1 per cent, and in one case 3 per cent of mica was present (CA65). In most samples however, the impurities did not amount to more than 0.1 per cent. A greater degree of purity was obtained with the calcites, which showed no more than one foreign grain in 1,000, i.e., 0.1 per cent.

The results of the analyses are given in Tables 3 to 13. The methods used have been described elsewhere (Moxham, 1958; Lapkowsky, 1959; Filby, 1957; Shaw, Wickremasinghe & Yip, 1958; Shaw, Wickremasinghe & Weber, 1960; Shaw, 1960a). In general, precision is of the order of 10 per cent of amount present, and accuracy appears satisfactory from the results of analysis of G-1, W-1 and other standard samples. The analyses for K appear to be the least reliable: a general discussion of the precision and accuracy has been given in the papers on scapolite (Shaw, 1960b, c). In the Tables of results the figures are given in parts per million (p.p.m.) except where otherwise stated; the symbols "tr," "*," and "–" signify "trace," "not detectable," and "no information," respectively. The ionic radii given correspond to the most common valence state of the element and are from Ahrens (1952). Almost all analyses have been given to two significant figures regardless of the amount present: this arises from the logarithmic working curves in spectrographic methods.

In calculating the averages in Table 5, the symbol "tr" has in each case been taken to represent a concentration of about half the sensitivity limit of the element in question: the symbol "*" has been taken as zero. In the pyroxenes, the two high Cu-figures of >500 and 120 p.p.m., and the two high Pb-figures of 340 and 220 p.p.m., are probably caused by contamination and have been ignored.

TABLE 2. SAMPLE LOCALITIES

Number	Locality	Detail Rock type	Company	Symbol	Minerals separated
CA1	27-VII, Grand Calumet Twp., Que.	Sc-px granulite	CUM	I	Sc
CA30	25-VII, Grand Calumet Twp., Que.	Sc-px gneiss	CCUM	I	Sc, px
CA44	28-VII, Grand Calumet Twp., Que.	Px syenite	CUM	IV	Px
CA45	28-VII, Grand Calumet Twp., Que.	Px syenite	CUM	IV	Px
CA46	28-VII, Grand Calumet Twp., Que.	Px pegmatite	CUM	IV	Px
CA47	28-VII, Grand Calumet Twp., Que.	Px granodiorite	CUM	IV	Px, am
CA49	30-VII, Grand Calumet Twp., Que.	Px syenite	CUM	IV	Px
CA51	30-VII, Grand Calumet Twp., Que.	Pegmatitic skarn	CUM	V	Sc
CA53	32-VII, Grand Calumet Twp., Que.	Px granite	CUM	IV	Px
CA56	13-North Range, Grand Calumet Twp., Que.	Sc-px gneiss	—	I	Sc, px
CA61	12-North Range, Grand Calumet Twp., Que.	Sc marble or skarn	—	III	Sc
CA63	31-VI, Grand Calumet Twp., Que.	Sc-px skarn	CUM	I	Sc, px
CA65	33-VI, Grand Calumet Twp., Que.	Sphene-sc-px skarn	CUM	I	Px
CA74	32-VIII, Grand Calumet Twp., Que.	Sc-px gneiss	CCUM	I	Sc, px
CA76	33-VIII, Grand Calumet Twp., Que.	Px-sphene-felds-qtz skarn	CCUM	IV	Px, am
CA83	28-IX, Grand Calumet Twp., Que.	Sphene-sc-ct skarn	—	III	Sc
CA92	29/30-VII, Grand Calumet Twp., Qu.	Px-am skarn	CUM	II	Px, am
CA105	22-V,Huddersfield Twp., Que.	Phlog-px-ct skarn	HUM	III	Px, ct
Q3	28-VII, Grand Calumet Twp., Que.	Px granodiorite	CUM	IV	Px
Q7	19-V, Huddersfield Twp., Que.	Sc-px-am gneiss	YUM	I	Sc, px, am
Q11	20-IV, Huddersfield Twp., Que.	Sc-px skarn	YUM	I	Sc, px
Q12	19/20-V, Huddersfield Twp., Que.	Sc-px-ct gneiss	YUM	I	Sc, px
Q13	20-IV, Huddersfield Twp., Que.	Sc-px-gneiss	YUM	I	Sc, px
Q16B	16/17-V, Huddersfield Twp., Que.	Sc-px-ct skarn	YUM	V	Px
Q16D	16/17-V, Huddersfield Twp., Que.	Sc-px-sphene skarn	YUM	V	Sc, px
Q19DS13	22-V, Huddersfield Twp., Que.	Sc-px skarn	HUM	I	Sc, px
Q19DS14	22-V, Huddersfield Twp., Que.	Pyroxenite	HUM	II	Px
Q23	26/27-VIII, Huddersfield Twp., Que.	Sc crystal from skarn	NML	III	Sc
Q24	38-II, Clapham Twp., Que.	Sc-px granite	—	IV	Sc
Q24C	38-II, Clapham Twp., Que.	Sc-px granite	—	IV	Sc, px
Q25	48/49-IV, Leslie Twp., Que.	Px crystal from skarn	—	—	Px
Q26	28-III, Clapham Twp., Que.	Sc crystal from skarn		III	Sc
Q27	29-V, Huddersfield Twp., Que.	Sc-px skarn		I	Sc, px
Q30	3-XIII, Clarendon Twp., Que.	Sc-px gneiss	QMI	I	Sc, px
Q31A	3-XIII, Clarendon Twp., Que.	Pyroxenite	QMI	II	Px
Q31B	3-XIII, Clarendon Twp., Que.	Sc-epidote skarn	QMI	I	Sc, px
Q31C	3-XIII, Clarendon Twp., Que.	Sc-px granulite	QMI	I	Sc, px
Q34	55-X, Masham Twp., Que.	Pyroxenite	SL	II	Px
Q64	27-I, Sicotte Twp., Que.	Px tonalite	ANM	IV	Px
Q 67	Mercier Dam, Mitchell Twp., Que.	Ct-qtz vein	DOM	III	Ct
Q69	Mercier Dam, Mitchell Twp., Que.	Px syenite	DOM	IV	Px
Q73	29-II, Baskatong Twp., Que.	Pyroxenite	GUM	II	Px
Q85	26-IV, Huddersfield Twp., Que.	Sc-px skarn	SDGM	I	Sc, px
Q87	16/17-V, Huddersfield Twp., Que.	Sc-ct-px skarn	YUM	V	Sc, px
ON1	34-VIII, Brudenell Twp., Ont.	Sc crystal from skarn	—	I	Sc
ON3	13-XVI, Lyndoch Twp., Ont.	Sc-px skarn	—	I	Sc, px, am
ON4	25-XV, Lyndoch Twp., Ont.	Sc crystal	—	—	Sc
ON5	Glendower Fe mine, Bedford Twp., Ont.	Sc-px-ct gneiss	—	I	Sc
ON6	13-XVI, Monmouth Twp., Ont.	Sc-px-ct gneiss	—	I	Sc, px, ct
ON7	32-XVII, Monmouth Twp., Ont.	Sc crystal from gneiss	—	—	Sc

TABLE 2 (continued)

Number	Locality	Detail Rock type	Company	Symbol	Minerals Separated
ON8	2½ miles east of Gooderham, Glamorgan Twp., Ont.	Sc crystal from syenite pegmatite	—	—	Sc
ON15	34-XIV, Monmouth Twp., Ont.	Sc-px-ct skarn	—	I	Ct
ON20	13-XVI, Monmouth Twp., Ont.	Sc marble	—	M	Sc
ON26	17-XII, Monmouth Twp., Ont.	Ct veins in granite	—	III	Ct
A2	17-XII, Monmouth Twp., Ont.	Ct-ap skarn	—	III	Ct
ON27	Olmsteadville, New York	Sc-px-ct skarn	—	I	Sc
ON30A	4/6-XXI, Cardiff Twp., Ont.	Ct-fluor-ap lens	—	V	Ct
ON30B	4/6-XXI, Cardiff Twp., Ont.	Ct-fluor-ap lens	—	V	Ct
ON30C	4/6-XXI, Cardiff Twp., Ont.	Ct-fluor-ap lens	—	V	Ct
ON31	17-VI, Glamorgan Twp., Ont.	Ct-ap vein	—	III	Ct
ON37	17-VI, Glamorgan Twp., Ont.	Sc-px-ct skarn	—	I	Sc
A5A	17-VI, Glamorgan Twp., Ont.	Ct mass in gneiss	—	III	Ct
A5B	17-VI, Glamorgan Twp., Ont.	Ct mass in gneiss	—	III	Ct
A5C	17-VI, Glamorgan Twp., Ont.	Ct mass in gneiss	—	III	Ct
ON38A3	McDonald Mine, 18-VII, Monteagle Twp., Ont.	Ct-qtz mass in pegmatite	—	III	Ct
ON39	6-IX, Monmouth Twp., Ont.	Ct vein	—	III	Ct
ON53	Trooper Lake, Glamorgan Twp., Ont.	Sc gneiss	—	—	Sc
M728	St. Lawrence Co., New York	Sc-px-ct skarn	—	I	Sc
M730	Grenville, Que.	Sc crystal (fluorescent)	—	—	Sc
M731	Sebastopol Twp., Ont.	Sc-ap-ct skarn	—	III	Sc
M733	Low Twp., Que.	Sc crystals	—	—	Sc
M1162	Renfrew Co., Ont.	Sc crystals	—	—	Sc
A1	27/28-XV, Glamorgan Twp., Ont.	Ct lens in gneiss	—	III	Ct
A4	27/28-XV, Glamorgan Twp., Ont.	Ct-magnetite mass in gneiss	—	III	Ct
A6A	22-VI, Glamorgan Twp., Ont.	Ct mass in gneiss	—	III	Ct
A6B	22-VI, Glamorgan Twp., Ont.	Ct. mass in gneiss	—	III	Ct

Twp. means Township. The figures e.g. 27-VII mean Lot 27, Concession or Range VII.
(Table 1 appears in Part 1, p. 440.)

Scapolite

The geochemistry of scapolite has been discussed in previous papers (Shaw, 1960b, c) from a general standpoint. Certain relevant aspects are summarized in the following.

Six specimens were analysed for major constituents in the Rock Analysis laboratory of the University of Minnesota. The results are given in Table 3 in wt. per cent, along with the cation-equivalents or gm.-atoms $\times 10^4$, calculated on the basis that Si + Al = 12,000. Also included are the quantities w and AN, where

$$w = \text{Ca}^* + \text{Na}^*; \text{Ca}^* = \text{Ca} + \text{Mg} + \text{Fe} + \text{Mn} + \text{Ti}, \text{Na}^* = \text{Na} + \text{K}$$

and

$$AN = \text{C} + \text{S} + \text{Cl} + \text{F}.$$

The composition may therefore be readily checked against the general formula

$$W_4 Z_{12} O_{24} \cdot R$$
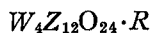
where W is mainly Ca, Na and K but includes small amounts of other

TABLE 3. CHEMICAL ANALYSES OF SIX SCAPOLITES

	M730	Q85	Q19DS13	Q87	ON6	ON8
SiO_2	45.91	47.17	51.83	52.10	54.73	57.89
Al_2O_3	28.19	26.29	24.29	23.79	22.85	21.62
TiO_2	.07	.03	.03	.02	.01	.01
$Fe_2O_3^a$	.11	.15	.07	.23	.08	.07
MgO	.46	1.00	.02	.18	.03	.03
MnO	.01	.01	tr	tr	.00	.01
CaO	15.76	14.31	11.66	11.13	8.29	4.81
Na_2O	2.44	3.82	6.40	6.86	8.55	10.50
K_2O	2.21	1.01	1.16	.87	1.08	1.16
H_2O+	1.12	.93	.22	.07	.13	.44
H_2O-	.03	.50	.04	.10	.00	.06
CO_2	2.86	2.66	2.28	2.14	1.69	1.11
Cl	.05	.56	1.66	1.85	2.19	2.96
SO_3	.94	1.42	.72	.80	.39	.03
F	.01	.04	.02	.11	.00	.00
O = Cl, F	.02	.14	.38	.46	.49	.67
Sum	100.15	99.76	100.02	99.79	99.53	100.03
Si	6963	7243	7732	7803	8046	8334
Al	5036	4757	4268	4197	3954	3666
Ti	8	4	4	2	1	1
Fe	14	18	8	26	9	8
Mg	105	231	5	41	7	7
Mn	1	1				1
Ca	2570	2362	1862	1786	1309	744
Na	717	1137	1854	1995	2435	2934
K	429	198	221	167	203	214
H	1132	950	219	70	127	422
C	592	558	464	438	339	218
Cl	13	146	418	471	544	721
S	107	163	81	90	43	3
F	5	19	9	52		
w	3844	3951	3954	4017	3964	3909
AN	717	886	972	1051	926	942

ANALYST: C. O. Ingamells, Rock Analysis Laboratory (Director: Dr. S. S. Goldich), University of Minnesota. The analyses are given in Wt.% in the upper part of the table, and in gm.-atoms$\times 10^4$ in the lower part (see text).

