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SILICA-POOR HASTINGSITIC AMPHIBOLES FROM METASOMATIC ALKALINE GNEISSES AT WOLFE, EASTERN ONTARIO

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ABSTRACT

The chemical characteristics of amphiboles in metasomatic alkaline gneisses of several lithological varieties have been studied utilizing fifteen new amphibole analyses. All can be classed as hastingsites, magnesian hastingsites, and sub-silicic magnesian hastingsites, and have Si contents ranging from 5.27 to 6.11 atoms in the half-unit cell. These fall amongst the most silica-poor amphiboles recorded in Leake's (1968) compilation. Progressive changes in composition relate directly to intensity of nephelinization in the individual rock layers and provide a useful index to this phenomenon even in the absence of nepheline. A pre-metasomatic tschermakitic hornblende to pargasitic hornblende composition is indicated for most of the amphiboles.

RÉSUMÉ

Les caractéristiques chimiques d'amphiboles dans des gneiss métasomatiques alkalines de plusieurs variétés lithologiques ont été étudiées à l'aide de quinze nouvelles analyses amphiboliques. Elles peuvent toutes être classées comme hastingsites, hastingsites magnésiennes et hastingsites magnésiennes sous-siliciques et elles contiennent du Si variant de 5.27 à 6.11 atomes dans une demi-maille élémentaire. Celles-ci se retrouvent parmi les amphiboles les plus pauvres en silice enregistrées dans la compilation de Leake (1968). Des changements progressifs dans la composition sont reliés directement à l'intensité de la néphélinisation dans les couches rocheuses individuelles et fournissent ainsi un index utile à ce phénomène même en l'absence de néphéline. De l'hornblende tschermakitique prémétasomatique à l'hornblende pargasitique, la composition est indiquée pour la plupart des amphiboles.

(Traduit par le journal)

INTRODUCTION

The classification of calciferous and subcalciferous amphiboles has occupied mineralogists for many years (Billings 1928; Hallimond 1943; Winchell 1945; Sundius 1946; Wilkinson 1961; Phillips 1963; Leake 1968). A number of general formulae have been proposed to represent the structural composition of the group, of which the one proposed by Ernst (1968) viz. $W_{0-1}X_2Y_5Z_8O_{22}(OH,F)_2$ will be used in this paper. In this formula $W = Na^A, K$; $X = Ca, Na^{M(4)}, Mn$; $Y = Mg, Fe^{2+}, Fe^{3+}, Al^{vi}, Ti, Cr, Li, Zn$; $Z = Si, Al^{iv}$.

Amongst the issues which have arisen are the extent to which Al^{iv} may substitute for Si in the Z positions and the reason why the $W+X$-group may appear to total more than 3.00. Phillips (1963), for example, has suggested that in a satisfactory amphibole analysis Si must occupy not less than 5.94 of the 8.00 Z-sites in the half-cell and the sum of the $W+X$-group must not be more than 3.03. Leake (1968), on the other hand, has shown that numerous modern amphibole analyses, some of which he considers to be of "superior quality", exceed Phillips' limitations. Leake accepts that Si may range down to 5.27 and that $Ca + Na + K$ may sometimes exceed the limitations of $W+X$-group occupancy.

Amphiboles from the alkaline gneisses of the Wolfe Nepheline Belt, Lyndoch Township, Renfrew County, Ontario have been studied as part of a wider investigation of the metasomatic origin of these rocks. The fifteen analyses discussed in this account were previously published in Leake's catalogue, though not described until now. Their compositions are relevant to the above problems and also provide other insights into the origin of the rocks in which they occur.

OCCURRENCE

The alkaline rocks of the Wolfe Belt comprise a group of banded gneisses of unusually sodic composition characterized by the occurrence of nepheline and mafic minerals with abnormally high Na contents. The stratigraphy, petrography, mineral paragenesis, structures and textures of the rocks have been described previously (Appleyard 1967, 1969). The rocks may be divided into two main units, (1) a lower unit of leucocratic feldspathic gneisses, generally nepheline-bearing, up to 350 feet thick and more than 4 miles in length in which are intercalated horizons of amphibolite, crystalline limestone and quartzite, and (2) an upper unit of calc-silicate gneisses, 230 feet thick, with enclosed layers of metamorphic pyroxenite and "iron-formation". The whole sequence is characterized by regular lithological layering which has been interpreted (Appleyard 1967, 1969) as being of supracrustal origin. The rocks were nephelinized (Gummer & Burr 1943, 1946; Baragar 1953; Tilley 1958; Gittins 1961) during the Grenville orogeny. The evidence for the timing of this event relative to other events during this orogeny is stated in Appleyard (1969).

