METASOMATISM IN THE KAMISKOTIA MAFIC COMPLEX

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ABSTRACT

Metasomatism was taken by Goldschmidt (1922) as being metamorphism involving introduction and removal of certain substances, with a corresponding change in the chemistry and mineralogy of the rock concerned. Using this definition, there is strong evidence of metasomatism having played an important role in the transformation of part of the Kamiskotia mafic intrusion from a norite to a greenschist facies rock.

The importance of metasomatism has generally proved difficult to evaluate because of disagreement on a quantitative approach to the problem. Two of the approaches suggested in the literature have been employed to characterize the chemical changes accompanying metamorphism of the Kamiskotia complex; one assuming constant volume, the other assuming constant alumina. The latter approach, supported by most recent work in this area (Carmichael, 1970; Korzhinsky, 1964) is favoured. It defines a mobility series that agrees guite well with Korzhinsky's for all elements except iron. It is concluded that metamorphism of the Kamiskotia norite has been accompanied by significant removal of potash, soda, iron and silica besides the addition of water and carbon dioxide.

Reactions, constructed on the basis of mineral relationships observed in thin section combined with the calculated

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chemical changes are proposed. The source of the metasomatic fluids and the site of deposition of removed material is speculated upon.

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INTRODUCTION

The Kamiskotia complex is a large mafic intrusive body which outcrops west of Timmins, Ontario in parts of Robb, Cote, Massey, Turnbull, Whitesides and Carscallen townships (see FIGURE 1). As part of an Ontario Department of Mines project undertaken by W.J. Wolfe, this intrusive was mapped and sampled during 1969. The author assisted in this aspect of the study.

Large parts of the mafic body consist of fresh noritegabbro, but a roughly circular zone in northern Whitesides and southern Massey townships has been regionally metamorphosed to a greenschist facies assemblage of epidote-chlorite-albitequartz-calcite. Whole rock analyses, performed by X-ray fluoresence spectroscopy, bring out significant chemical differences between the fresh and altered rocks. If it can be assumed that the original composition of the metagabbroic rocks were similar to that of the norite-gabbros, then these chemical differences can only be explained in terms of different relative mobility of components during regional metamorphism.

Various petrologic calculations have been proposed for studying metasomatic changes in rock composition; Barth (1948), Poldervaart (1953), Korzhinsky (1964), etc. Two of these techniques have been used to compare the fresh and altered rocks; first, by the oxygen standard cell proposed by Barth and

modified by Chidester (1962), and secondly by assuming constant alumina, as proposed by Korzhinsky.

THE KAMISKOTIA MAFIC COMPLEX

General Geology

FIGURE 1 (modified after Wolfe, 1970) summarizes the general geology of the Kamiskotia-Whitesides area and locates all samples referred to in this report. Wolfe's geological map has been simplified for the sake of clarity by omitting a number of north-south trending diabase dikes and some structural information.

The Kamiskotia mafic complex has been intruded into a diverse sequence of Archean metavolcanics; these consist of mafic and felsic flows, tuffs and pyroclastics. The intrusive contact between the volcanic series and the Kamiskotia complex has been described as transitional (Berry, 1944) or as a hybrid reaction zone (Wolfe, 1970).

The texture and grain size of the norite-gabbro and hornblendite are quite variable, ranging from fine grained to coarse pegmatitic phases. In Whitesides and Massey townships there is a gradational change from fresh gabbroic rocks to amphibole metagabbro and finally to a zone of strongly altered leucocratic metagabbro. Data from an airborne magnetic survey can be used to delineate this area of altered gabbroic rocks. Wolfe correlates the low magnetic profile of these rocks with the virtual absence of oxide and sulphide phases in them.

TABLE 1

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TABLE OF FORMATIONS FOR THE KAMISKOTIA-WHITESIDES AREA (from Wolfe, 1970)

CENOZOIC

RECENT

Swamp, stream and lake deposits

PLEISTOCENE

Massive and varved lacustrine clays

Sand and gravel (esker deposits, re-worked esker material, beach deposits)

UNCONFORMITY

PRECAMBRIAN

ARCHEAN

LATE MAFIC INTRUSIVE ROCKS

Diabase, porphyritic diabase

IGNEOUS CONTACT

FELSIC INTRUSIVE ROCKS

Granite, quartz monzonite, trondhjemite, quartz porphyry, aplite

Intrusive breccia, hybrid granitic rocks

IGNEOUS CONTACT

EARLY MAFIC AND ULTRAMAFIC ROCKS

Norite, clinopyroxene norite, orthopyroxene gabbro, anorthositic norite, hornblendite, amphibole metagabbro, leucocratic metagabbro, serpentinite

IGNEOUS CONTACT

METAVOLCANIC ROCKS

Rhyolite and dacite flows and fragmentals

Basalt and andesite flows, pillowed lavas and fragmentals.





(modified after W.J. Wolfe, 1970)

Many small granitic stocks and dikes intrude the eastern margin of the mafic complex, while its western extent is cut off by a large younger granitic batholith.

Petrography

The norite-gabbro was subclassified by the relative modal abundance of plagioclase, orthopyroxene and clinopyroxene, using the classification scheme shown in FIGURE 2. By this classification the Kamiskotia mafic rocks include norite, clinopyroxene norite, anorthositic norite and orthopyroxene gabbro (referred to collectively as norite-gabbro). Other rock types are hornblendite, amphibole metagabbro, leucocratic metagabbro and serpentinized peridotite. Hornblendite is distinguished from amphibole metagabbro by the presence of primary, euhedral hornblende. It is not uncommon for the norite-gabbros to display an igneous lamination, defined by the parallel alignment of plagioclase and pyroxene grains. In southern Robb and northern Massey townships a layered series consisting of pyroxene-rich and plagioclase-rich beds is exposed.