[a]Total Fe as Fe_2O_3.

metals, Z includes Si and Al, and where R is CO_3, SO_4, $(OH)_2$, Cl_2 or F_2 for meionite and Cl, F, HCO_3, HSO_4 or OH for marialite. The sum w should therefore approximate 4,000. The anion sum AN is however, not simply related to R, except in solid solutions of the type Cl-Ma—CO_3-Me, where AN would be 1,000: by contrast R usually includes hydroxyl in units of OH or $(OH)_2$, and in addition the halogens must be assigned in units of F_2 or Cl_2 when combined with Ca. There is no simple procedure to work out the formula in an unequivocal manner, and it is necessary to assign the anions and OH to cations in a rational but empirical sequence. The writers' procedure has been described in detail (op. cit.) and was used to obtain the data in Table 4.

TABLE 4. RECALCULATED SCAPOLITE ANALYSES WITH DENSITIES
AND REFRACTIVE INDICES

	M730	Q85	Q19DS13	Q87	ON6	ON8
Ca*	2698	2616	1879	1855	1326	761
Na*	1146	1335	2075	2162	2638	3148
w	3844	3951	3954	4017	3964	3909
AN	717	886	972	1051	926	942
H for AN	269	169	92	18	116	66
MeCO$_3$	61.5%	56.5%	46.9%	43.6%	33.5%	19.4%
MeSO$_4$	8.6	9.7	.5	2.6		
MaCl	1.4	14.8	42.3	46.9	54.8	73.8
MaHCO$_3$					.7	2.9
MaHSO$_4$	2.5	6.8	7.7	1.8	4.3	.3
MaOH	25.5	10.3	1.6		6.7	3.6
MaF	.5	1.9	.9	5.2		
% Me	70.1	66.2	47.5	46.2	33.5	19.4
Resid. H	+863	+781	+127	+52	+11	+356
Resid. Si	+337	+315	+250	+155	+121	+109
Resid. Al	+129	−168	−101	−208	−14	+163
Resid. anions				+46 S		
G	2.703	2.705	2.686	2.689	2.660	2.619
ω	1.587	1.581	1.569	1.568	1.560	1.549
ϵ	1.555	1.557	1.551	1.550	1.547	1.541
ω-ϵ	.032	.024	.018	.018	.013	.008
n_m	1.571	1.569	1.560	1.559	1.554	1.545

Elements are given in gm.-atoms$\times 10^4$, scapolite molecules in Mol. %.
With H, Si, Al and Anions the symbol "+" indicates a residue and "−" a deficiency.

The range in composition is from about 20–70 per cent Me and in five specimens the main components are Cl-Ma and CO$_3$-Me: one sample (M730) is mainly composed of OH-Ma and CO$_3$-Me.

Sample ON8 is considerably more sodic than any of the others, and it should be pointed out that it came from a vein of pegmatitic syenite associated with nepheline syenite.

In addition to the six samples just discussed, thirty-four other scapolites were separated. Refractive indices were determined for all, and all were analysed for trace (and some major) elements. It is unnecessary to reproduce all the refractive indices here, since they have already been discussed (op. cit.), but it may be noted that the values of n_m and the contents of Na$_2$O and CaO indicate that most of the skarn scapolites lie in the composition range 25–75 per cent. Me.

Individual spectrographic analyses are given in Shaw (1960c, Table 6) and are summarized in Table 5, along with the other minerals analysed and crustal abundances. Interpretation of the behaviour of the trace elements is mostly summarized in Table 5A, except for B and Li.

It is likely that B either occurs as the anion BO$_3^{-3}$ and substitutes for

TABLE 5. SUMMARY OF ELEMENTS DETERMINED IN SCAPOLITE, PYROXENE, AMPHIBOLE AND CALCITE

	rÅ	Crust	Scapolite			Pyroxene			Amphibole			Calcite		
			Range	No.	Mean	Range	No.	Mean	Range	No.	Mean	Range	No.	Mean
B^{+3}	.23	3	tr-270	40	30	7-80	38	20	19-29	5	24	6-48	19	21
Be^{+2}	.35	2	tr-37	40	9.0	tr-19	38	3.5	tr-14	5	5.0	*		*
Ga^{+3}	.62	19	12-71	40	36	*-27	38	11	21-62	5	35	*		*
Cr^{+3}	.63	100	tr		tr	tr-210	38	32	tr-120	5	33	*		*
Tl^{+4}	.68	4400	*-590	40	79	150-930	38	309	590-1200	5	760	7-46	19	21
Li^{+1}	.68	29	5-190	40	51	tr-160	35	63	30-150	4	98	–		–
Ni^{+2}	.69	80	tr		tr	1-39	38	13	2-50	5	28	tr		tr
Mo^{+4}	.70	1	*		*	*		*	*		*	*		*
Sn^{+4}	.71	2	*		*	*		*	*		*	–		–
Co^{+2}	.72	23	*		*	4-45	38	15	5-35	5	22	*		*
Cu^{+2}	.72	70	1-24	40	4.6	tr-15	36	4.5	tr-8	5	3.4	–		–
V^{+3}	.74	100	*		*	7-76	38	32	38-86	5	57	*		*
Zr^{+4}	.79	156	*-130	40	13	10-68	38	38	43-120	5	66	*		*
Mn^{+2}	.80	1000	20-160	40	53	590-2800	38	1350	710-2200	5	1290	380-3000	19	1490
Sc^{+3}	.81	15	*		*	tr-48	38	8.9	tr-23	5	8.2	–		–
Ag^{+2}	.89	0.1	*		*	*		*	*		*	tr		tr
Y^{+3}	.92	40	tr		tr	tr-30	38	9.1	6-18	5	13	–		–
Sr^{+2}	1.12	450	120-3700	40	1870	17-120	38	70	52-260	5	94	530-6600	19	2350
La^{+3}	1.14	20	*		*	*		*	*		*	–		–
Pb^{+2}	1.20	15	*-110	40	45	*-50	36	(7)	tr		tr	4-60	19	22
Ba^{+2}	1.34	250	14-580	40	133	tr-65	38	15	12->500	5	?	6-100	19	53
Rb^{+1}	1.47	120	5-130	34	21	tr-32	33	8	4-13	2	(9)	–		–
Si^{+4}	.42											.01-1.1%	19	.247%
Al^{+3}	.51		tr-1.1%	40	.149%							.003-.170	19	.040
Mg^{+2}	.66											.06-1.3	19	.443
Fe^{+2}	.74											.13-.62	19	.391
Ca^{+2}	.99		3.1-14.0			tr-2.4						–		
Na^{+1}	.97		1.7-8.8			tr-21						–		
K^{+1}	1.33		.10-1.7									–		

B to Rb inclusive are given in p.p.m.: Si to K are given in Wt. %.
Crustal abundances taken from various sources (see Shaw, 1959).

TABLE 5A. SUMMARY OF TRACE ELEMENT BEHAVIOUR IN SCAPOLITE

Elements more abundant than in the crust	
B	See text
Be, Ga	Substitute for Si, Al
Li	See text
Sr, Pb	Substitute for Ca, Na
Other elements present	
Mn, Ba, Rb	Substitute for Ca, Na
Ti	Substitution for Si, or contamination from sphene, or adsorption
Cu, Zr	Uncertain significance; low concentrations in any case
Elements negligible or not found	
Cr, Ni, Co, V, Sc, Y	No octahedral sites available

the usual anions, or substitutes for Al in 4-fold co-ordination (see Eugster & McIver, 1959): an alternative explanation would be contamination by tourmaline. The latter is most unlikely, unless at a sub-microscopic level, since (see later) B also occurs in the pyroxenes, amphiboles, feldspars and calcites, and not a single grain of tourmaline (which is very easy to recognize) was detected during microscopic examination of all the grains when checking for impurities. In addition, tourmaline was only rarely recorded in the parent rocks, although in other parts of the world it is a common companion of scapolite.

Li is unexpectedly high. It does not normally substitute for either Al or Na, but usually follows Mg and Fe. Contamination by Li-rich mica is most unlikely, and the possibility must be entertained that the Li is not in isomorphous substitution, but adsorbed. It is of interest to note that the average ratio Li/Mg is 34×10^{-3}: this figure is much higher than the values of $0.1–4.0 \times 10^{-3}$ obtained by Nockolds & Mitchell (1948) for a series of differentiated Caledonian igneous rocks from Scotland. However, their results showed a clear increase of the ratio towards the latest stages of differentiation. The figure of 34 here would suggest perhaps a prolongation of this trend to pegmatitic, pneumatolytic or hydrothermal conditions. The marked concentration of B and Be in scapolite agrees well with such an interpretation, since both are well-known from deposits in these categories. On the other hand one would also have expected Rb to be concentrated, and it is not.

In this connection it is of interest to compare scapolite with plagioclase feldspar, since the two minerals are similar in metallic constituents and frequently are intimately related petrographically. For the three elements Pb, Ba and Rb, the scapolite averages are 45, 133 and 21 p.p.m. respectively. Recent literature gives ranges in plagioclase of 9–20, 150–840

and *–120 p.p.m. for these elements (Nockolds & Mitchell, 1948; Wager
& Mitchell, 1951; Howie, 1955; Wedepohl, 1956). It is clear that Pb is
relatively more abundant in scapolite, whereas the reverse is true for
Ba, and Rb is perhaps at the same level in each. These relations are not
easily explained, since Ba^{+2} and Rb^{+1} generally tend to follow K^{+1}
(radii 1.34, 1.47, 1.33 Å), and K_2O is usually more abundant in scapolite
(up to at least 3.6 per cent) than in plagioclase (Emmons *et al.*, 1953,
show the range of K_2O in 18 plagioclase specimens to be .19–.62 per cent).
By contrast Pb^{+2}, with a radius of 1.20 Å, is intermediate in size between
K^{+1} and Ca^{+2} (.99 Å), and its relative concentration in scapolite is there-
fore explicable. It may also be noticed that the Li content of plagioclase is
usually very much less than scapolite, and seldom exceeds 10 p.p.m.
except in samples from Li-rich pegmatites.

None of the groups of elements examined, whether major or minor,
showed any sympathetic variations, of the kind usually found in studies
of minerals of igneous or quasi-igneous origin.