Amphiboles were analyzed from the leucocratic feldspathic alkaline gneiss, amphibolite, calc-silicate and "iron-formation" lithologies. In several places series of specimens were collected along the strike of individual layers in order that a uniform initial composition of the specimens might be assumed and the metasomatic effects thereby determined. Amphiboles from such suites show progressive compositional changes reflecting the variable intensity of nephelinization which can be used to indicate their pre-metasomatic composition.

ANALYTICAL METHODS

The rocks from which the amphiboles were separated consist of medium-grained gneisses crystallized under upper-amphibolite facies conditions. The amphiboles are unaltered and usually free of inclusions. In some specimens of the calc-silicate gneisses, amphibole occurs as rims and patches around clinopyroxene as well as in separate grains. Special care was taken with such specimens to avoid mixed grains in the concentrate. The concentrates were prepared in two stages, (1) an initial concentration in an isodynamic magnetic separator, followed by (2) repeated centrifuging in Clerici solution. This procedure allowed concentrates to be prepared which are believed to contain less than 2 per cent impurities on the basis of optical examination. The impurities observed were principally clinopyroxene in mixed grains. Three to five grams of concentrate of each sample were prepared so that the standard amounts required by the analytical methods did not have to be reduced.

Standard gravimetric analytical methods were used for SiO_2, Al_2O_3, CaO, MgO and H_2O. TiO_2, MnO and P_2O_5 were determined colourimetrically and Na_2O and K_2O by flame emission photometry. Fe was reduced by passing the solution through an Ag reduction column followed by titration with ceric sulphate to determine Fe^{total}. FeO was determined on a separate sample by the ammonium vanadate-ferrous ammonium sulphate method. F was determined volumetrically by titration with standard thorium nitrate solution. Amphibole proved to be refractory to the normal digestion technique, *i.e.* boiling perchloric acid, so Willard's method (1933, p. 9) of preliminary digestion of the sample was used. This yielded consistent results for F on duplicate determinations, but the accuracy of the technique was not checked against natural mineral standards.

The trace-element determinations were carried out by R. Allen, Department of Mineralogy and Petrology, University of Cambridge, using the optical spectrographic technique essentially as described in Nockolds & Allen (1953).

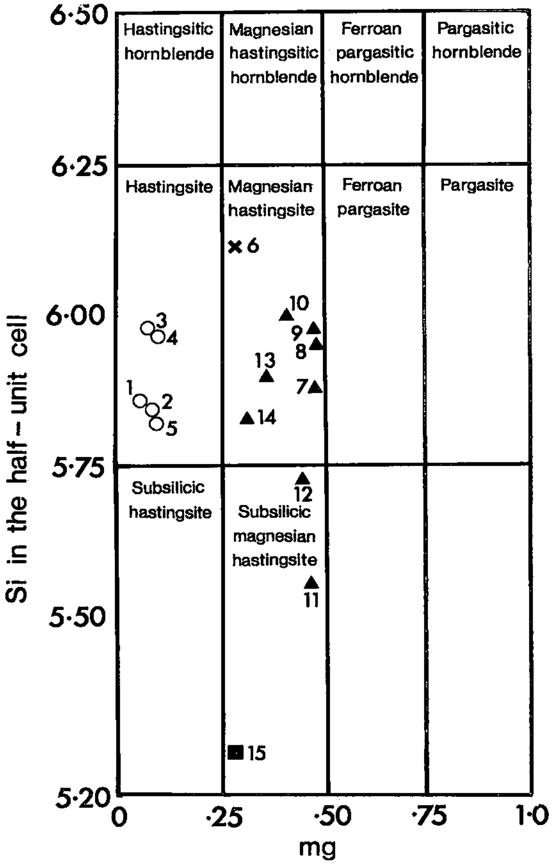

FIG. 1. Classification of the Wolfe Belt amphiboles following Leake's (1968) system of nomenclature. Symbols are: open circles — amphiboles from leucocratic alkaline gneisses, X — from nephelinized amphibolite, triangles — from calc-silicate gneisses, square — from the "iron-formation" unit.