Clear, unclouded plagioclase usually makes up more than one-half of the norite-gabbros. These plagioclase grains are albite and pericline twinned and consistently give compositions in the An_{50} to An_{60} range, as determined by the Michel-Levy method. Hypersthene is the predominant pyroxene in most samples; it occurs as subhedral grains or as large anhedral grainspoikiolitically enclosing plagioclase laths. In some

FIGURE 2 CLASSIFICATION OF KAMISKOTIA NORITE-GABBROS



rocks, hypersthene has exsolved clinopyroxene as thin lamallae parallel to (100). Occasionally, there are two sets of exsolution lamallae, a narrow set exsolved parallel to (100) as well as a coarser set, crystallographically unrelated to the hyperstheme host. Such well-developed exsolution features are typical of pyroxenes from large, slowly cooled mafic intrusions such as the Bushveld, Skaergaard and Stillwater. The textures and optical properties of these pyroxenes have been described by Poldervaart and Hess (1951), and quantitatively analyzed by electron probe by Boyd and Brown (1969). The double set of exsolution lamallae described for some Kamiskotia pyroxenes appears to be similar to that of the Bushveld pvroxenes. Thick lamallae of augite exsolved parallel to (001) of monoclinic pigeonite prior to its inversion to orthorhombic hypersthene. The exsolution of the calcic pyroxene, augite, from the calciumpoor host continued as narrow lamallae parallel to (100) of hypersthene.

Clinopyroxene also occurs as a primary phase, but tends to be interstitial, schillerized and of smaller grain size than plagioclase or hyperstheme. Opague minerals, oxides and sulphides, make up the remainder of the fresh norite-gabbros, but their quantity is guite variable.

Modal analyses of five typical noritic gabbros are tabulated in TABLE 2(A).

The transition from fresh norite-gabbro to the metagabbroic facies is gradational. Attempts to trace the alteration

TABLE 2 MODAL ANALYSES

(A) NORITE-GABBROS (500 point counts)

Rock Type	Norite	Clino No	pyroxene rite	Anorthosit Norite	ic Ortl	hopyroxene Gabbro
Sample No.	236	33	97	171		330
Plagioclase	53.7	52.3	55.3	67.1		57.4
Hypersthene	31.0	25.8	31.7	19.6		13.9
Clinopyroxene	8.9	19.2	12.2	3.5		19.5
Amphibole (afte hypersthene)	er 1.0	1.4		8.0		3.2
Oxides and Sulphides	5.4	1.3	0.8	1.8		6.0
Total	1.00.0	100.0	100.0	100.0		100.0
(B) METAGABBROS	5 (750 point	counts)				
Sample No.			117		119	
	and the second	are a sumal survey and				And the second se

Clinozoisite	44.8	54.2	
Amphibole (tremolite)	10.0		
Chlorite (ripidolite)	35.1	27.1	.*
Quartz and Albite Calcite Oxides	2.3 7.5 0.3	13.1 5.0 0.6	
Total	100.0	100.0	

sequence are hindered by the lack of good outcrop exposure, but the changes can be followed reasonably well in the rocks of north-central Whitesides township. Fresh clinopyroxene norite passes into amphibole metagabbro with the formation tremolitic amphiboles from primary pyroxenes. Amphibole appears first as mantles on pyroxene grains, but in the more highly altered rocks they occur grouped as large clusters. If oxides are present, they are reduced to aggregates of ragged grains, surrounded and embayed by pale yellow-green iron-bearing epidote. Plagioclase remains clear and unclouded in these rocks.

The next step in the alteration sequence is marked by the almost simultaneous appearance of chlorite and clinozoisite. In some cases all plagioclase grains lose their twinning and become strongly clouded before minute grains of high-relief clinozoisite appear. In other cases the replacement is irregular as both clinozoisite and unaltered plagioclase may occur in the same thin section. Chlorite usually forms radiating mantles on amphiboles, but it also occurs as fan-shaped crystal aggregates. It is typically colourless, or at most, only very faintly green and pleochroic. Its colour and crystal form, along with very low birefringence and nearly parallel extinction characterize this chlorite as ripidolite. A trace amount of secondary quartz is often present, associated with the mafic minerals, tremolite and chlorite.

With the disappearance of plagioclase in favour of clinozoisite and the replacement of tremolite by chlorite,

these rocks grade into the most intensely altered group. The final mineral assemblage in these fine grained rocks is clinozoisite-chlorite-calcite-albite-guartz. Albite and guartz may occur as very small, clear grains associated with chlorite. The presence of both these minerals was verified by an X-ray diffraction trace. Finally, calcite, present in narrow stringers in some of the less altered rocks, is present throughout these more altered rocks.

Modal analyses of two leucocratic metagabbros are given in TABLE 2(B).

CHEMICAL ANALYSIS

Analytical Procedure

Analyses for Si, Al, Ti, Mg, Ca, Na, K and total Fe were performed by X-ray fluoresence, using the method developed by Rose et al (1962). The method used is as follows:

- 0.1250 grams of rock powder (-200 mesh), 0.1250 grams of cerium oxide and 1.0000 grams of anhydrous lithium tetrabroate were weighed into a carbon crucible.
- 2. The crucible and contents were placed in a pre-heated muffle furnace at 1100°C for 30 minutes and then quenched in air to produce a glass bead.
- The glass bead was reweighed and the weight made up to 1.2500 grams with powdered boric acid.
- The glass bead and boric acid were ground and mixed in a Spex Mix-Grinder to produce a powder.
- 5. A pellet was made from the powder, applying 20 tons of pressure for 30 seconds in a pellet press, and using a backing of powdered boric acid.

Pellets of six rock standards (W-1, GSP-1, G-2, PCC-1, AGV-1 and DTS-1) and fourteen samples were prepared by this method. In addition, as a check on internal consistency, duplicate pellets were prepared for two samples. For each element analyzed, the six standards were used to prepare a calibration curve. One of these pellets, generally W-l or AGV-1, was selected as a running standard and was included with each group of three samples. After all the samples had been analyzed the position of the calibration curve was checked by running the standards once again. A Philips, Model 1540, X-ray fluoresence vacuum spectrograph, with a chromium target tube and flow proportional counter were used for all analyses. The instrumental conditions used for each element are listed in TABLE 3.