Pyroxene

The 38 pyroxene specimens have already been discussed in detail
(Moxham, 1960), except for the elements Li, Na, K and Rb, whose
analyses were carried out later. Six samples were analysed in the Rock
Analysis Laboratory of the University of Minnesota and the results are
given in Table 6. The analyses were recalculated by the procedure of
Hess (1949) and the lower part of Table 6 contains three groups of com-
position parameters, expressed in atomic per cent. Since no ortho-
pyroxenes were encountered in any of the rocks under discussion, the
term "pyroxene" will, for brevity be taken to mean clinopyroxene
throughout this paper.

The detailed relationship between optical properties and chemical
composition will be discussed elsewhere, but it may be noted here that
the varieties rich in Fe show marked dispersion and also vary in their
optics from grain to grain, and within grains. For example, in one thin
section of Q3 the values of $2V$ (in Na light) measured on different grains
and different parts of single grains were 61, 61, 63, 72, 74, 74 and 80°:
similarly the angle $Z \wedge c$ gave the values 39.5, 43, 50, 54.5, 59 and
59.5°. These effects are presumably caused by compositional variation,
but this is irregular and zoning is not evident.

From Table 6 it is seen that the Ca/(Ca + Mg + Fe) percentage is
close to 50 and that only small amounts of Al substitute for Si; in addition
the content of Al and Ti is low. Accordingly the pyroxenes may be classed
as members of the diopside-hedenbergite series: Q19DS14, Q31A and
Q19DS13 are diopside, ON6 and Q87 are salite, Q3 is ferrosalite. How-

TABLE 6. CHEMICAL ANALYSES OF SIX PYROXENES

	Q19DS14	Q31A	Q19DS13	ON6	Q87	Q3
SiO_2	54.47	54.01	53.78	53.44	52.20	50.69
Al_2O_3	.95	1.02	1.29	1.41	1.31	1.49
TiO_2	.07	.05	.08	.08	.06	.08
Fe_2O_3	.41	.88	.80	2.17	1.72	3.64
FeO	1.51	2.66	3.89	4.36	8.49	14.51
MgO	17.16	16.11	15.08	13.99	11.89	6.77
MnO	.09	.13	.19	.28	.28	.56
CaO	24.81	24.50	24.21	23.10	22.73	20.71
Na_2O	.31	.41	.50	.84	.65	1.16
K_2O	.02	.02	.06	.03	.06	.09
H_2O+	.10	.07	.06	.03	.18	.09
H_2O-	.00	.00	.00	.13	.16	.14
F	.03	.00	.02	.01	.04	.02
Cl			.01		.03	
O = F, Cl	.01		.01		.02	.01
Sum	99.92	99.86	99.96[a]	99.87	99.78[a]	99.94
Ca	49.5	49.4	49.6	48.6	48.2	47.1
Mg	47.6	45.2	43.0	41.0	35.1	21.4
Fe[b]	2.9	5.4	7.4	10.4	16.7	31.5
Mg	94.2	89.3	85.4	79.8	67.8	40.4
Fe[b]	5.8	10.7	14.6	20.2	32.2	59.6
Si	99.2	99.0	98.9	98.4	98.5	97.8
Al	.8	1.0	1.1	1.6	1.5	2.2
β	1.6758	1.6797	1.6826	1.6885	1.6957	1.7218
G	3.26	3.26	3.33	3.31	3.35	3.40

ANALYST: C. O. Ingamells, Rock Analysis Laboratory (Director: Dr. S. S. Goldich), University of Minnesota. Analyses in wt.%.
[a]Includes traces BaO, Li_2O: no detectable S.
[b]Total Fe.

ever the content of Fe_2O_3 is rather high in the last three, which therefore deviate somewhat from the diopside-hedenbergite series. The expected values of n_γ, interpreted from Plate I of Hess (*idem*) for these three pyroxenes are less than the measured values[a] by .003, .002 and .010 respectively. The difference is greatest for Q3, which has the highest Fe_2O_3 content and which also contains 1.16 per cent Na_2O.

The iron content correlates generally with the intensity of green colour: thus Q19DS14 is nearly white in hand-specimen, whereas Q3 is very dark green. The lighter-coloured varieties are from marble or pyroxenite, whereas the darker varieties are from coarse skarns and the syenite-granite group.

Individual spectrographic analyses are given by Moxham (1960, Table 3) but the additional alkali determinations are given here in Table 7.

[a]Indices were measured on the U-stage at constant temperature, varying the wavelength of the light used and calibrating the oil simultaneously on a refractometer: the indices given are for 5890 Å.

TABLE 7. SPECTROCHEMICAL ANALYSES OF PYROXENES FOR
ALKALI METALS

	Li	Na	K	Rb
r Å	.68	.97	1.33	1.47
Sensitivity	3	.1%	.01%	5
CA30	84	.81	.17	6.6
CA44	73	1.2	.016	11
CA45	70	.71	.018	10
CA46	—	—	—	—
CA47	160	1.4	.16	8.2
CA49	140	1.3	.050	11
CA53	73	1.1	.062	6.0
CA56	21	.63	.017	13
CA63	66	.80	.027	4.9
CA65	100	1.1	.21	9.2
CA74	96	.87	.071	8.6
CA76	110	1.1	.070	7.9
CA92	110	tr	.099	11
CA105	7.4	.11	tr	tr
Q3	110	2.1	.16	32
Q7	14	.45	.058	tr
Q11	33	.42	tr	tr
Q12	26	.71	.045	3.7
Q13	27	.58	.036	tr
Q16B	43	.82	.013	12
Q16D	50	.74	.016	8.0
Q19DS13	31	.68	tr	6.7
Q19DS14	18	.45	.047	tr
Q24C	93	.95	.18	tr
Q25	20	.44	.034	-6.0
Q27	tr	.54	.13	3.0
Q30	—	—	—	—
Q31A	tr	.59	.016	4.7
Q31B	70	.61	.19	4.0
Q31C	57	.54	.072	tr
Q34	53	.43	.028	4.4
Q64	44	.68	.064	10
Q69	100	1.1	.049	6.2
Q73	—	—	—	—
Q85	95	2.4	tr	30
Q87	—	—	—	—
ON3	81	—	—	—
ON6	110	1.1	tr	4.9

The results for Na and K are of uncertain accuracy (see Shaw, 1960c) but Mn and Ti agree reasonably well in the case of the six samples analysed chemically. The results are summarized and compared with the other minerals in Table 5, and are compared with a number of igneous pyroxenes in Table 8. Behaviour of individual elements is tabulated in Table 8A.

Comparing generally with igneous pyroxenes, the skarn varieties are more "pure," i.e., the content of most trace elements is relatively lower.

TABLE 8. TRACE ELEMENTS IN PYROXENES FROM VARIOUS ROCKS

	Skarn Pyroxenes Range	Mean	Igneous Pyroxenes Range
B	7–89	20	–
Be	tr–19	3.5	–
Ga	*–27	11	3–15
Cr	tr–210	32	*–3000
Ti	150–930	309	4200–19200
Li	tr–160	63	*–50
Ni	1–39	13	*–650
Mo	*	*	*–10
Sn	*	*	–
Co	4–45	15	15–170
Cu	tr–15	4.5	50–720
V	7–76	32	25–900
Zr	10–68	38	30–300
Mn	590–2800	1350	600–6000
Sc	tr–48	8.9	60–250
Ag	*	*	–
Y	tr–30	9.1	30–500
Sr	17–120	70	10–200
La	*	*	*
Pb	*	*	*
Ba	tr–65	15	5–60
Rb	tr–32	8	*
Li/Mg[a]	< .1–2.7		.03–1.9
Ga/Al[a]	< 1–2.5		.2–.8

[a] $\times 10^3$.
Data for igneous pyroxenes taken from the following sources:
Nockolds & Mitchell (1948), 1 specimen.
Wager & Mitchell (1951), 5 specimens.
Cornwall & Rose (1957), 2 specimens.
Storm & Holland (1957), Ni in 20 specimens.
Howie (1955), 3 specimens.
Sen, Nockolds & Allen (1959), 2 specimens.
Snyder (1959), 45 specimens.
Wilkinson (1959), 7 specimens.

This concept of purity may be made more quantitative by using the coefficient of accumulation R (Shaw, 1961) which is calculated as follows: for each mineral the concentration (k_i) of each trace element (i) is divided by the crustal abundance (K_i), the ratios are then added and divided by the number of elements (n) to obtain R:

$$R = \frac{1}{n}\sum_{i=1}^{n} k_i/K_i$$

If most of the structurally non-essential elements have been determined, the coefficient R has some value, for purposes of comparison: in the present case the only serious lack is in data for rare earths, Zn, U and Th.

For the pyroxenes analysed R lies between .315 and 1.862, with an average value of .664: by contrast the igneous pyroxenes cited in Table 8

TABLE 8A. SUMMARY OF TRACE ELEMENT BEHAVIOUR IN PYROXENE

Elements more abundant than in the crust

B	Substitution for Si or contamination
Li	Substitution for Mg, Fe; more abundant than in most igneous augites
Mn	Substitution for Mg, Fe and also for Ca (more likely)

Elements at concentrations similar to the crust

Be	Substitutes for Si; rarely detected in other pyroxenes
Ga	Substitutes for Al
Co	Substitutes for Mg, Fe; Co and Ni have similar concentrations; this is only found in igneous pyroxenes from silicic rocks; Co and Ni also show clear positive correlation.
Sc, Pb	Substitution for Ca; it is unlikely that much of the Pb is radiogenic, since several strongly radioactive specimens have low Pb content.

Elements less abundant than in the crust

Cr, Ti, Ni, Cu, V, Zr	Substitution for Mg, Fe; all are more abundant in igneous pyroxenes, especially Cr, Ti.
Y, Sr, Ba, Rb	Substitution for Ca; Y is much more abundant in igneous pyroxenes.

from the papers by Wager & Mitchell (1951), Cornwall & Rose (1957) and Howie (1955) have a range of .990–3.024 with an average of 2.016. The crust has an R-value of 1.000, by definition. In this manner the skarn pyroxenes are purer than igneous varieties: this conclusion is relevant to the conditions of genesis and will be discussed later.

It remains to discuss correlations between elements: the positive correlation between Ni and Co has already been mentioned. For the six specimens analysed chemically there is a rough positive correlation between the ratio Fe/(Mg + Fe) and the contents of Ni, Co, V and Mn: this might be expected from the chemical similarities between these elements, and, in the case of Mn, does not seem to be modified by the tendency for that element to follow Ca also. The Fe/(Mg + Fe) ratio is not known for the other specimens, but can be roughly estimated from the intensity of colour, as mentioned earlier. It was found (Moxham, 1960) that when the analyses are arranged in order of increasing colour there is again a positive correlation with the content of Ni, Co, V and Mn, and also with Ga. The Ga variation may be related to an increase of both Fe and Al but is not very clear when only the chemically analysed samples are examined. Slight correlation with colour was also shown by Be, Sc, Zr and Ti.

Amphibole

No amphiboles were analyzed for major elements, and only five samples were analysed spectrographically. The results were presented by Moxham (1960, Table 3) and are summarized in Table 5.

All the amphiboles studied occurred in association with pyroxenes which were also analysed: their detailed discussion will come later. At this point it is sufficient to note that their trace and minor elements show no unusual features. The elements which substitute at tetrahedral and octahedral positions include Ga, Cr, Ti, Li, Ni, Co, Cu, V, Zr and perhaps Mn, all of which are relatively abundant: several appear to be more abundant than in pyroxenes. Eightfold-coordinated elements include Mn, Sc, Y and Sr. Traces of Pb and Rb are present, and Ba is also low except in one unusually rich sample (CA76). In addition it may be noticed that Be and B are again prominent: both are probably in tetrahedral coordination. B, Be, Ga and Li are generally more abundant than in the crust.