TABLE 1. ANALYSES OF AMPHIBOLES FROM ROCKS OF THE WOLFE NEPHELINE BELT, LYNDOCH TOWNSHIP, ONTARIO*

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.
SiO_2	36.45	36.53	37.20	37.30	36.35	38.90	38.64	39.05	39.47	38.90	36.69	37.74	38.16	37.70	33.50
Al_2O_3	13.44	13.98	12.13	12.48	14.09	9.67	16.22	15.74	15.30	14.70	19.90	17.71	14.81	15.52	17.89
TiO_2	1.75	1.66	1.36	1.36	1.75	1.04	1.35	0.97	1.07	0.85	1.58	1.00	1.24	1.76	3.26
Fe_2O_3	8.19	7.55	11.09	11.96	8.89	12.21	3.51	4.43	4.42	5.55	3.44	3.85	5.88	4.52	6.65
FeO	21.91	21.39	19.97	18.03	20.19	15.20	13.24	12.83	12.90	14.49	12.93	13.24	15.81	17.49	16.49
MgO	0.95	1.50	1.42	1.52	1.66	6.07	8.64	8.95	8.77	7.78	8.07	7.77	6.88	5.61	5.00
CaO	9.89	9.63	7.36	7.16	8.51	8.95	11.67	11.46	11.66	10.79	11.42	11.14	10.48	11.40	10.30
Na_2O	3.10	2.99	4.22	4.60	3.67	3.78	2.40	2.67	2.73	2.94	2.46	2.61	2.97	2.30	3.14
K_2O	2.36	2.42	2.43	2.35	2.35	2.21	2.15	2.20	2.03	2.24	2.34	2.57	2.19	2.29	1.48
MnO	0.41	0.59	1.14	1.33	0.99	0.75	0.28	0.25	0.30	0.29	0.10	0.14	0.40	0.30	0.26
P_2O_5	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.05
H_2O^+	1.23	1.28	1.33	1.29	1.23	1.16	1.32	0.81	1.00	0.76	1.32	1.16	0.89	1.42	1.37
H_2O^-	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.04	0.04	0.00	0.03	0.00	0.01	0.04
F	0.89	0.90	0.75	0.77	0.67	1.04	0.63	1.17	1.24	1.14	0.31	1.62	1.17	0.31	0.25
	100.57	100.42	100.40	100.15	100.35	100.99	100.05	100.55	100.93	100.47	100.56	100.58	100.88	100.63	99.68
$O \equiv F$	0.37	0.38	0.32	0.32	0.28	0.44	0.26	0.49	0.52	0.48	0.13	0.68	0.49	0.13	0.10
	100.20	100.04	100.08	99.83	100.07	100.55	99.79	100.06	100.41	99.99	100.43	99.90	100.39	100.50	99.58
Si	5.86	5.85	5.98	5.97	5.82	6.11	5.88	5.95	5.98	6.01	5.55	5.73	5.90	5.84	5.27
Al^{iv}	2.14	2.15	2.02	2.03	2.18	1.79	2.12	2.05	2.02	1.99	2.45	2.27	2.10	2.16	2.73
Al^{vi}	0.41	0.49	0.28	0.33	0.48	0.01	0.79	0.78	0.71	0.68	1.09	0.91	0.60	0.67	0.59
Ti	0.21	0.20	0.16	0.16	0.21	0.12	0.15	0.11	0.12	0.10	0.18	0.11	0.14	0.21	0.39