Determinations for ferrous iron, carbon dioxide and water were performed under the direction of Mr. J. Muysson using standard wet chemical methods. Ferric iron was determined by difference, using the X-ray fluoresence value for total iron and the separate determination for ferrous iron.

Results

Duplicate analyses were performed on one representative sample of fresh clinopyroxene norite and one leucocratic metagabbro. The two pairs of analyses are compared in TABLE 4, and the close agreement of these two duplicate samples implies good internal consistency.

The analytical results are given in TABLE 5, grouped according to rock type. In addition three analyses by Wolfe (1970) of leucocratic metagabbros are presented as they will be referred to in subsequent interpretations. Molecular norms have been calculated for each analyses and these are

Element	X-ray line	Peak Position (°20)	Vacuum	Collimator	Excitation Voltage (kv)/Tube Current (ma)	Counter Voltage	Analyzing Crystal
Si	K	73.36	On	Coarse	50/30	460	PET
Ti	K	86.16	On	Fine	50/30	505	LiF (200)
Al	K	114.61	On	Coarse	50/30	425	PET
Fe	K	57.54	Off	Fine	50/30	505	LiF (200)
Mg	K	106.99	On	Coarse	50/30	475	ADP
Ca	K	113.24	On	Fine	40/20	505	LiF (200)
Na	K	24.27	On	Coarse	50/30	450	RBAP
K	К	20.58	On	Coarse	50/30	505	PET

Element	Pulse Height	Analysis	Time	Counts	Counts	
	Lower Level	Window	(sec.)			
Si	_ /	-	200	1 x 10 ⁶		
Ti	-	4	100	4×10^{5}		
Al	125	100	200	1×10^{5}		
Fe	-	-	40	1 x 10 ⁶		
Mg	120	160	200	1×10^4		
Ca	· · · · ·		100	1×10^{6}		
Na	100	180	200	1×10^{4}		
K	-	-	100	1 x 10 ⁶		

Oxide	Samp] A	e 97 B	Sample A	117 B	Largest Error on the Mean
sio ₂	51.7	52.0	45.1	45.5	±0.2
TiO2	0.13	0.13	0.0	0.0	±0.0
Al ₂ 0 ₃	15.5	14.9	18.4	18.9	±0.3
FeO+ Fe2 ⁰ 3	7.41	7.52	5.37	5.26	±0.06
MgO	7.65	7.25	8.77	9.30	±0.3
CaO	14.2	13.9	13.8	13.8	±0.2
Na20	2.89	2.42	0.41	0.33	±0.3
к20	0.11	0.15	0.08	0.08	±0.02
Total	99.6	98.3	91.9	93.2	±0.7

TABLE 4. REPRODUCIBILITY OF ANALYSIS

tabulated with the chemical data.

Comparison of Analytical Results

Four of the samples have also been analyzed by the Ontario Department of Mines laboratory in Toronto and have been published by Wolfe (1970). They analyzed Si, Al, total Fe, Ca, Mg, Ti and Mn by X-ray fluoresence spectroscopy; ferrous iron was determined separately and ferric iron by subtraction. Na and K were determined by flame photometry and P, CO₂ and H₂O

Rock Type		Clinopyroxene	e norite
Sample	3	3 38	97 ¹
SiO_2 TiO_2 Al_2O_3 FeO MgO CaO Na_2O K_2O H_2O+ H_2O- CO_2	51 0 13 1 10 6 12 2 0 1 1 0 0	.4 51.0 .92 1.03 .6 13.8 .06 1.74 .0 8.62 .59 7.41 .6 12.5 .28 2.35 .15 0.17 .17 1.53 .06 0.05	51.9 0.13 15.2 1.67 5.80 7.42 14.1 2.66 0.13 0.84 0.31 0.04
TOTAL	100	.1 101.4	100.2
Density ²	3	.02 3.03	2.88
Sample	3	338	97
Quartz Corundum Orthoclase Plagioclase Hypersthene Augite Olivine Ilmenite Magnetite Calcite	1 0 48 17 29 0 1 1 0	.28 0.75 .00 0.00 .91 1.02 .10 48.67 .83 17.47 .28 28.64 .00 0.00 .31 1.46 .14 1.86 .16 0.13	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
TOTAL	100	.0 100.0	100.0
Mol % An Mg/Fe	56 0	.57 56	55 0 .73

TABLE 5 CHEMICAL ANALYSES AND MOLECULAR NORMATIVE MINERALS

TABLE 5/... continued

Rock Type	Opx	Anorthositic	Norite
Sample	Gabbro 330	Norite 171	172
SiOn	50.8	52.3	48.6
TiO2	1.17	0.24	1.88
AlaÓa	15.4	18.3	14.9
Fe ₂ O ₂	2.95	1.02	1.66
FeŐ	11.2	8.05	11.6
MgO	6.11	5.71	8.56
CaO	10.8	10.7	10.9
Na ₂ O	2.15	2.61	1.59
K2Ō	0.18	0.14	0.11
H ₂ O+	0.87	1.13	1.01
H20-	0.27	0.24	0.26
CO2	0.07	0.12	0.18
TOTAL	101.9	99.5	101.3
Density ²	3.05	2.92	3.06
Sample	330	171	172
Quartz	2.60	2.28	0.00
Corundum	0.00	0.00	0.00
Discission	1.01	0.84	0.00
PidyiOciase	22.20	21 50	30.03
Augito	17 25	11 72	16 02
Olivine	0.00	0.00	0.25
Ilmenite	1 65	0.34	2.66
Magnetite	3,12	1.08	1.76
Calcite	0.18	0.31	0.46
TOTAL	100.0	100.0	100.0
Mol % An	62	62	70
Mg/Fe	0.55	0.58	0.62