Calcite

The calcite specimens analysed have been discussed in detail elsewhere (Lapkowsky, 1959). Forty-two samples were analysed, of which 19 came from the Skarn Series, 10 came from miscellaneous marbles of the Grenville Series and 13 were from Palaeozoic Limestones (for comparison). The last group was kindly supplied by Professor F. W. Beales, Department of Geology, University of Toronto, who had extracted the calcite grains by careful hand-picking: since these samples were considered to be too fine-grained for heavy liquid and magnetic separation, they may not be as pure as the other samples analysed. Individual analyses of the skarn calcites are presented in Table 9, and the averages are presented in Tables 5 and 10, the latter also containing the averages of the other groups of calcites.

In discussing the elements present in calcite it should first be noted that several elements sought in the other minerals were not sought in the calcites: these include Li, Sn, Cu, Sc, Y, La and Rb. Secondly, the elements Be, Ga, Cr, Ni, Mo, Co, V, Zr and Ag were either not detected or were present in concentrations near the limit of detection (1–5 p.p.m.). By contrast, Si, Al, Mg and Fe, which are major elements in most of the other minerals analysed, usually occur as minor constituents in calcite.

The elements not detected provide no problem: all are rare, and would not be expected to be attracted to the calcite lattice from considerations of size and charge, nor would be expected to come from normal kinds of contaminating grains (except perhaps Zr in zircon in the skarns). The elements which were determined fall into three groups: (*a*) Si, Al and Ti, which would not be expected to substitute for Ca: (*b*) Mg, Fe, Mn, Sr, Pb and Ba, which by reason of their radius, charge and chemical properties can replace Ca isomorphously in the calcite or aragonite structures: (*c*) B, which must be considered separately.

TABLE 9. SPECTROCHEMICAL ANALYSES OF CALCITES

No.\ r Å \Sensy.	.23 B 5	.42 Si 100	.51 Al 30	.66 Mg 10	.68 Ti 5	.74 Fe 30	.80 Mn 10	1.12 Sr 30	1.20 Pb 3	1.34 Ba 5
CA105	22	860	74	1300	9	1400	650	3700	12	6
Q67	28	4400	380	600	7	1900	700	2500	27	100
ON6	48	1500	540	5500	23	2600	1200	1100	18	16
ON15	10	1900	470	1700	10	3500	940	1000	13	16
ON26	25	5400	1100	4700	20	5800	2400	5200	18	79
A2	20	110	25	3000	13	3700	2000	5800	44	98
ON30A	41	600	83	2000	45	6000	3000	1900	45	57
ON30B	21	600	97	2000	46	5500	2900	1400	29	50
ON30C	20	1100	300	2100	44	5500	2900	1700	26	38
ON31	26	930	78	13000	10	1300	430	2500	12	54
A5A	12	3000	460	1300	10	3500	830	760	21	10
A5B	12	3700	710	2000	10	4400	930	740	16	90
A5C	11	2300	670	2500	9	5100	950	1300	22	11
ON38 (A3)	6	1700	230	1700	13	3200	1200	970	60	15
ON39	44	3600	180	12000	17	1500	890	6600	16	96
A1	23	420	110	3200	16	6200	2600	3800	17	36
A4	17	1200	140	2700	17	5800	3000	2500	17	30
A6A	9	2600	260	10000	36	3700	440	570	4	98
A6B	10	11000	1700	13000	43	3700	380	530	4	98

All figures are the averages of triplicate analyses and are expressed in p.p.m.
Traces of Ag (1 p.p.m.) and Ni (5 p.p.m.) were present in most samples.
Be, Ga, Cr, Mo, Co, V, Zr were not detected in any sample.

The possibility of contamination must be raised for group (a). The average Si and Al contents of the skarn calcites are about .25 and .04 per cent, respectively. One grain of scapolite, feldspar or pyroxene in every 100 calcite grains would supply all the Si, as would one grain of quartz in 200: one grain of scapolite or feldspar in 300 would supply all the Al. In the case of Ti, one grain of sphene in 10,000 would supply the average value of 21 p.p.m. The separation methods yielded calcite fractions which were free of foreign grains and intergrowths, to a limit of one per 1,000. Thus gross contamination was avoided, and, moreover, the material for analysis was hand-picked before weighing: however, there remains the possibility of sub-microscopic inclusions or adsorption. It is interesting to note that the Palaeozoic calcites show only slightly greater Si, Al and Ti contents than the coarser-grained and recrystallized specimens, which underwent more rigorous separation methods. Accordingly the possibility remains that at least some of the Si and Al is not present as contamination, and may have some crystal chemical significance.

With regard to group (b) it may first be noted that Mg and Fe are of course normal constituents of calcite: the values for Mg are not great enough to allow the presence of much dolomite, and none was recognized

TABLE 10. ANALYSES OF CALCITES EXTRACTED FROM SKARN ROCKS,
GRENVILLE MARBLES AND PALAEOZOIC LIMESTONES

Element	Skarn Average of 19	Grenville Marble Average of 10	Palaeozoic Limestone Average of 13	C %
B	21	18	8	7.5
Ti	21	15	41	6.5
Mn	1490	190	150	8.0
Sr	2350	300	310	12.0
Pb	22	2	*	11.0
Ba	53	42	4	5.0
Si	2470	3410	3450	8.0
Al	400	390	740	9.0
Mg	4430	34100	7630	7.0
Fe	3910	1680	970	7.0

The results are expressed in p.p.m. The standard error C was obtained from the results of analysing one sample 10 times.
The Palaeozoic calcites also contained 2 p.p.m. Cr.

in thin section or grain study, but it may nevertheless be present in exsolution (see Goldsmith, Graf & Joensuu, 1955): the amounts of Mg and Fe determined however, are small enough that both could be present in solid solution, without necessitating the presence of an additional phase.

The other elements in group (b) are Mn, Sr, Pb and Ba. The first three are present in the skarn calcites at higher concentrations than in the crust as a whole, this being especially marked in the case of Sr. Pb shows less enrichment, while Ba is not enriched at all. It is possible that this pattern is related to the progressively greater difficulty of accommodating large ions in the calcite lattice, but if this were the sole explanation one would expect Mn to show the greatest degree of enrichment rather than Sr. The availability of each element at the time of crystallization and facility of entry into other minerals are important factors and will be considered later. It should be noted here, however, that the data of Table 10 indicate a strong enrichment of Mn, Sr, Pb and perhaps Ba in skarn calcites, by comparison with calcite from normal marbles and unmetamorphosed limestones.

The significance of B is uncertain (see later). It is possible that the element occurs in submicroscopic inclusions of tourmaline, but this is unlikely for the same reasons discussed earlier in connection with scapolite. The small size and high valence of B^{+3} and C^{+4} (radii .23 and .16 Å respectively) give them some stereo-chemical similarities, and it is likely that B substitutes for C in the carbonate radicle. It is well known that small amounts of B are found in marine sediments and it is therefore possible that the B in the skarn calcites represents an original constituent

of the carbonates: however, it should be noted that the skarn and marble calcites contain from 2 to 3 times more boron than limestone calcite. The latter group can probably be considered representative, since Runnels & Schleicher (1956) and Ostrom (1957) found average values of 6.9 and 18 p.p.m. B in limestones, which were certainly less pure than the calcites analysed.

A feature of interest in the skarns is the variability in grain-size and colour of the calcite; most of the samples analysed were the coarse salmon-pink variety, but a few other varieties were analysed in the hope of obtaining some information on the source of the pink colouration. Thus, A6A and B were pink and white respectively: A5A, B, C were pink, grey, white: ON30A, B, C, were coarse-grained pink, medium-grained pink, fine-grained pink. In each case the varieties came from the same hand-specimens. Field evidence, in the form of segregations and veins of coarse pink calcite in the marbles and other rocks, indicates that these samples can be taken to represent steps in the recrystallization sequence as follows:

white ct → coarse white ct → grey ct → fine pink ct → coarse pink ct

$$\text{marble} \nearrow\!\!\!\nearrow \frac{\text{skarn group}}{\text{increasing degree of recrystallization and mobilization}} \longrightarrow$$

On examining the analyses for ON30 it is seen that there is an increase in B, Ba, Pb and a decrease in Al, Si, on going from fine to coarse grain: in A6 there is an increase in Mn and a decrease in Al, Si, Mg, on going from white to pink: in A5 there is a decrease in Al, Fe, Mg, Sr, Mn, on going from white to pink, with no increase in any element, but an intermediate maximum for Ba and Si in the grey variety. If more specimens had been available the trends might have been more definite, but it seems that continued recrystallization within the skarns has usually led to an expulsion of Al, Si and Mg, which corresponds to a continuation of the same decrease observed on passing from sedimentary calcite to marble and skarn. Conversely, the concomitant increase in B, Fe, Mn, Sr, Pb and Ba does not continue clearly within the skarn group in every case.

As far as the pink colour is concerned, if it is due to the presence of colour-giving cations the most likely source is Mn or Fe or both together, since the salmon colour partakes of both the bright pink colour of rhodochrosite and the more brownish colour of siderite. This conclusion was also reached by Walker & Parsons (1923, 25).

Six skarn calcites from radioactive properties in Ontario were analysed by W. O. Taylor for Dr. J. Satterly of the Ontario Department of Mines, who kindly allowed the writer to see the results: the figures for Mn, Sr,

Fe, Zr, Co, Ni, Ti, V, Ba, Pb, B, and Cr agreed very well with the present results, although values for Fe reached 1 per cent: in addition values of 1–50 p.p.m. Cu and 200–800 Y were also obtained. The Cu figures are of little significance but it is interesting that such large amounts of Y are present (a marble calcite analysed for comparison gave only 2 p.p.m. Y), which are of the order of 10 times the crustal abundance. Traces of Ce and La were also noticed.

Feldspars

The two feldspars occurring with pyroxene Q3 were carefully separated. It was possible to obtain a plagioclase fraction in which only 1 per cent of the grains showed intergrowths of microcline, and a microcline in which 2 per cent showed plagioclase inclusions and alteration: R. H. Filby made these and other careful separations. Each feldspar was analysed by the University of Minnesota Rock Analysis Laboratory, then spectrographically: the results are presented in Table 11, which includes calculations to gm.-atoms $\times 10^4$ (lower left-hand side), and to constituent molecules (lower right-hand side).

The chemical analyses showed rather low sums, in spite of careful checks (personal communication: Dr. S. S. Goldich). The spectrographic analyses indicate that small amounts of Sr and Mg are present, but it is unlikely that Sr exceeds .2 per cent in each case. It is interesting to note that small amounts of Cl are present in both feldspars.

The trace element suite of each feldspar is conspicuous by the absence of most elements of interest except for B, Ga, Sr and Ba. B may replace Al (Eugster & McIver, 1959), but Ga, Sr and Ba are well-known constituents of feldspars. Since only one specimen of each feldspar was analysed, few general comparisons can be made, but plagioclase feldspars from igneous rocks usually show small amounts of many of the other elements listed, especially Ti, Ni, Co, Cu, V and Zr, and in addition Mn is usually more abundant (see references given in Table 8). It seems likely that the plagioclase from these skarns is also "purer" than in igneous rocks, as was the case for pyroxene.

The refractive indices of both feldspars were measured in Na light, using a calibrated set of index oils and applying temperature corrections. The greatest and least indices of cleavage flakes of the plagioclase were 1.543 and 1.533, corresponding to compositions An_{14} and An_{12}, respectively. Three determinations of $2V$ (about X) on the universal stage gave values of 88–90°, corresponding to An_{15}: the maximum extinction angle on albite twins is 12° (An_9), and the extinction angle in a section perpendicular to the a-axis is 10° (An_{10}), both measured on the universal stage.