Fe^{3+}	0.99	0.91	1.34	1.44	1.07	1.44	0.40	0.51	0.50	0.64	0.39	0.44	0.68	0.53	0.79
Fe^{2+}	2.95	2.86	2.69	2.42	2.71	1.99	1.68	1.64	1.63	1.87	1.63	1.68	2.05	2.27	2.17
Mn	0.06	0.08	0.15	0.18	0.13	0.10	0.04	0.03	0.04	0.04	0.01	0.02	0.05	0.04	0.03
Mg	0.23	0.36	0.34	0.36	0.40	1.42	1.96	2.03	1.98	1.79	1.82	1.76	1.59	1.30	1.17
Ca	1.70	1.65	1.27	1.23	1.46	1.51	1.90	1.87	1.89	1.78	1.85	1.81	1.74	1.89	1.74
Na	0.97	0.93	1.31	1.43	1.14	1.15	0.71	0.79	0.80	0.88	0.72	0.77	0.89	0.69	0.96
K	0.48	0.49	0.50	0.48	0.48	0.44	0.42	0.43	0.39	0.44	0.45	0.50	0.43	0.45	0.30
OH	1.32	1.37	1.42	1.38	1.31	1.22	1.34	0.82	1.01	0.78	1.33	1.18	0.92	1.47	1.44
F	0.45	0.46	0.39	0.39	0.34	0.52	0.30	0.56	0.59	0.56	0.15	0.78	0.57	0.15	0.12
O	22.23	22.18	22.19	22.23	22.35	22.27	22.36	22.61	22.40	22.66	22.52	22.05	22.51	22.38	22.44
$\Sigma W+X$	3.15	3.08	3.08	3.14	3.08	3.10	3.03	3.09	3.09	3.11	3.02	3.08	3.06	3.03	2.99
ΣY	4.84	4.90	4.96	4.89	5.00	5.08	5.02	5.10	4.99	5.12	5.13	4.92	5.12	5.00	5.14
ΣZ	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Ga	20	28	28	35	20	18	20	20	28	28	20	20	20	20	20
Cr	n.d.	5	n.d.	n.d.	n.d.	2	40	83	48	115	2	n.d.	12	12	n.d.
V	n.d.	22	n.d.	22	32	74	220	400	120	100	45	32	220	100	250
Li	25	10	32	100	55	50	100	150	--	55	32	100	45	18	100
Ni	5	5	5	5	5	4	46	56	32	22	2	2	10	10	n.d.
Co	10	10	n.d.	10	10	10	46	46	32	22	15	22	22	22	46
Sc	--	--	--	--	--	--	18	26	n.d.	--	--	--	--	--	--
Zr	465	465	465	800	465	220	150	150	220	115	220	220	220	100	150
Y	7	10	5	7	17	40	10	n.d.	n.d.	n.d.	n.d.	n.d.	12	5	25
Sr	110	110	33	74	63	190	140	140	--	110	248	331	110	110	320
Ba	22	22	5	5	120	100	216	216	--	100	220	100	45	220	216
Rb	100	100	120	120	100	85	120	100	--	100	100	120	18	120	80
S.G.	3.469	3.454	3.454	3.437	--	--	--	--	--	--	3.296	3.308	--	--	--
α	--	--	--	--	--	--	--	--	--	1.674	1.675	1.674	1.676	1.685	1.687
β	--	--	--	--	--	--	--	--	--	--	--	--	1.688	--	--
γ	--	--	--	--	1.716	--	--	--	--	1.689	1.689	1.690	1.695	1.704	1.700
mg	0.054	0.085	0.075	0.083	0.092	0.287	0.480	0.483	0.476	0.412	0.471	0.451	0.363	0.314	0.282