TABLE 5/... continued

Rock Type	Amphibole Metagabbro				
Sample	133	143	150	163	213
SiO_2 TiO_2 Al_2O_3 FeO MgO CaO Na_2O K_2O H_2O+ H_2O- CO_2	50.6 0.09 14.4 1.37 4.67 9.12 14.6 2.12 0.22 2.74 0.37 0.21	50.3 0.18 13.8 1.6 6.03 11.2 11.7 1.39 0.40 2.51 0.33 0.13	49.4 0.26 14.6 1.97 6.16 10.8 10.3 1.63 0.47 3.03 0.35 0.47	48.7 1.31 16.3 1.83 3.12 8.07 13.0 0.89 0.97 2.48 0.30 1.89	47.9 0.13 16.2 1.49 4.86 8.13 13.3 1.89 0.18 2.90 0.34 0.49
TOTAL	100.5	99.6	99.5	98.9	97.8
Density ²	2.88	2.96	3.04	2.96	2.96
Sample	133	143	150	163	213
Quartz Corundum Orthoclase Plagioclase Hypersthene Augite Olivine Ilmenite Magnetite Calcite	0.0 0.0 1.32 48.84 10.49 34.04 3.19 0.13 1.45 0.54	$\begin{array}{c} 0.76 \\ 0.0 \\ 2.42 \\ 43.7 \\ 28.75 \\ 22.08 \\ 0.0 \\ 0.26 \\ 1.71 \\ 0.34 \end{array}$	0.66 0.0 2.86 47.09 31.71 13.98 0.0 0.37 2.12 1.22	7.07 0.0 5.93 47.19 18.67 12.35 0.0 1.89 1.98 4.94	0.0 0.0 1.11 54.58 16.62 23.17 1.41 0.19 1.63 1.30
TOTAL	100.0	100.0	100.0	100.0	100.0
Mol % An Mg/Fe	60 0 <u>.</u> 8	71 0.8	68 0.79	82 0.93	67 0.78

TABLE 5/... continued

Rock Type	Leucocratic Metagabbro						
Sample	167	1171	119	65	177 ³	176 ³	
SiO_2 TiO2 Al ₂ O3 Fe ₂ O3 FeO MgO CaO Na ₂ O K ₂ O H ₂ O+ H ₂ O+ H ₂ O- CO ₂	44.6 0.13 17.3 2.15 5.50 8.44 10.8 0.57 0.11 4.09 0.41 3.64	45.3 0.0 18.7 0.78 4.54 9.04 13.8 0.37 0.08 4.48 0.27 3.92	45.7 0.02 18.1 1.24 3.52 7.51 14.1 0.81 0.06 4.89 0.32 4.37	45.2 0.02 22.1 0.71 3.04 9.29 14.4 0.84 0.07 2.89 0.37 0.11	42.4 0.12 21.3 0.41 3.69 9.74 13.3 0.76 0.07 4.35 0.44 3.46	42.5 0.06 19.7 0.0 5.71 13.3 11.1 0.42 0.08 5.83 0.28 0.18	
TOTAL	97.7	101.8	99.6	99.0	100.0	99.2	
Density ²	2.92	2.98	2.91	2.98	2.90	3.03	
¹ Average of two ² Densities from 3Analyses from	pellets N Wolfe (1 Wolfe (19	1970) 970)					
Sample	167	117	119	65	177	176	
Quartz Corundum Orthoclase Plagioclase Hypersthene Augite Olivine Ilmenite Magnetite Calcite	$ \begin{array}{r} 11.2\\ 5.85\\ 0.69\\ 37.9\\ 32.01\\ 0.0\\ 0.0\\ 0.19\\ 2.39\\ 9.78\end{array} $	$ \begin{array}{r} 6.43\\ 2.17\\ 0.48\\ 47.93\\ 32.05\\ 0.0\\ 0.0\\ 0.0\\ 0.83\\ 10.11 \end{array} $	8.42 1.34 0.37 51.08 26.05 0.0 0.0 0.03 1.34 11.38	0.0 0.42 65.33 11.32 11.73 10.08 0.03 0.76 0.28	1.74 4.79 0.42 50.34 32.75 0.0 0.0 0.17 0.44 8.89	0.0 0.49 57.78 17.07 1.85 22.17 0.09 0.0 0.48	
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	
Mol % An Mg/Fe	86 0.77	93 0.79	85 0.82	88 0.86	86 0.83	93 0.81	

by standard rapid wet chemical methods.

Their analyses compare quite favourably with those presented in this study. The two sets of analyses are similar for Al, Ti, total Fe, Ca, K, H₂O and CO₂. The author's analysis for Si appears, on the basis of the four comparisons, to be consistently 0.5 to 1.5 weight per cent higher. Probably a more significant difference in the two sets of analyses is the general disagreement of the ferrous to ferric iron ratio. The author's analysis in three of the four duplicates have a slightly lower ferrous to ferric ratio, but the difference becomes more acute if the leucocratic metagabbros analyzed by the Ontario Department of Mines laboratory (samples 65, 176, 177) are compared with those analyzed in this study (samples 117, 119, 167).

Because of the low intensity of the K_{α} fluoresence line of Na and Mg these elements are difficult to determine by X-ray fluoresence spectroscopy. Consequently the reproducibility and the agreement for Na and Mg is not as good as for the other major elements.

As an indication of the extent of agreement between the two laboratories, analyses for the four samples are compared in TABLE 6.