TABLE 11. ANALYSES OF MICROCLINE AND ALBITE FROM Q3

	Mc	Ab		Mc	Ab
SiO_2	64.44	66.66	B	12	23
TiO_2	.01	.01	Be	*	1.4
Al_2O_3	18.36	20.17	Ga	20	27
Fe_2O_3[a]	.20	.21	Cr	*	*
MgO	.00	.00	Ti	*	*
MnO	tr	tr	Li	–	–
CaO	.00	1.83	Ni	*	*
Na_2O	1.33	9.91	Mo	*	*
K_2O	14.52	.58	Sn	–	–
H_2O+	.11	.07	Co	*	*
H_2O-	.00	.00	Cu	*	2.2
Cl	.05	.02	V	*	*
BaO	.24	.01	Zr	*	*
Rb_2O	.08	.00	Mn	16	16
Cs_2O	.00	.00	Sc	*	*
			Ag	*	*
Sum	99.34	99.47	Y	*	21
			Sr	>800	>800
			La	*	*
			Pb	–	–
			Ba	>500	84
			Rb	–	–
			Mg	260	370

				Microcline		
Si	10729	11099				
Al	3602	3957		metal	Al, Fe	Si
Fe	25	26				
Ca	0	326	Feldspar	3537	3627	10729	At.% Wt.%
Na	429	3197				
K	3083	123	Or	3083	3083	9249	87.8 88.3
Ba	16	1	Ab	429	429	1287	12.2 11.7
Rb	9	0	Ba	16	32	32
H	122	78	Rb	9	9	27
Cl	14	6				
			Residue	0	74	134

ANALYST: C. O. Ingamells, Rock Analysis Laboratory (Director: Dr. S. S. Goldich), University of Minnesota.
Oxides in Wt.%. Minor and trace elements in p.p.m.

			Albite		
		metal	Al, Fe	Si	
Feldspar		3647	3983	11099	At.% Wt.%
Or		123	123	369	3.4 3.6
Ab		3197	3197	9591	87.6 87.0
An		326	652	652	9.0 9.4
Ba		1	2	2	
Residue		0	9	485	

[a]Total Fe as Fe_2O_3.

Diagrams of Tsuboi (in Winchell, 1951) were used to interpret these compositions. Using the x-ray diffraction method of J. V. Smith (1956) the 2θ-spacing $(\bar{1}32)-(131)$ was $2.62°$, indicating a low temperature sodic

feldspar, and the spacing $(111)-(1\bar{1}1)$ was $0.54°$, corresponding to the composition An_{10}: the x-ray determination was made by P. S. Simony and A. E. Edgar. These results all agree fairly well with the chemical analysis, which indicates $An_{9.4}$ if Or is added to Ab, $An_{13.0}$ if Or is added to An, or $An_{9.8}$ if Or is ignored (all wt.%).

The indices of the microcline on cleavage flakes were γ', 1.525; β, 1.523; α', 1.520. Cross-hatched twinning is visible in thin section and in addition the extinction varies in a rather irregular, patchy manner. Measurements on the universal-stage show considerable variation in the optic parameters from point to point in a given grain, and show also that $2V$ is not symmetrical about X in some cases:

	V_1	V_2	$2V$	$X \wedge a$	$001 \wedge OAP$
	34.5	34.5	69.0		
Grain 1	28.0	43.5	71.5	4.5	6
	32.0	32.5	64.5		
Grain 2	38.5	42.0	80.5	8	10
	37.0	29.5	66.5	7	7

The measurements were made in Na light, making the usual corrections for tilt and repeating all settings several times. Grain 1 was measured at three points extinguishing in different positions, Grain 2 in two. The cleavages in each case extended right across the grains without any interruption or change of orientation, but could not be measured as accurately as the positions of the optic axes: the extinction angles given above are therefore less reliable than the values of V_1 and V_2, which depend only on accurate location of the indicatrix planes. Error of $0.5°$ in V is possible, but differences in $V_2 - V_1$ of 2.5, 3.5 and $15.5°$ must be real.

Neglecting the apparent asymmetry of $2V$ at some points in the crystals, the values of $2V$ range from 64 to $81°$. This might be due either to compositional variation or to variations in properties due to structural changes. The analysis shows the bulk composition to be $Or_{88}Ab_{12}$, and Tuttle's (1952) curves for the four series of alkalic feldspars show that the values of $2V$ conform to microcline and to a phase intermediate between microcline and orthoclase: the average value of $2V$ is about $70°$, which would be the expected value for microcline of this composition. Hewlett (1959) has investigated the optical properties of the alkali feldspars in more detail and recommends that Tuttle's curves be used to indicate the crystallographic state of a feldspar when the composition is known: accordingly the overall value of $2V$ indicates that the feldspar is a microcline, but some of the individual values suggest that a phase

intermediate to orthoclase is also present. The asymmetry in $2V$ may be associated with areas of structural indeterminancy.

In several recent papers (e.g., 1955), Barth has discussed a geological thermometer based on the partition of Na between two coexisting alkali feldspars which have crystallized together in equilibrium. The theoretical basis of the method and its present uncertain calibration have been criticized (see discussion following the paper of Barth, *op. cit.*), but in practice the temperatures obtained from its application seem realistic. The temperature is evaluated from the ratio of mol. per cent Ab in the potassic phase to mol. per cent Ab in the plagioclase: for the present pair of feldspars, which appear from petrographic evidence to have formed in equilibrium, the ratio is 0.12 which corresponds to a temperature of 330° C. on Barth's scale. The significance of this figure will be discussed later.

Other Minerals

Two other minerals were analysed qualitatively. These were a phlogopite (Q30) and a sphene (CA83). The phlogopite showed less than 10 p.p.m. of B, Be, Ga, Ti, Li, Cu, Mn, Pb, Ba, Rb: the sphene contained less than 10 p.p.m. of B, Be; 10–100 p.p.m. of Cr, Li, Cu, Mn, Sr; 100–1,000 p.p.m. of V, Ba.

It thus appears probable that B and Be are present in all the skarn minerals.

Distribution of Trace Elements between Minerals

The minerals discussed here represent a metamorphic-metasomatic origin in which it may be assumed that adjacent minerals for the most part crystallized simultaneously. The elements found in a given mineral would therefore depend on several factors:

(*a*) the supply of elements in the original rocks,
(*b*) the supply of elements in any mobile phase,
(*c*) the crystal chemical features of the mineral in question,
(*d*) the crystal chemical features of other phases crystallizing simultaneously,
(*e*) the relative proportions of the different phases,
(*f*) subsequent alteration and recrystallization.

However, the elements themselves must be discussed in three groups according to their manner of occurrence within each mineral: (i) those which occur in isomorphous solid solution at lattice sites; (ii) those which occur in lattice cavities, structural imperfections and by surface adsorption; (iii) those which are present by virtue of contamination by other

minerals (geometrical intergrowth, exsolution, alteration) or by liquid or gaseous inclusions. None of these groups is mutually exclusive and a given element may be present in all three categories (e.g., perhaps Fe in feldspar).

For the elements which are present in true solid solution the laws of solutions apply, and the factors (a) to (e) above allow the concentration k_i of a given element in mineral i to be expressed as

$$k_i M_i = K_o + K_m - \sum k_j M_j$$

where M_i is the proportion of the mineral in the rock, K_o is the concentration of the element in the original rock, K_m is the concentration added by any mobile phase, and $\sum k_j M_j$ represents the amounts of the element held in other minerals. If the total concentration in the rock is $K_t (= K_o + K_m)$, then we can write

$$D_i = \frac{k_i}{K_t}$$

where D_i is the distribution factor for that element between the mineral and the rock as a whole. The supply of the element, the crystal chemical features of all the minerals (i.e., those which govern the ease of entry of an element into the minerals) and the relative proportions of the different phases are all expressed in the parameters k_i and K_t, and therefore in D_i. If only trace elements are considered (dilute solutions) and if equilibrium be assumed, then the value of D_i would be a function of temperature and pressure (the system is assumed to be closed at the time of equilibrium).

Evidently numerical values for D_i are unknowable in the present case, since the skarns do not possess any homogeneity and the value of K_t cannot be determined. However, one can readily determine the partition D_i^{ab} of an element between the two coexisting minerals a and b, since

$$D_i^{ab} = \frac{k_i^{a}}{k_i^{b}}$$

Again assuming equilibrium conditions and the laws of ideal solutions, the value of D_i^{ab} will be a function mainly of temperature and pressure, and will express the relative ease of entry of the element into the two structures. Considering several minerals it should therefore be rare to find that the values D_i^{ab}, D_i^{bc}, D_i^{ca}, etc., were all equal to unity.

For elements which are in category (ii) however, the position might be different. These elements are in lattice cavities, structural imperfections and adsorbed on various surfaces: their distribution is not controlled by bonding requirements at specific lattice sites.

To have elements present in lattice cavities it is obviously necessary that the mineral possesses such cavities: clearly in this case there would be a preferential enrichment of suitable elements in such a mineral. Secondly, submicroscopic inclusions of crystal nuclei should be restricted to inclusions of minerals which occur as principal phases of the rock: it is inherently unlikely that elements in trace concentrations should occur as inclusions of minerals in which they are themselves major constituents. The effect of trace elements in the major phases occurring as inclusions should be negligible, and the principal contamination supplied would be the major elements: e.g. inclusions of pyroxene in scapolite grains, would add Si, Fe, Mg and Ca, but a few p.p.m. of Li in the pyroxene would contribute little to the scapolite. However, inclusions of minerals rich in a few minor elements are possible (e.g., Ti in sphene, Zr in zircon) and could introduce significant contamination. The significance of these effects depends on the particular element, and also on the growth history of a given rock: for most trace elements, however, (e.g., Ga, Mn) one cannot envisage the presence of minerals in which they are major constituents, and this effect can be neglected.

In category (ii) there remain the elements which are present by more or less random adsorption and incorporation on surfaces and other structural imperfections. It is difficult to analyze such effects, but it is apparent that the concentration of the "foreign" element would depend on its abundance in the solutions depositing the crystals. For example, Li is not an expected constituent of scapolite, but if Li were present in a solution from which scapolite were forming one would expect a certain amount to be trapped within the structure. However, there would be a similar opportunity for the Li to be trapped in any other minerals forming at the same time: in other words the partition ratio of an element between two minerals and foreign to both should be unity. Such foreign elements are what Jedwab (1953) refers to as "éléments typochimiques," in that they indicate something of the environment of formation rather than the crystal chemical characteristics of the minerals. By analysis of this kind it might be possible to distinguish "éléments typochimiques" from the "éléments cristallochimiques" which occur at lattice sites and have a structural significance.

Elements of category (ii) pass into those of category (iii) by increase of particle and unit size. Ideally it should be possible to separate minerals completely one from another, but in practice it is very difficult. Solid and liquid inclusions and alteration products are present in every grain of a mineral and some must be regarded as having been "part of" the mineral (e.g., exsolution effects). Even with gem quality material it is difficult to know how pure the mineral is. However, negative evidence is

sometimes of value. For example, most of the scapolites contain small amounts of Pb, which might be suspected to be contamination from radioactive minerals: however, four gem varieties which appeared to be absolutely pure, occurred as single transparent crystals and required no separation, were also analyzed and showed similar amounts of Pb (see Shaw, 1960c). It must be concluded that Pb is a normal trace constituent of scapolite.

The above considerations form a reference framework in which to discuss the distribution of elements between the minerals analyzed.

The summaries in Table 5 indicate in a general way the distribution of elements between the different minerals. Individual analyses of pairs and trios of minerals have, however, also been reproduced in Table 12.

It is unfortunate that more examples of calcite and amphibole occurring with the other minerals were not available, but it is evident that most elements show varying degrees of concentration, which can be expressed as follows:

e.g. $\qquad$ Sr $\quad$ ct > sc > px = am

In a few cases these trends are reversed but this usually occurs when an element has about the same concentration in two minerals. The relations are summarized in Table 13, which includes the observation of W. O. Taylor (see above) that Y is strongly concentrated in the skarn calcites.