*Half-unit cell contents calculated on the basis of 24(O,OH,F). All trace element values in ppm; n.d.=below the limits of detection, -- = not determined. S.N.=sample number in the petrology collection of the Department of Mineralogy and Petrology, University of Cambridge, where the specimens are deposited; L.N.=analysis number in Leake's (1968) catalogue.

1. *Hastingsite* from microcline-plagioclase-nepheline-amphibole-garnet-calcite gneiss, Kargus ridge. Garnet also analyzed. S.N.-91722; L.N. 933.
2. *Hastingsite* from microcline-plagioclase-nepheline-amphibole-calcite gneiss, Kargus ridge. Nepheline also analyzed. S.N.-91724; L.N.-932
3. *Subcalcic sodic potassic hastingsite* from plagioclase-microcline-nepheline-amphibole-magnetite gneiss, Kargus ridge. S.N.-91727; L.N.-926.
4. *Subcalcic sodic hastingsite* from plagioclase-microcline-nepheline-magnetite-biotite-(sphene)-(calcite)-(amphibole) gneiss, Kargus ridge. Nepheline and biotite also analyzed. S.N.-91728; L.N.-925.
5. *Subcalcic sodic hastingsite* from plagioclase-amphibole-microcline-nepheline-calcite-(biotite) gneiss, Remus ridge. Biotite also analyzed. S.N.-91639; L.N.-934.
6. *Sodic magnesian hastingsite* from plagioclase-amphibole-nepheline-calcite-sphene gneiss (nephelinized amphibolite) Remus ridge. S.N.-91659b; L.N.-905.
7. *Magnesian hastingsite* from scapolite-amphibole-clinopyroxene-garnet-plagioclase-sphene gneiss (calc-silicate gneiss), Heiderman ridge. Clinopyroxene and garnet also analyzed. S.N.-91568; L.N.-909.
8. *Magnesian hastingsite* from scapolite-clinopyroxene-nepheline-amphibole-vesuvianite-garnet-plagioclase-sphene gneiss, Heiderman ridge. Clinopyroxene, garnet and vesuvianite also analyzed. S.N.-91563; L.N.-904.
9. *Magnesian hastingsite* from clinopyroxene-scapolite-nepheline-amphibole-vesuvianite-calcite-sphene gneiss, Heiderman ridge. Clinopyroxene and vesuvianite also analyzed. S.N.-91576; L.N.-896.
10. *Magnesian hastingsite* from plagioclase-nepheline-amphibole-scapolite-clinopyroxene-garnet-calcite-sphene-(vesuvianite) gneiss, Remus ridge. Clinopyroxene and garnet also analyzed. S.N.-91638; L.N.-906.
11. *Subsilicic alumino-magnesian hastingsite* from scapolite-amphibole-garnet-apatite-plagioclase-(nepheline) gneiss, Kargus ridge. Garnet also analyzed. S.N.-91732; L.N.-931.
12. *Subsilicic magnesian hastingsite* from nepheline-vesuvianite-garnet-amphibole-scapolite-plagioclase gneiss, Kargus ridge. Garnet and vesuvianite also analyzed. S.N.-91729; L.N.-920.
13. *Magnesian hastingsite* from plagioclase-amphibole-calcite-sphene-microcline-apatite gneiss, Remus ridge. S.N.-91633a; L.N.-915.
14. *Magnesian hastingsite* from plagioclase-amphibole-clinopyroxene-scapolite-sphene-apatite gneiss, Remus ridge. Clinopyroxene also analyzed. S.N.-91635; L.N.-921.
15. *Subsilicic titaniferous magnesian hastingsite* from amphibole-scapolite-magnetite-apatite-(spinel)-(biotite) gneiss ("iron formation"), Kargus ridge. S.N.-91735; L.N.-936.

COMPOSITION AND CLASSIFICATION

The fifteen amphiboles analyzed in this study are listed in Table 1. The half-cell contents are given on the basis of 24(O,OH,F) rather than 23(O) because of Borg's (1967) criticism of the latter procedure. Leake's terminology has been adopted for the samples. The basic terminology is displayed in Figure 1 and the following additional prefixes are used where applicable:

subcalcic: Ca less than 1.50
sodic: Na 1.00 and above
alumino: Al^{vi} 1.00 and above
titaniferous: Ti 0.25 and above
potassic: K 0.50 and above
subsilicic: Si less than 5.75

The amphiboles from the leucocratic alkaline gneisses classify as hastingsites; the original "hastingsite" described by Adams & Harrington (1896) was obtained from similar rocks in Dungannon Township and plots close to the Wolfe Belt hastingsites (Si = 5.75, *mg* = 0.07). The calc-silicate gneisses are characterized by magnesian hastingsites, including two that are subsilicic. The most extreme case of subsilicic character is found in the magnesian hastingsite of the so-called "iron-formation". The most siliceous amphibole amongst those analyzed occurred in the amphibolite unit.

The occurrence of $W+X$-group cell contents greater than 3.00 and Y-group cell contents greater than 5.00 are often considered to be due to analytical error. Phillips (1963) suggested that the sum of the $W+X$-group must lie between 1.98 and 3.03 and the sum of the Y-group between 4.95 and 5.05 but Leake (1968) broadened these limits to 1.75-3.05 for the $W+X$-group and 4.75-5.25 for the Y-group. The most likely sources of error are discussed by Leake (1968).