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Oxide	33 This Study	3 ODM	38 This Study	ODM	17 This Study	1 ODM	330 This Study	ODM
SiO2	51.4	50.6	51.0	50.5	52.3	51.8	50.8	49.5
TiO2	0.92	0.85	1.03	1.02	0.24	0.33	1.17	1.04
A1_0	13.6	13.2	13.8	14.6	18.3	18.2	15.4	14.5
Fe203	1.06	0.92	1.74	0.81	1.02	0.72	2.95	2.97
FeO	10.0	9.62	8.62	9.18	8.05	8.31	11.2	10.3
MgO	6.59	7.42	7.41	7.05	5.71	5.91	6.11	5.70
CaO	12.6	12.3	12.5	12.4	10.7	10.5	10.8	11.0
MnO	n.d.	0.22	n.d.	0.21	n.d.	0.21	n.d.	0.23
Na ₂ 0	2.28	2.41	2.35	1.52	2.61	2.28	2.15	1.95
к20	0.15	0.11	0.17	0.13	0.14	0.16	0.18	0.15
H20+	1.17	1.03	1.53	1.21	1.13	0.91	0.87	0.78
H ₂ 0-	0.25	0.22	0.23	0.25	0.24	0.22	0.27	0.18
co ₂	0.06	0.05	0.05	0.05	0.12	0.13	0.07	0.07
P205	n.d.	0.12	n.d.	0.12	n.d.	0.01	n.d.	0.02
S	n.d.	0.10	n.d.	0.07	n.d.	0.04	n.d.	0.20
TOTAL	100.1	99.2	101.4	99.1	99.5	99.7	101.9	98.6
								,

n.d. = no determination

INTERPRETATION

General Statement

Gradational changes in chemical composition parallel the gradational changes in petrographic character of the altered rocks. These changes are, of course, only apparent since a chemical analysis is a closed array of numbers; that is, the oxides must always total 100%. Thus, the weight per cent of an oxide may be different in two rocks, not because of a difference in the number of atoms of that element per unit volume, but because of differences in the number of atoms per unit volume, but because of differences. For example, the replacement of K^+ by H^+ necessarily leads to an increase in the weight per cent of all other elements in the rock, simply because of the lighter weight of hydrogen compared to potassium.

The apparent chemical changes that occur in the progression from fresh norite-gabbro to highly altered metagabbro can be followed in the table of analyses. The composition of the fresh rocks appears to be quite similar as most oxides show a limited range of values. Si, Al, Ca, Mg, Na and K tend to be constant in the fresh rocks whereas Fe and especially Ti can be seen to vary more widely. With progressive alteration:

 Silica content decreases gradually from about 51% to 45% or less.

- 2. Alumina content increases from about 15% to 20%.
- The data for magnesium shows more scatter but it appears to indicate an increase from about 7% to 9%.
- As for magnesium, the pattern for lime is not pronounced, but there may be a moderate increase from 12% to 13%.
- The soda content drops off markedly, decreasing from
 2.5% to about 0.5%.
- 6. The pattern for potash is more complex; it increases from 0.15% to more than 0.5% in the amphibole metagabbros but then decreases abruptly to about 0.07% in the leucocratic metagabbros.
- 7. Though the iron content of all the rocks is variable there is a decrease from about 10% to 5%. The author's analyses indicate that ferric iron remains nearly constant, but the Ontario Department of Mines' analyses show a pronounced decrease in ferric iron.
- 8. As with iron, the titanium content of the fresh rocks is rather variable but the data points to a sharp decrease in the altered rocks.
- 9. Volatiles show a pronounced increase; H₂O from 1% to 5% and CO₂ from 0.1% to about 4%.

Molecular Norms

The modal analyses and the norms of the fresh rocks are quite similar with respect to plagioclase and total pyroxene content as reference to TABLE 2 and TABLE 5 will show. Minor amounts of quartz, or occasionally olivine are present in the norms of the fresh rocks, in keeping with their tholeiitic character. With increasing addition of water to the rock, the anhydrous normative minerals become increasingly difficult to relate to the actual mineralogy. While normative albite, quartz and calcite correspond to the actual mineralogy, normative anhydrous pyroxene and anorthite appear in thin section as the hydrous minerals chlorite and clinozoisite.

The presence of substantial amounts of CO_2 in the altered rocks requires that a large amount of CaO be used in forming normative calcite. This results in an excess of Al_2O_3 and SiO_2 over CaO in the formation of anorthite. Since this excess Al_2O_3 and SiO_2 cannot all be used by forming pyroxene, they are left over as normative corundum and quartz. In the rock, excess Al_2O_3 is accommodated by the Al-rich minerals clinozoisite and ripidolite chlorite, while the excess SiO_2 appears as free quartz.

Normative orthoclase reflects the K_2O content of the sample and therefore the decrease described for K_2O is paralleled by the orthoclase molecule. The decrease in Na_2O in the metagabbroic rocks, compared to the nearly constant amount of CaO results in a marked increase in the anorthite content of the normative plagioclase.

Finally, the altered rocks show a decrease in normative magnetite and ilmenite, corresponding to the observed decrease in oxides in thin section and to the decrease in iron and titanium in the chemical analyses.

Metasomatism - Nature of the Problem

In the previous discussion the evidence has been shown to indicate that metamorphism of part of the Kamiskotia mafic pluton coincides with an area of significantly different chemical composition. Both the mineralogical and the chemical changes have been shown to be gradational and to parallel each other, which strongly suggests that the chemical changes are genetically related to the metamorphism. The remaining objective is to describe these chemical changes in a more quantitative manner.

Direct comparison of chemical analyses given in terms of weight per cent oxides cannot result in an accurate description of metasomatic changes, because material added to or lost from the system is not taken into account. The problem may be stated mathematically as (Chidester, 1962):

 $W_{\rm F} = W_{\rm O} + x - y$

where W_0 is a given weight of the original rock, x is the weight of material gained, y is the weight of material lost and W_F is the final weight of the given rock. Because x and y are both unknowns, a direct solution is not possible. Various indirect methods have been proposed to calculate the chemical changes accompanying metamorphism. One approach is to assume constant volume and therefore to compare equal volumes of rock, while another approach is to assume that some constituent of the rock, such as silica or alumina, is inert to metasomatic processes.