The results indicate that with the exception of Li, Cu and perhaps B, each element shows varying degrees of concentration in the different mineral species: that is, the values of D_i^{ab} are not usually equal to unity. Moreover, there is a general tendency for the cations which demand six-fold coordination to concentrate in pyroxene and amphibole. These facts indicate clearly that most elements occur in true solid solution.

Li and Cu, however, are rather evenly distributed throughout scapolite, pyroxene and amphibole. From their behaviour in igneous minerals one would expect both Li and Cu to concentrate in the mafic minerals to a marked degree. In the case of Cu it is possible that small amounts were adsorbed indiscriminately in each mineral: by contrast Li could be adsorbed by scapolite but would be incorporated in the structures of the mafic minerals, and that is probably what happened. The solutions effecting the crystallization were richer than usual in Li, consequently the mafic minerals accepted more Li than is usually found in igneous rocks. At the same time Li was adsorbed to an unusually high degree in scapolite. The only other reasonable explanation would be that contamination of the scapolite by a Li-rich mica has taken place, which is unlikely on petrographic grounds.

B is also rather constant in abundance, but shows some preferential

TABLE 12. TRACE-ELEMENT ANALYSES FOR MINERAL PAIRS AND TRIOS

		B	Be	Ga	Cr	Ti	Li	Ni	Co	Cu	V	Zr	Mn	Sc	Y	Sr	Pb	Ba	Rb	
CA30	Sc	9.8	1.6	28	*	50	57	*	*	4.5	*	50	35	*	*	1900	96	150	—	Sc
	Px	16	1.8	7.3	tr	320	84	15	27	4.0	39	58	890	11	3.5	74	59	30	6.6	Px
CA56	Sc	tr	8.2	39	*	110	30	*	*	3.5	*	39	49	*	*	2700	51	80	17	Sc
	Px	17	tr	23	15	480	21	1.0	9.0	3.7	27	41	1100	4.7	4.1	92	*	1.0	13	Px
CA63	Sc	tr	6.8	32	*	21	58	*	*	3.8	*	*	51	*	*	2900	45	120	11	Sc
	Px	26	2.0	16	43	230	66	17	15	1.5	32	32	1400	5.5	9.0	120	tr	10	4.9	Px
CA74	Sc	tr	7.7	32	*	*	82	*	*	3.8	*	*	71	*	*	2500	67	210	18	Sc
	Px	27	tr	16	16	390	96	31	26	tr	46	56	1500	12	8.2	84	*	10	8.6	Px
Q7	Sc	22	4.5	15	*	87	26	*	*	3.3	*	6.8	46	*	*	2100	105	23	22	Sc
	Px	9.0	1.5	6.2	210	610	14	39	45	1.0	30	40	730	28	4.5	72	tr	2.6	tr	Px
	Am	25	tr	22	120	650	30	45	25	tr	54	43	720	23	12	260	*	20	4.5	Am
Q11	Sc	tr	6.5	36	*	27	12	*	*	2.8	*	37	41	*	*	2900	9	160	27	Sc
	Px	16	1.8	6.4	tr	230	33	10	10	1.5	23	68	950	tr	7.4	86	*	30	tr	Px
Q12	Sc	22	4.4	33	*	36	24	*	*	3.6	*	*	33	*	*	2600	71	80	30	Sc
	Px	17	1.5	8.8	24	440	26	11	10	2.0	29	32	1020	tr	13	100	*	12	3.7	Px
Q13	Sc	13	6.9	39	*	*	21	*	*	3.4	*	tr	32	*	*	2000	23	58	15	Sc
	Px	8.0	1.5	5.6	tr	300	27	2.8	8.0	1.0	14	16	950	tr	tr	99	tr	12	tr	Px
Q16D	Sc	tr	8.4	33	*	110	41	*	*	1.6	*	19	39	*	*	2200	tr	60	11	Sc
	Px	24	1.6	9.6	46	220	50	27	20	2.0	42	28	1600	8.4	30	94	*	5.0	8.0	Px
Q19DS13	Sc	19	5.0	39	*	43	50	*	*	2.2	*	16	34	*	*	1700	93	82	13	Sc
	Px	15	tr	11	20	170	31	13	9.0	15	23	21	940	3.0	4.8	82	*	25	6.7	Px
Q24C	Sc	tr	34	52	*	46	110	*	*	8.8	*	*	74	*	*	280	34	14	—	Sc
	Px	13	8.9	13	10	320	93	31	18	3.5	30	55	2200	6.5	8.6	48	*	15	tr	Px
Q27	Sc	20	10	43	*	tr	24	*	*	2.3	*	tr	97	*	*	1100	62	31	22	Sc
	Px	17	2.7	5.6	tr	180	tr	3.2	9.4	4.0	14	16	920	tr	4.0	59	*	13	3.0	Px

TABLE 12 (cont'd.)

		B	Be	Ga	Cr	Ti	Li	Ni	Co	Cu	V	Zr	Mn	Sc	Y	Sr	Pb	Ba	Rb	
Q30	Sc	11	8.6	57	*	11	64	*	*	2.1	*	tr	44	*	*	1050	21	80	17	Sc
	Px	13	1.0	11	11	150	—	1.7	5.2	4.0	8.0	12	730	2.0	8.0	52	15	20	—	Px
Q31B	Sc	tr	9.6	46	*	20	50	*	*	5.2	*	7.3	36	*	*	1150	23	58	18	Sc
	Px	42	1.0	9.0	29	230	70	3.0	4.5	3.0	9.0	18	870	tr	6.2	41	*	21	4.0	Px
Q31C	Sc	37	7.0	51	*	520	56	*	*	3.6	*	18	35	*	13	1300	tr	98	12	Sc
	Px	24	1.3	13	120	860	57	9.0	6.0	3.1	33	36	810	15	27	38	*	15	tr	Px
Q85	Sc	36	8.4	20	*	32	53	*	*	2.2	*	60	83	*	8.3	3300	99	86	61	Sc
	Px	31	tr	27	tr	350	95	1.0	4.5	47	10	50	590	tr	6.6	120	*	31	30	Px
Q87	Sc	14	6.9	45	*	tr	24	*	*	3.2	*	7.3	37	*	*	3700	36	47	9.8	Sc
	Px	17	tr	11	44	160	—	24	19	1.5	36	29	1010	9.4	7.4	94	tr	6.0	—	Px
ON3	Sc	14	5.1	39	*	56	20	*	*	2.5	*	tr	59	*	*	2800	39	170	5.6	Sc
	Px	14	1.0	19	tr	710	81	2.8	4.3	8.4	34	28	1020	48	tr	48	tr	26	—	Px
	Am	29	4.5	21	tr	660	—	2.0	5.0	3.4	40	50	1000	tr	9.2	53	*	13	—	Am
ON6	Sc	39	29	52	*	11	185	*	*	4.3	*	*	43	*	*	950	33	64	24	Sc
	Px	89	9.0	19	15	260	110	12	8.0	3.5	16	43	1600	2.6	23	36	tr	tr	4.9	Px
	Ct	48	*	*	*	28	—	*	*	—	*	*	1200	—	—	1100	18	16	—	Ct
CA47	Px	16	19	20	44	170	160	10	16	4.0	27	39	2800	10	11	64	15	8.0	8.2	Px
	Am	20	6.0	47	15	710	150	15	22	tr	38	44	2200	5.4	18	52	tr	12	—	Am
CA76	Px	12	5.9	26	tr	930	110	29	30	9.0	63	66	960	23	tr	47	*	8.2	7.9	Px
	Am	19	tr	62	tr	1200	70	50	35	8.2	86	71	710	5.4	18	52	*	>500	13	Am
CA92	Px	14	9.1	7.4	26	290	110	22	18	1.5	57	41	1900	14	4.5	88	tr	5.2	11	Px
	Am	27	14	24	24	590	140	27	22	4.6	68	120	1800	5.4	6.7	52	*	33	—	Am
CA105	Px	14	1.5	*	tr	160	7.4	1.0	5.5	120	6.8	10	1300	tr	16	78	30	1.5	tr	Px
	Ct	22	*	*	*	9	—	*	*	—	*	*	650	—	—	3700	12	6	—	Ct

concentration in amphiboles in individual rocks: the averages in Table 5, however, are very close, and the two feldspars also show similar quantities. For the silicates it is possible that the B occurs in 4-fold sites replacing Al (and Si), since the B-bearing analogues of alkali feldspars have recently been synthesized (Eugster & McIver, 1959). However, it must be borne in mind that although the Al-content of pyroxene is much less than the feldspars, nevertheless, the B content is similar: one would expect pre-ferential concentration in feldspar and scapolite, calcite (in 3-fold sites), amphibole then pyroxene. The possibility must, therefore, be entertained that B also occurs as an adsorbed phase, or alternatively, that it is present in fluid inclusions. If the latter is, however, the case, the concen-tration of B within the inclusions would have to be considerable, since their volume must be very small. Adsorption is more likely.

The elements Ti, Ni, Co, V, Zr, Cr, Mn, Sc, all show preferential concentration in the mafic minerals: the first five are most abundant in amphibole, Cr and Sc in pyroxene, and Mn about as abundant in each. These elements substitute at 6-fold or 8-fold sites and show chemical similarities to Mg, Fe and Ca which are major constituents. Feldspar and calcite usually contain less of these trace elements than the other minerals, however, Mn is an important constituent of calcite, as would be expected.

Y belongs to the previous group of elements, in that, it is clearly associated with the ferromagnesian minerals. However, it seems likely that it is most strongly concentrated in calcite: it would be interesting to know whether this also is the case for Sc. The substitution of Y^{+3} for Ca^{+2} in calcite would necessitate the substitution of a trivalent element for C^{+4}: this could be B^{+3} but the evidence suggests that not enough is present.

Ga shows similar concentrations in amphibole and scapolite, which may be ascribed to a replacement of Al: similar amounts also appear in the feldspars. With low Al contents in pyroxene and calcite the concen-tration of Ga is also low.

Be, Pb, Rb and Ba all show preferential concentration in scapolite, Ba also being abundant in the feldspars. The first replaces Si at 4-fold sites and it is not clear why it should prefer scapolite to the other silicates. The others replace Ca and Na. The only element which is preferentially concentrated in calcite, apart from Y, is Sr: it is chemically similar to both Ba and Ca but the lower abundance of Ba in calcite must be ascribed to its larger size.

In the lower part of Table 13 it is indicated which elements are concen-trated in amounts exceeding the crustal abundances. The commonest assemblages in the skarns consist of scapolite, pyroxene and calcite,

together with phlogopite and sphene which have not yet been examined in detail but which both contain B and Be. Accordingly, it can be stated that the skarns are enriched in B and Be, and probably also in Ga, Li, Mn, Y, Sr and Pb. Of these elements, B and Li may occur to some extent in adsorbed phases, but the other elements can best be explained as occurring at lattice sites in the various minerals.