If one distributes Ca, Na and K into the $W+X$-group and Al^{vi}, Ti, Fe^{3+}, Fe^{2+}, Mn and Mg into the Y-group, then the analyses in this study have $W+X$-group cell contents between 2.99 and 3.15 and Y-group cell contents between 4.84 and 5.14. The Y-group total must contain the cumulative error of determinations of both Y-group and Z-group elements since the Z-group is arbitrarily fixed at 8.00 atoms. However, many of the errors within this group normally compensate one another in the total, so only when a substantial proportion of the errors are positive or negative will the Y-group total be abnormally high or low, respectively. One would expect that analyses by different techniques would have different patterns of errors, but this is not apparent from compilations of data. A further scrutiny of these relationships seems in order.

The major consistent errors affecting X- and Y-group totals are probably those in the OH, F and Cl group. Due to the requirements of the cell-content calculations, analyses with less than 2.00 atoms of OH, F and Cl, whether by real or by by analytical deviations, will yield cell contents with high $W+X$ and Y-group totals. The error will be distributed proportionally between the groups in the ratio: error in $W+X$/ error in Y = 2-3/13. These errors will be positively correlated. The $W+X$- and Y-group totals of the Wolfe amphibole analyses are plotted in Figure 2. Line A-B gives the theoretical limit to the field of amphibole analyses whose only errors lie in their volatile determinations. The Wolfe analyses fall predominantly outside this field. The points are scattered but there appears to be a tendency for high $W+X$-group totals to be associated with low Y-group totals. If so, an effect having a negative correlation between the $W+X$- and Y-groups may be superimposed on the sum of the effects of the volatile error and the real analytical and concentrate errors. Phillips (1963) suggested that in-

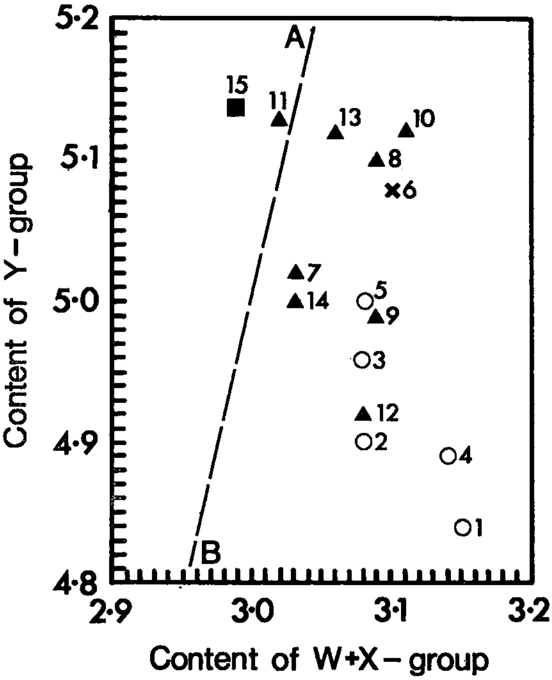

FIG. 2. Relation between the contents of the $W+X$-group elements (Ca+Na+K) and the Y-group elements (Al^{vi}+Ti+Fe^{+3}+Fe^{+2}+Mn+Mg) in the Wolfe Belt amphiboles. Symbols as in Figure 1.

versely-correlated errors in these groups may result from compensating errors in Ca and Mg determinations by gravimetric analysis due to the similar chemical behaviour of these elements. On the other hand, Binns (1965) and Leake (1968) suggested that Ca may enter sites normally occupied by *Y*-group elements. Arguments such as these have led some to augment low *Y*-group totals up to the ideal 5.00 atoms with Ca from the *W*+*X*-group.