Modified Standard Cell

Barth (1948) has proposed a method to calculate metasomatic changes based upon the fact that oxygen constitutes about 94% of the volume of most rocks. Therefore comparing rock volumes of equal oxygen content is nearly equivalent to comparing equal volumes of rock. A cell of 160 oxygen ions was chosen because it contains about 100 cations and gains or losses can be regarded as percentage changes, to a good approximation. Chidester (1962) has proposed a modification to Barth's standard cell because many rocks differ appreciably in cell size if they contain minerals of very different equivalent volumes. Precise definition, instructions for calculation, and sample calculations are given by Chidester and are summarized in the Appendix of this paper. Modified standard cells have been calculated for all samples presented in TABLE 5 and are compared as groups in FIGURE 3. These groups are:

1. Fresh norite-gabbros (33, 38, 97, 171, 172, 330)

2. Amphibole metagabbros (133, 143, 150, 163, 213)





3. Leucocratic metagabbros (65, 117, 119, 167, 176, 177).

The modified oxygen standard cell model shows that metamorphism of these Kamiskotia complex rocks has been accompanied by:

- 1. Removal of Na, Si, Fe(II) and Ti.
- 2. Addition of K to the amphibole metagabbro but removal from the leucocratic metagabbro.

3. Addition of Al and to a lesser extent Mg.

The trends for Fe(III) and Ca are not conclusive, some Fe(III) may have been lost, whereas minor amounts of Ca may have been added.

Immobile Aluminum

The concept of constant alumina has become more popular in the consideration of metasomatic processes than Barth's oxygen standard cell approach. Carmichael (1969) on a thin section scale and Korzhinsky (1968) on a crustal scale, find that alumina is always the least mobile component and therefore the one most nearly held constant. Bryant (1966) in a study of phyllonites in North Carolina, considered alternately that alumina or silica remained constant during metamorphism, and found that better agreement with other lines of evidence was obtained using constant alumina. But he concluded that no matter which of the two he considered constant, Na, Ca, Fe and Mg must have been removed during metamorphism. Assuming constant alumina, Burwash and Krupicka (1970) found significant removal of Ca, Mg and Na and addition of K in the metasomatism of Precambrian schists and gneisses of the western Canadian Shield. They conclude that "immobile alumina (and TiO₂) and only slightly mobile silica seem to have been a kind of chemical pivot around which changes in other chemical constituents were taking place."

Clearly, the results of the modified standard cell calculation do not agree with the findings of the authors listed above. Consequently the analyses have been recalculated assuming a constant alumina content (equal to the average of the alumina content of samples 33, 38, 97, 171, 172 and 330). This average is biased somewhat by the high Al-content of sample 171 and it could be argued that this sample should not be included. However, since samples were collected on a random basis there is no justification in omitting it because its alumina content is greater than that of the other fresh rocks. The metagabbroic rocks are compared to the norite-gabbros in FIGURE 4. The graphical representation shows that:

- There has been a removal of Na, K, Fe(II) and Si from the leucocratic metagabbros.
- There has been an addition of K to the amphibole metagabbros.
- The trends for Ca, Mg, Fe(III) and Ti are not conclusive.

Mg has probably remained constant while some Ca may have been removed. The trend for Fe(III) is uncertain, the samples





analyzed in this study indicate little change in ferric iron, but the analyses reported by Wolfe (1970) indicate significant loss of ferric iron. Because ferric iron commonly substitutes for aluminum in crystal lattices, it seems more reasonable that ferric iron has also been immobile. Also, it is more likely that chemical processes in which water is involved would be associated with oxidation rather than reduction. The higher ferric to ferrous iron ratio of the author's analyses agree with this hypothesis better than those of the Ontario Department of Mines published by Wolfe. The trend for Ti is difficult to interpret also. Although the graphical presentation of both models point to a significant loss of Ti, the fresh rocks show such a range in Ti-content that this apparent trend may not be real. Consequently no final conclusions will be made with respect to the behaviour of Ti under these metasomatic conditions.

Conclusions

A comparison of the results for the models of metasomatism shows them to be quite similar; both point to the removal of Na, K, Si and Fe from the leucocratic metagabbros and to the addition of K to the amphibole metagabbros. This is undoubtedly due to the fact that the changes are large enough that the general pattern of the metasomatic processes can be modified but not greatly changed by the two different approaches. It may also be due to the partial validity of either approach;

that is, both volume and alumina content are constant to a first approximation.

Using the constant alumina model, a relative mobility series has been deduced (on the basis of percentage change of the oxide). In decreasing order the series is:

CO₂, H₂O, Na, K, Fe(II), Si, Ca, Fe(III), Mg, Al. This agrees fairly well with Korzhinsky's (1964) low temperature mobility series:

 H_2O , CO_2 , S, K, Na, O_2 , Si, Ca, Mg, Fe, P, Al, Ti, except for the position of iron. There are two possible reasons for the anomalously high mobility of iron suggested by these conclusions.

First, it was pointed out that the iron content of the fresh norite-gabbros was guite variable. It could be that the low-iron fresh rocks, such as 97 or 171, provide a more accurate estimate of the original iron content of the metagabbroic rocks. If this were the case then a considerably smaller amount of iron would need to have been removed from the metagabbros to fit the observed pattern.

Secondly, the unusually high mobility of iron may be a real effect, and have been facilitated by the role of sulphur acting as a transporting agent. Wolfe (1970) found that the altered rocks were very low in iron and sulphur compared to the unaltered rocks, despite the presence of high Ni concentrations. Combining data from three selective acid leaches he concluded that nickel in the leucocratic metagabbro facies is present largely in secondary carbonate or silicate minerals. Because there is a "general coincidence of metal sulphur patterns ... in all areas of clinopyroxene norite and hornblende lithology" Wolfe suggests the association of high Ni with low S and low Fe in the metagabbroic rocks, together with the occurrence of Ni-poor pyrite-pyrrhotite deposits bordering the metagabbroic rocks, may be due to "large-scale metasomatic transfer" of Fe and S. In support of this mechanism of iron transfer, Turner and Verhoogen (1960) consider it possible that sulphur may act as a carrier of iron.