TABLE 13. PREFERENTIAL CONCENTRATION OF TRACE
ELEMENTS IN THE MINERALS ANALYSED

Elements	Order of concentration	No data
Li, Cu	sc = am = px	ct
B	am > px = sc = ct	
Ti, Ni, Co, V, Zr	am ⩾ px > sc = ct	
Cr	px > am > sc = ct	
Mn	am = px > ct > sc	
Sc	px > am > sc	ct
Y	(ct) > am > px > sc	
Ga	am = sc > px > ct	
Be, Pb, Rb	sc > px = am ⩾ ct	Rb in ct
Ba	sc > am > ct > px	
Sr	ct > sc > px = am	

Mineral	Elements more abundant than in the crust
Calcite	B, Mn, Sr, Pb (Y)
Scapolite	B, Be, Ga, Li, Sr, Pb
Pyroxene	B, Be, Li, Mn
Amphibole	B, Be, Ga, Li
All three silicates	B, Be, Li
All minerals	B

GENERAL GEOCHEMISTRY

Recapitulation

Before considering the genesis of the Skarn series it is convenient to state some generalizations which arise out of the foregoing:

(i)   the skarns were formed in part from pre-existing Grenville rocks;

(ii) the processes of formation included in situ metasomatism, meta-morphic diffusion or differentiation, vein deposition, possibly bulk injection or flowage, possibly pegmatitic contamination;

(iii) skarn assemblages III, IV and V frequently contain radioactive minerals and are confined to regions of intense tectonic and migmatitic activity: assemblages I and II do not always contain radioactivity;

(iv) some radioactive deposits are not associated with skarns;

(v)   some radioactive deposits appear to be cogenetic with their enclosing rocks: others were clearly emplaced by fracture control and have no evident relation to the host rock;

   (vi) the elements, Ca, B, Be, Ga, Li, Mn, Y, Sr, Pb are commonly enriched in the skarn minerals; to these may be added U, Th, Zr, RE, Ti, F, Cl, S, and P in many cases; B is always richer than in the crust, and the same is probably true for Cl, Be, Li, Mn, Y, Sr and Pb;

  (vii) Cr, Ni, Co, Cu, V, and various other less important elements are at notably low concentrations in the skarn minerals; Mo is also low, although some pyroxenites are mineralized with molybdenite;

 (viii) most trace elements occur at lattice sites in their minerals, but Li may be in an adsorbed phase in scapolite, and the status of B is uncertain; camouflaged trace elements in scapolite show no sympathetic variation with major elements, but in pyroxene there is correlation between Fe (+ Al) and Ga, Ni, Co, V and Mn;

  (ix) intercalated pelitic horizons in drill-cores at many radioactive deposits have sillimanite-garnet-microcline-mica assemblages, indicating upper amphibolite facies;

   (x) the coarse massive fabric of most skarns indicates a post-tectonic crystallization;

  (xi) the conditions of genesis appeared to favour equilibrium assemblages, composed of rather few minerals;

  (xii) assemblage I occurs on a regional scale in various parts of the world;

 (xiii) the fluorite skarns are the most differentiated, in the sense that they show the least resemblance to any country rocks.

The last three points need further discussion. Number xi will be examined immediately and the others later.

Scapolite-Diopside Assemblages

    The assemblage scapolite-green pyroxene-sphene, with amphibole, phlogopite, garnet, calcite or feldspars as additional phases has been found all over the world in areas rich in highly metamorphosed calcareous rocks. The literature has already been reviewed in detail (Shaw, 1960*b*) and need not be recapitulated here. As far as one can judge from published descriptions the pyroxene is usually a member of the diopside-salite-ferrosalite series, but the rocks of the Shai Hills, Ghana, described by von Knorring & Kennedy (1958) differ from most others in that the pyroxenes are rather rich in Al and show eclogitic affinity. Apart from this example the other assemblages appear to have formed in the upper amphibolite facies, and this is also the case for the Quebec and Ontario rocks considered here.

The question arises as to whether the assemblage fulfils the conditions necessary for the erection of a special metamorphic facies. It is widespread, it appears to represent equilibrium conditions, it is known to form from various parent rocks and it indicates special chemical conditions (high p-CO_2 and p-Cl, medium p-H_2O). Since, however, rather similar assemblages occur in the sanidinite and granulite-eclogite facies, the assemblage scapolite-pyroxene alone would be too broad to be of value. To be considered as a facies two conditions would have to be met:

(a) potash feldspar must be microcline or orthoclase, and not sanidine;

(b) pyroxene must be a (virtually) non-aluminous variety of the diopside-hedenbergite series.

Since these assemblages represent a rather unusual conjunction of geological conditions the concept of a scapolite-diopside facies might be of value. This would generally overlap the almandine amphibolite facies (Fyfe, Turner & Verhoogen, 1958) as far as external conditions are concerned, but is characterized by the chemical environment mentioned above, together with richness in the trace elements B, Be and Li (whose presence has been found in scapolites from other areas also [Shaw, *op. cit.*]).

Physical Conditions During Genesis

Pelitic assemblages intercalated here and there with the Skarn Series and associated rocks demonstrate a metamorphic grade reaching the upper amphibolite facies, recently re-named the almandine amphibolite facies by Fyfe, Turner & Verhoogen (1958). According to their tentative correlation of facies with physical conditions, this facies extends from about 500 to nearly 700° C. under p-H_2O of 6,000 to more than 10,000 kg/cm²: by contrast Ramberg (1952, p. 156) suggests a temperature range of 400–500° C.

From discussions of the scapolite-diopside assemblages, it is evident that the recrystallization cannot solely be related to conditions expressed in water vapour pressure. More important for the present rocks were p-CO_2, p-Cl, p-SO_3 and, in some rocks, p-F. Moreover, since there is evidence that some of the skarns migrated and accumulated in pods, lenses and veins, these loci must have been under lower confining pressure than the surrounding rock framework; consequently the total volatile vapour pressure was different from the hydrostatic pressure. In fact, it is not reasonable to use a single hydrostatic rock pressure, since the evidence of flowage indicates that the force distribution within the "solid" rock was not isotropic, and the carbonates yielded in response to the maximum stress vector.

In a decrepitometric study of pegmatite minerals (pyrite, quartz,

fluorite, oligoclase) possibly cogenetic with the skarns in Monteagle Twp., Ontario, Peach (1951) found indications of pressures in the range 2,800–3,000 bars and temperatures of 430–650° C. (mostly 450 to 550° C.). On the other hand Currie, using a similar approach to the phlogopite-apatite pyroxenites in southeastern Ontario (1951), found temperatures of formation in the range 500–750° C. The stability of phlogopite has been investigated experimentally by Yoder & Eugster (1954): its lower stability limit is not known but it remains stable up to at least 770° C.

The depth at which the skarns were formed is problematical. With the present state of stratigraphic studies in the Grenville province there is little information regarding the thickness of beds to be seen, largely owing to insufficient knowledge of the extent of flowage and repetition of beds by faulting and folding, let alone the thickness which might have been eroded away. The only information one can use is general; for example, Engel & Engel (1953) estimate the Grenville series in the Haliburton–Bancroft region and adjacent areas to have a present thickness of 10,000–20,000 feet (3–6 km), and Buddington (1939) estimates the metamorphism in the Adirondack mountains to have taken place at a depth of 20,000–30,000 feet (6–10 km).

The only numerical result from the present study is the temperature of 330° C. from Barth's temperature scale for the crystallization of the feldspars in Q3 (a pyroxene granodiorite from CUM). In spite of various theoretical and practical objections which can be made to the use of this scale, the results which Barth has obtained from its use appear to be of the right order of magnitude. Moreover, the influence of volatile elements other than water on the partition of albite between potash and plagioclase feldspar should not be great, since these volatile components take no part in the reaction. The influence is indirect, in part by exerting a total pressure which would have a little affect on the reaction by virtue of slightly different molar volumes of the various phases, and in part with regard to obtaining equilibrium, which should be easier in the presence of abundant volatiles. The former effect should be small, however, and it may be taken that the figure of 330° C. represents the order of magnitude of the temperature actually obtaining.

The calibration of Barth's scale is however not very certain, and the composition of the feldspar pair (Q3) may also be examined in the light of recent experimental studies in the system Or–Ab–An–H_2O by Yoder, Stewart & Smith (1957) and Orville (1958). Assuming that the Q3 feldspars crystallized in equilibrium with each other and with a gaseous phase under high pressure, the position of their tie-line in the system Or–Ab–An (i.e. low An and Or content of the plagioclase and low Ab content of the microcline) indicates a low temperature of formation. The

precise relationship of ternary composition to pressure and temperature has not been determined, but the An content of both phases is so low that we can consider them (as with Barth's method) to be binary solid solutions in the Or–Ab system. Extrapolation of the solvus in Fig. 38 of Yoder *et al.* (*op. cit.*, p. 208) would give a temperature in the range 300–400° C. at p-H_2O of 5,000 bars. The solvus has been shown to be relatively independent of pressure and we might accept a temperature of 350 $\pm$ 50° C. at a pressure determined in part by the depth of burial and in part by the quantity of volatiles present.

This temperature is considerably lower than the estimates for related minerals by Currie (*op. cit.*), and also lower than the limits proposed by Fyfe, Turner & Verhoogen for the almandine amphibolite facies. It is, however, not very different from Peach's interpretation.

From heat flow and conductivity values Tuttle (1955) has estimated the geothermal gradient, and a temperature of 350° C. might be expected at crustal depths of 4 to 10 km. By contrast the data used by Birch (1955) suggest depths of 15 to 30 km, depending on the thermal model chosen for the crust: he also comments that (p. 114)

in parts of the Canadian Shield, where the heat flow seems to be no greater than 0.9 microcal/cm²/sec., the temperature at 30 km might be as low as 240° C.

This, however, refers to the present temperature gradient, which is different from the one which prevailed at the time of metamorphism and orogenesis.

From analysis of the thermal conditions within the crust MacDonald (1959) concludes that (p. 1983):

In both continental and oceanic regions the temperature at a depth of 30 km should be of the order of 500° C. . . . A temperature much in excess of 600 to 700° C. appears unreasonable. Local variations are to be expected . . . (and) temperatures at a depth of 30 km in areas of Tertiary sedimentation should be a hundred degrees or more above temperatures in ancient shield areas.

The temperatures suggested by MacDonald for the depth of 30 km in a crust of intermediate rock composition are 345 and 415° C., depending on the conductivity. Since we are interested in events at a time when the present shield resembled more closely an "area of Tertiary sedimentation" we might add 100° C. to these figures and accept 500° C. at the base of a 30 km crust. This would give a temperature of 350° C. at a depth of 20 to 25 km.

Another line of reasoning assumes that in rocks such as Q3, microcline, sodic plagioclase and quartz crystallized simultaneously. For this to

occur the pressure must have been great enough to prevent the prior formation of a single feldspar (sanidine); experimental realization of these conditions has not quite been attained, but a pressure of at least 6,000 kg/cm.² at about 500° C. is suggested by extrapolation (Tuttle & Bowen, 1958): this corresponds to a minimum depth of 22 km, but in terms of the experimental studies is a water vapour pressure, somewhat different from the conditions in the skarns.

The presence of carbon dioxide, chlorine, fluorine, calcite and pyroxene would certainly be expected to modify the silica-two feldspar cotectic, but probably in the direction of lower temperatures. However, Wyllie & Tuttle (1959) have shown that carbon dioxide has very little or no effect on the melting of granitic liquids. A depth of about 25 km and temperature of about 350° C. would lie within Birch's and MacDonald's limits for the geothermal gradient, although decidedly deeper than Tuttle's estimate. Similarly, the opportunities for erosion since late Precambrian time (1,000 m.y.) suggest a deep crustal level to be exposed now, even supposing that the main features of the Shield had been carved out by early Palaeozoic times. Finally the abundance of migmatites, suggestions of anatexis and granitization, tectonic complexity and obliteration of most primary sedimentary features agree better with a deep-seated than a shallow history.

Chemical Features of The Skarns

Figure 1 summarizes the relations between the skarns and related country rocks, and indicates that the evolution of the skarns can be considered as a convergence towards assemblages of relatively few minerals, eleven in all: plagioclase, microcline, scapolite, quartz, pyroxene, amphibole, calcite, phlogopite, sphene, fluorite, and apatite. Accessory minerals (allanite, zircon, uranothorite, uraninite, etc.) can be ignored, since they do not determine the major assemblages. Most contact skarns from younger rocks show a far greater wealth of mineral species.