Further ambiguity arises when the distribution of Na is considered. Na is accommodated within the amphibole structure in two different sites, the smaller 6-8-fold coordinated M_4 sites at the margins of adjacent, opposite-facing (Si, Al)O_4 chains, and larger 10-12-fold coordinated *A* site situated between the back-to-back double chains. The actual distribution of Na between these two sites is unknown. Since the *A* site may be unoccupied, the procedure has been adopted to fill the M_4 site with 2.00 atoms before allocating the remainder to the *A* site. Thus, in the present account the M_4 site is considered to contain (a) all the Ca present in excess of that amount required to achieve full occupancy of *Y*-sites, (b) divalent ions, possibly Fe^{+2} and/or Mn, representing any excess in the *Y*-group, and (c) sufficient Na to fill the *X*-group to its capacity of 2.00 atoms. The *W*-group, comprising atoms in the *A* site, contains all the K present plus the excess Na left after the *X*-group is allocated.

COMPOSITIONAL VARIATION DURING NEPHELINIZATION

The abundance of nepheline, the sodic content of the rocks, and related paragenetic features vary both along and across the strike of individual layers. These effects were studied by collecting suites of samples along and across strike where primary rock compositions are assumed constant. It is recognized that this assumption is less tenable in the case of the suites collected across strike, but such samples were collected from apparently homogenous layers.

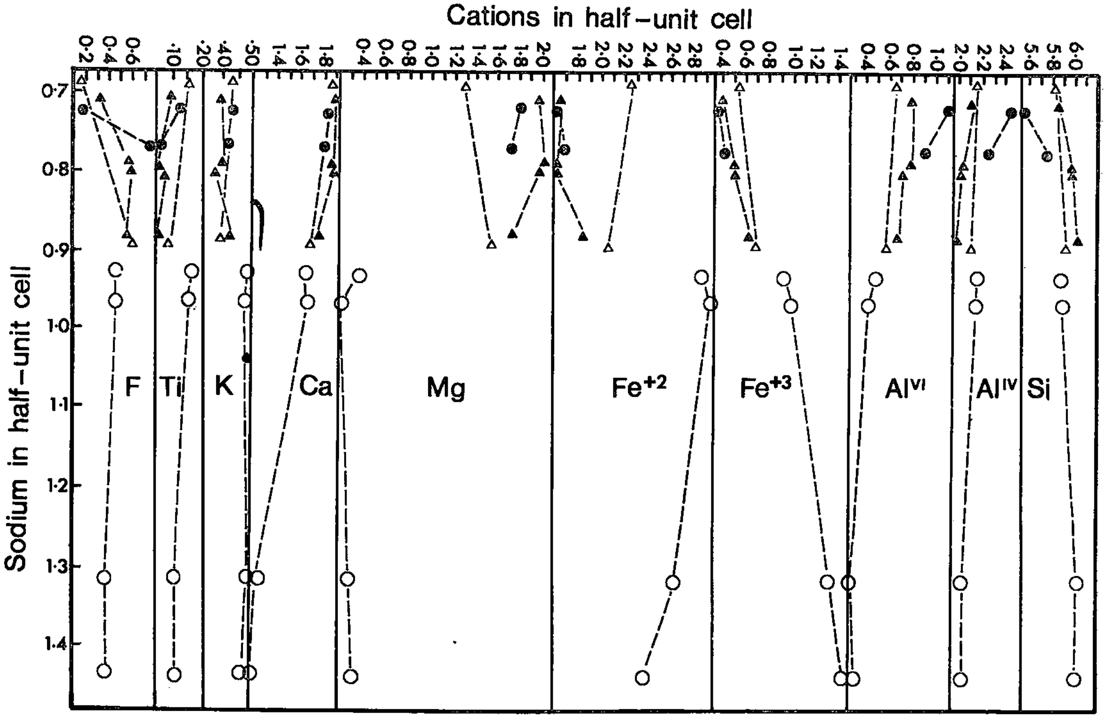

FIG. 3. Compositional variation of Wolfe amphiboles relative to their Na contents. Open circles — specimens 1, 2, 3, and 4 collected over 780 feet (240 m) along strike of leucocratic alkaline gneisses; solid triangles — specimens 7, 8, and 9 collected over 850 feet (260 m) along strike of calc-silicate gneiss, specimen 10 collected 7200 feet (2.2 km) along strike to west; solid circles — specimens 11 and 12 collected from two similar calc-silicate layers separated by an 18-inch (45 cm) layer of leucocratic alkaline gneiss; open triangles — specimens 13 and 14 collected 8 feet (2.44 m) apart across strike of a megascopically homogeneous calc-silicate layer.