For three reasons the author favours the constant alumina approach over the modified standard cell (constant volume) approach to metasomatism in the Kamiskotia complex:

- It defines a mobility order that agrees more closely with Korzhinsky's (1964).
- There is no strong field evidence to suppose that the volume has remained constant, because of the poor outcrop control in the area.
- 3. The bulk of the recent research as well as general success of the constant alumina approach support the immobile aluminum hypothesis.

However, in areas where field mapping gives good reason to believe that volume changes have been minimal, then the modified standard cell may still be a very worthwhile calculational tool to use in studies of metasomatism. In such an area it would be especially interesting to compare it with the constant alumina

approach.

The metasomatic alteration of the Kamiskotia mafic complex is visualized as a process in which water and carbon dioxide have been added and alkalis, silica and iron have been removed. Immobile aluminum, magnesium and nearly immobile calcium have remained in the rock as the stable mineral assemblage clinozoisite-ripidolite chlorite-calcite-quartz. Deduced from the observed petrographic relationships and the calculated chemical changes, the following metasomatic reactions are proposed:

1. 3(Mg,Fe)SiO₃ +2Ca(Mg,Fe)(Si,Al)₂O₆ + 2H⁺
hyperstheme augite

Ca₂ (Mg,Fe)₅ (Si₃AlO₁₁)₂ (OH)₂ tremolite

 $Ca_2(Mg_4Fe)(Si_3AlO_{11})_2(OH)_2 + 6H^+$ tremolite

> $Mg_5Al_2Si_3O_{10}(OH)_8 + 3SiO_2 + Fe^{2+} + 2Ca^{2+}$ ripidolite

2. $CaAl_2Si_2O_8 + (Na,K)AlSi_3O_8 + 2Ca^{2+} + H^+ + CO_2$ Plagioclase, An₅₀

Ca2Al3(SiO4)3(OH) + 2SiO2 + CaCO3 + (Na⁺,K⁺)
clinozoisite

By these reactions the pyroxene-plagioclase assemblage of the fresh rock is converted to the clinozoisite-chlorite-quartzcalcite assemblage of the altered rock. Albite in the altered rocks is believed to represent either incomplete reaction or an excess of that reactant. In any event its presence is not surprising since albite is a stable mineral in the greenschist facies. Some silica is removed in solution, along with ferrous iron, soda and potash ions, and some silica is left behind, precipitating as quartz. Some calcium is transferred from the mafic minerals in order to form clinozoisite, and interchange of other ions probably occurs, but the mafic minerals and the felsic minerals may still be considered as two sub-systems, that can react somewhat independently of each other.

The question of where added material has come from, and where removed material has gone to is at least as difficult and important a problem to solve as a description of the metasomatism itself. Very little attention has been paid to this problem, partly because it is beyond the scope of this thesis and partly because the conclusions are largely speculative. Addition of material has been limited to water and carbon dioxide and there are at least three possible sources of these fluids.

First, they could have been drawn into the hot gabbroic magma during and shortly after its intrusion from the surrounding basic volcanic rocks. Secondly, water and carbon dioxide could represent the residual volatiles of the gabbroic magma

itself and hence an autometamorphic phenomenon, or thirdly, they could be the residual volatiles of a younger intrusive event, injected into the mafic pluton from below. If the country rocks, the volcanics, had acted as a source for the metasomatic fluids then the alteration should be most intense closest to the volcanic rocks. But, the field relationships suggest that the most intensely altered rocks lie within the mafic pluton and that relatively unaltered rocks border the volcanics. Consequently the first alternative can be rejected as an unlikely solution to the problem. Since there is no definite external source of the volatiles, the autometamorphic hypothesis cannot be complately rejected but there is a possible external source of the fluids. As mentioned in the general geology, there are a number of small granitic stocks that intrude the eastern margin of the Kamiskotia complex, as well as a large younger granitic batholith to the west. Although appeal to a hidden granite at depth is a somewhat less than satisfactory answer, it does seem to be the most plausible alternative. One objection to it is that no indications of metasomatic alteration were noted around any of the small granitic stocks; contact effects appeared minimal. However, there is some evidence for the development of a spotted texture, due to the formation of clusters of amphiboles, in the gabbroic rocks adjacent to the granitic batholith, which is rather similar to that described for the amphibole metagabbros.

The second half of the metasomatism problem is concerned

with where the K, Na, SiO2 and Fe have gone. Evidence has already been cited that the amphibole metagabbros are relatively enriched in potash. Petrographic evidence supports this as one thin section was observed to contain amphiboles with biotite mantles. Clearly, the suggestion is that potash, leached from the most altered rocks has been relocated in the surrounding less altered zone. With respect to iron, it has been mentioned that Wolfe (1970) considers it possible that the iron and sulphur in the pyrite-pyrrhotite occurrences of central and western Whitesides townships could have been derived from the altered rocks. The author supports this suggestion and points out that the anomalously high mobility of iron, compared to Korzhinsky's mobility series may be due to the increased mobility of iron as ferrous sulphide complexes. No areas of relative enrichment in Na or SiO2, spatially related to the zone of metasomatic alteration, were recognized during field mapping or in the chemical analyses. It is possible, however, that such zones of enrichment could be present, either within the amphibole metagabbro facies, along the contact with the volcanic rocks, or within other rock lithologies.

RECOMMENDATIONS FOR FUTURE WORK

1. A greater number of analyses of both the fresh and altered rocks would provide a better characterization of their average compositions and thereby a more quantitative understanding of the metasomatic processes. Also a zone of enrichment in Na and SiO₂ might be discerned by such a program.

2. According to Korzhinsky's (1964) definition of metasomatic zoning, the number of mobile components should gradually increase from the unaltered rocks to the zone of greatest alteration. This should correspond to a gradual decrease in the number of mineral phases since,

 $\phi = c - c_m = c_i$ where ϕ is the number of phases, c the number of components in the fresh rock, c_m the number of mobile components and c_i the number of independent components.