This suggests that the skarns represent assemblages of a group of minerals stable in a particular physical and chemical environment, and that these conditions persisted long enough for equilibrium to be reached: that is, they constitute a metamorphic–metasomatic facies, rather than a series of products of incompleted reactions. The metamorphic or physical environment was that of the amphibolite facies, while the metasomatic processes depended on the availability of certain less common elements and will now be discussed.

The movement of elements cannot be presented quantitatively, because of the variable nature of the skarns, for which modal and bulk analyses were not feasible. The qualitative relations can, however, be

interpreted from the mineralogy, assuming volumetric replacement, and are shown in Fig. 2.
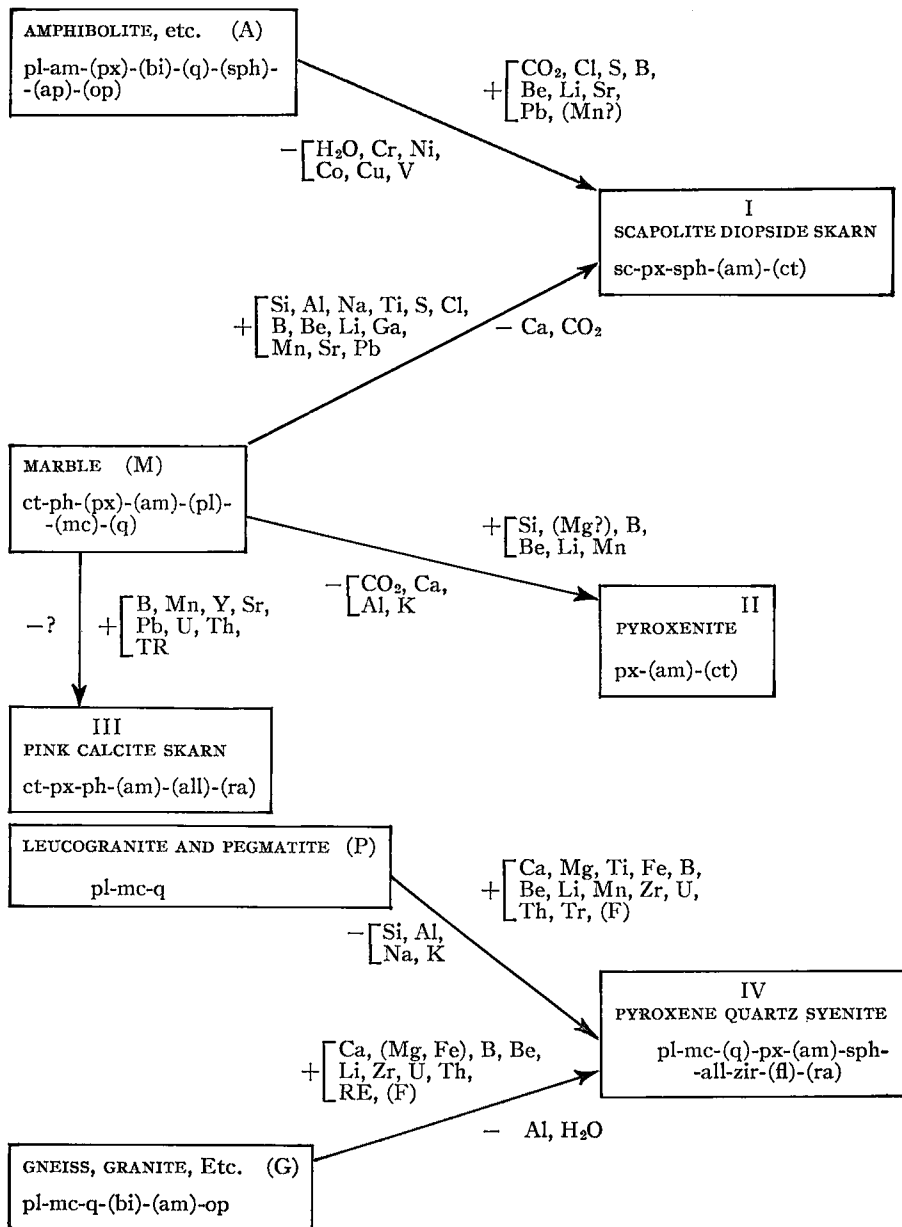

FIG. 2. Chemical relationships between skarns and country rocks
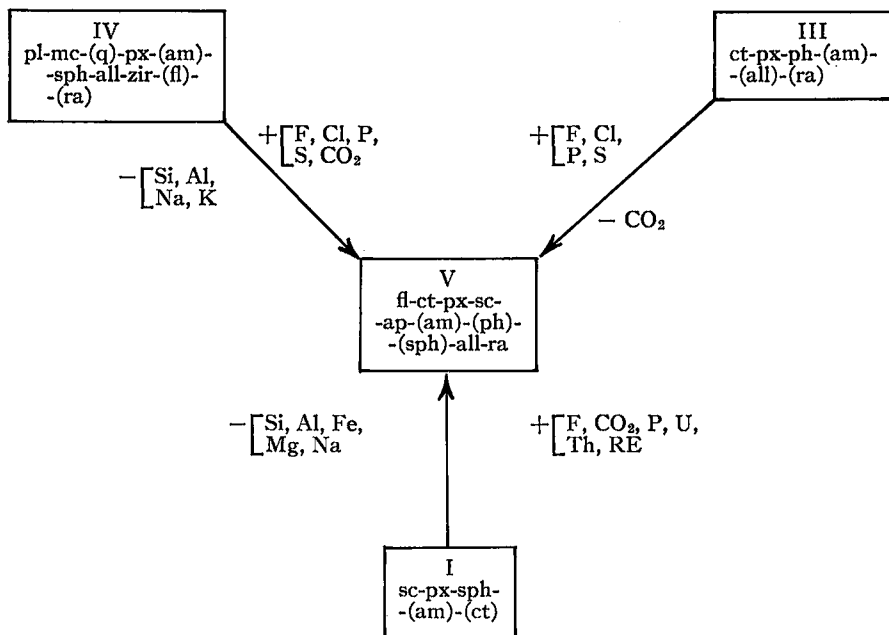[rare earth elements: RE, TR or Tr—EDITOR].

FIG. 3. Relationships of fluorite rocks to the other skarns.

The behaviour of some of the trace elements is postulated on the basis of their distribution in common rocks and minerals, and the interpretation would be more secure if more analyses of the country rocks were available (however, see Engel & Engel, 1958a, b).

The relative abundance of the different skarns cannot be assessed, nor can the question of whether any of these reactions were complementary: e.g., whether Si and Al released during the alteration of leucogranite to pyroxene syenite was available for the development of scapolite in marble. It is probable that such complementary reactions (i.e., metamorphic differentiation) took place in the many localities where there is a close spatial relation between different skarn-types, but the trace element evidence indicates that the reactions were not entirely a matter of redistribution of material in a closed system and did, in fact, necessitate introduction of elements from outside.

The compositional relations between the fluorite rocks and the other skarns are summarized in Fig. 3. These reactions are again based on volumetric replacement. If there was partial assimilation of skarn by a migrating fluid or solution the relations would be similar, except that no elements need have been removed if the volume of assimilated material was small in relation to the volume of the whole deposit.

The most critical problem which emerges from this discussion concerns the origin of the elements specially concentrated, i.e., F, P, Cl, S, B, Be, Li, Mn, Y, Sr, Pb, U, Th, and possibly Ga and RE.

Origin of the Skarns

It is evident that the origin of the skarns cannot yet be explained in detail. However, a tentative hypothesis can be attempted.

The skarns originated at a depth of about 25 km, at temperatures of 300–400° C., after the climax of a period of strong crustal movement or orogenesis over a wide area. The coarse massive textures which are common indicate that they were late in the plutonic history. Solutions (fluids) permeated the metamorphic rocks and began to react: their composition was a mixture of CO_2, H_2O, Cl and SO_4 (or related compounds), containing B, Be and Li as well. One cannot expect uniformity in nature, and local concentrations of F, P, Ga, Mn, Y, Sr, Pb, RE, U and Th can be admitted, if it is assumed that minerals crystallized faster than diffusion operated.

The rocks which were formed depended on several factors, which chiefly involved the particular country rock and the amount of bulk movement: the principal factor, however, was a reaction with marble. As a result the solutions either dissolved a limited amount of marble, then reacted with other rocks (e.g., to develop pyroxenic and scapolitic assemblages), or were completely spent in reacting with marble (e.g., pink calcite or fluorite skarns). In both cases varying degrees of movement operated, varying from in situ metasomatism, to local migration to points of lower pressure to form pods or tumours, to vein deposits and replacements (true cavities or open fissures cannot be envisaged). In some cases the migrating fluid was a dilute "liquid-like" solution, in others it was rich in carbonate and other minerals and approached our normal concept of a magma (not carbonatic, however). In all cases, however, volatiles were abundant, diffusion to crystal nuclei was rapid and coarse, pegmatitic fabrics developed. The fresh unaltered appearance of many minerals suggests the possibility that the initial cooling, which would be expected to have attendant alteration effects in many minerals, was succeeded by a later rise in temperature and annealing.

So far the hypothesis is largely an interpretative synthesis of the data obtained. Discussion of the exact nature of the solutions, their source and means of access, the significance of the radioactive deposits and causes of their concentration, needs rather wider speculation.

It is evident that the genesis of the skarns is only one facet of the plutonic history of the region, and cannot be considered alone. For instance, Engel & Engel (1958b) have demonstrated that the course of

metamorphism of an amphibolite in the north west Adirondacks released large quantities of H_2O, F, Cl, while the associated paragneiss was also depleted in the same elements plus Si and K. Similar rocks are widespread in the Grenville province of Ontario, although the grade of metamorphism in amphibolite does not commonly reach the level reported by Engel & Engel (i.e., development of orthopyroxene). The chemical changes reported by Engel & Engel were syntectonic and therefore older than the skarns: the same is true of many of the vast granitic complexes which dominate the geology of Southern Ontario and Quebec, but post-tectonic granites are also known (e.g., Loon Lake Pluton, Chandos Twp., Ontario).

In the opinion of the writers, the skarn-forming solutions were products of plutonic metamorphism of the country rocks (compare Rowe, 1952) and developed as a result of crustal depression of a complex of marbles, amphibolites, gabbros, paragneisses and granites (the products of earlier metamorphism) into hotter regions. Increasing temperatures and pressures mobilized pore-liquids and released volatile components from solid minerals, in a reversal of the familiar sequence of late magmatic fluid evolution: continuation of this process of "sweating" led to extensive solution of silicates and eventual anatexis or production of magma. It seems likely, however, that the processes under particular discussion took place below the temperature of extensive silicate melting, in a pneumatolytic or hydrothermal frame of reference. The solutions were highly active, however, and leached B, Be, Li, U, Th and RE from the rocks: the region was already a Th–U geochemical province in all probability. Moving upwards through fractures the solutions came in contact with cooler rocks and consequently reacted during a period sufficiently long for equilibrium to be attained. Where the host rocks were carbonatic, or contained abundant intercalated marbles, skarns were produced: the products of the reactions concealed the fracture systems along which the fluids entered. Elsewhere the solutions deposited radioactive minerals in silicate host rocks and, in the absence of skarns, the Th–U deposits are more clearly related to fracturing and appear in a wide variety of host-rocks. Partial anatexis in the lower region led to local generation of pegmatite solutions or magma: these also received a share of the Th & U and migrated under pressure to form bodies of radioactive minerals, accompanied by skarn minerals (during assimilation), pegmatitic in some cases and leucocratic in others.

The theory is evidently controversial and leaves numerous features unsatisfactorily explained. In particular the abundance of Th–U minerals in the Ontario-Quebec segment of the Grenville province has not been explained by relegating it to an earlier phase of the plutonic history, nor has the relative richness of Li in the skarn minerals in a region known to

be poor in Li-deposits. However, if the arguments provoke the replacement of the theory by a more satisfactory one, so much the better.

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