More detailed investigation of the mineralogy of the metagabbroic facies in the Kamiskotia complex might define other zones which could be correlated with a decreasing number of phases and an increasing number of mobile components.

3. The speculation of a felsic intrusive pluton beneath the metasomatized rocks could be investigated by a gravity survey of the area. 4. If the pyrite-pyrrhotite deposits of central and western Whitesides township are of metasomatic origin they should show evidence of a low temperature of formation (i.e. temperatures no greater than greenschist facies). This could be determined by sulphur isotope partitioning between coexisting sulphide minerals (Grootenboer and Schwarcz, 1969).

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APPENDIX: THE MODIFIED STANDARD CELL

DEFINITIONS (FROM CHIDESTER)

Equivalent mineral unit is defined so that the sum of electropositive ions or atoms in a mineral formula equals one. For example one equivalent mineral unit of quartz is 1 SiO₂, of albite is 1/5 NaAlSi₃O₈.

- Equivalent molecular numbers are determined by dividing the weight per cent of an oxide in a chemical analysis by its equivalent molecular weight.
- Equivalent volume is the volume of one equivalent mineral unit and is equal to the equivalent weight divided by the density of the mineral.
- Oxygen equivalent (O_{eq}) is an amount of an ion or atom that occupies a volume approximately equal to that of an oxygen ion.

The Modified Standard Cell

Because shale is the most abundant sedimentary rock Chidester used Leith and Mead's calculated mode of an average shale as the standard by which the size of the modified standard cell was calculated.

The total number of equivalent mineral units in the shale, represented by the mode in volume per cent was obtained by dividing the volume per cent of each mineral by its equivalent volume, and summing the quotients. The volume of the modified standard cell was then obtained by dividing the sum of the volume percentages in the mode (100.00) by the sum of the equivalent mineral units (4.8432) giving the volume per equivalent mineral unit or per cation. The volume of 100 cations was obtained by multiplying by 100, giving $V_{100} = 2064.8$.

The modified standard cell of the standard shale is defined as 2064.8xN⁻¹cc where N is Avogadro's Number.

CALCULATION OF THE CELL CONTENTS

The contents of the modified standard cell can be calculated directly from the chemical analysis if the density of the rock is known. The procedure is as follows and may be followied in the sample calculation:

- The chemical analysis in weight per cent, is converted to equivalent molecular numbers by dividing each oxide by its equivalent weight.
- 2. The equivalent molecular numbers are converted to equivalent molecular per cent by dividing each term by the sum of the equivalent molecular numbers, less the value for $HO_{1/2}$ and any other electronegative ions.
- 3. The oxygen equivalents are obtained by multiplying the equivalent molecular percentage of

each constituent by the number of oxygen ions in the equivalent weight symbol. Summation gives the total number of oxygen equivalents.

- 4. The weight of 100 equivalent molecules of rock, W_{100} , is determined by dividing the total weight per cent of the analysis by the total number of equivalent molecular numbers corrected for $HO_{1/2}$. This quotient is multiplied by 100.
- 5. V_{100} , the volume of 100 equivalent molecules of rock is obtained by dividing the weight by the density, D. That is, $V_{100} = \frac{W_{100}}{D}$. 6. The cell factor, F_{rk} , is the ratio of the volume of the standard cell to V_{100} ,

$$F_{rk} = \frac{2064.8}{V_{100}}$$

 F_{rk} is the number by which the volume of 100 equivalent molecules must be multiplied to convert it to the volume of the modified standard cell. Therefore F_{rk} multiplied by the equivalent molecular percentages gives the contents of the modified standard cell (7).

Chidester has retained Barth's concept of a rock formula and the contents of the modified standard cell are expressed as a rock formula in the example. Net chemical changes may be determined by direct comparison of the modified standard cells. Sample Calculation of the Modified Standard Cell for Sample 33

		(1)	(2)	(3)	(7)
v Pe	leight r cent	Eq. Mol. Nos.	Eq. Mol. Per Cent	No. of ^O eq	Cell Contents
sio ₂	51.4	0.8671	48.81	97.62	54.13
A103/2	13.6	0.2704	15.22	22.83	16.89
FeO _{3/2}	1.06	0.0135	0.75	1.13	0.83
FeO	10.0	0.1411	7.94	7.94	8.81
MgO	6.59	0.1657	9.32	9.32	10.34
CaO	12.6	0.2277	12.81	12.81	14.21
NaO1/2	2.28	0.0746	4.19	2.20	4.65
^{KO} 1/2	0.15	0.0032	0.18	0.09	0.20
HO1/2	1.17	0.1300	7.30	3.66	8.11
TiO2	0.92	0.0117	0.65	1.30	0.72
co ₂	0.06	0.0014	0.07	0.14	0.08
TOTAL LESS HO	99.8	1.9064 0.1300	107.24 7.30	159.04 3.66	118.97 8.11
TOTAL LESS (HO _{1/2}	+C02	1.7764	100.00	155.38	110.86
Oxygen				151.58	÷
4. W ₁₀₀ = -	99.8 x	100 = 5619			
5. $V_{100} = -$	$\frac{7}{100} = \frac{56}{3}$	$\frac{519}{02} = 1861$			
6. $F_{rk} = \frac{2}{3}$		1.109			

6.
$$F_{rk} = \frac{2064.8}{1861} = 1.109$$

Rock Formula is

 $[K_{0.20}^{Na}4.65^{Ca}14.21^{Mg}10.34^{Fe}_{8.81}^{2+}A^{1}16.89^{Fe}_{0.83}^{3+}T^{i}0.72^{Si}54.13^{O}168.0$ $(OH)_{8.11}(CO_{2})_{0.08}] \text{ cations} = 110.9 \qquad O_{eq} = 176.3$