The longest strike length over which samples were collected is 840 feet, except in the case of sample 10, which was collected from the same layer as specimens 7, 8 and 9 but 7200 feet to the west. Assuming equilibrium and ideal sampling, the amphiboles within each suite should have had identical compositions prior to nephelinization, the present variation in composition being the effect of metasomatism.

As Na is the most characteristic element introduced, the amount of Na in the amphibole half-unit cell can be taken as an index of the extent of metasomatism within each of the four suites of amphiboles (Fig. 3). The patterns of compositional change are generally consistent regardless of the parent lithology. In general, as Na increases, Fe^{+3}, Si and F increase and Ca, Fe^{+2}, Al^{iv} and Al^{vi} decrease. Ti decreases very slightly and K is practically constant. Some of the exceptions appear to correspond with changes in paragenesis, *e.g.* F decreases in the hastingsites from the leucocratic alkaline gneisses as F-rich biotite and fluorite appear in the mode. These irregularities, however, are not thought to detract from the general validity of the major trends. If one takes the suite of hastingsites from the leucocratic alkaline gneisses, the changes in composition are as follows:

Additions	Subtractions
0.14 Si	0.14 Al^{iv}
0.47 Fe^{+3}	0.13 Al^{vi}
0.04 Mg	0.46 Fe^{+2}
0.12 Mn	0.49 Ca
0.50 Na	0.04 Ti

These changes can be distributed amongst certain idealized substitutions in the amphibole structure. This is a subjective procedure as actual site occupancies are unknown, but it appears that the most important substitutions may be $Na^{M(4)}Si \rightarrow CaAl^{iv}$ (0.14 atoms), $Na^{M(4)}Fe^{+3} \rightarrow CaFe^{+2}$ (0.35 atoms), and (Mg, Mn) $Fe^{+3} \rightarrow Al^{vi}Fe^{+2}$ (0.12 atoms). Other substitutions are required to adjust Ti and the remainder of the Mn.

The substitution of Na for Ca in the M_4 site proceeds concomitantly with the substitution of Si for Al^{iv}. The required negative correlation between $Na^{M(4)}$ and Al^{iv} is illustrated in Figure 4A. All groups of analyses seem to show this relationship although the group of four amphiboles from calc-silicate gneisses plot in a very irregular fashion. Other simultaneous substitutions affect $Na^{M(4)}$ and possibly also Al^{iv} so the slopes of the tie-lines will not necessarily be identical nor conform to a 1 to 1 ratio. This substitution has the surprising effect of increasing both Na and Si contents of the cells. Since the Wolfe amphiboles are already extremely Si-poor in comparison with most amphiboles, it is unlikely that their pre-metasomatic antecedents could have been even more Si-poor. It seems reasonable then that the substitution $Na^{M(4)}Si \rightarrow CaAl^{iv}$ has been neither the sole, nor possibly even the principal, mechanism whereby the amphiboles acquired their present compositions. This point will be re-examined in the next section.

One of the most striking compositional changes paralleling the increase of Na^{total} is an increase in the iron oxidation ratios. This is illustrated in Figure 4B. The only analyses that depart significantly from a linear distribution are the amphibole from the amphibolite member on the Wolfe Belt, and a 19th-century analysis from Adams & Harrington (1896). The remainder of the analyses define a line with the equation:

Iron Oxidation Ratio $= 5.72 + 21.2$ Na (linear regression equation, variance $F = 169.7$). On further inspection, this general relationship seems to be the result of two simultaneous substitutions, both of which require the conversion of Fe^{2+} to Fe^{+3}, viz. $Na^{M(4)}Fe^{+3} \rightarrow CaFe^{+2}$ and (Mg, Mn) $Fe^{+3} \rightarrow Al^{vi}Fe^{+2}$. Figure 4C indicates that Fe^{+3} is partly balanced by Na in M_4. If this were the only substitution responsible for Fe^{+3} in the structure, then the points would be on the diagonal. However, they lie consistently above the line, indicating that an appreciable amount of Fe^{+3} enters the amphibole by another substitution. If $Fe^{+3} \rightarrow Al^{vi}$ is responsible, there should be a negative correlation between Al^{vi} and the amount of Fe^{+3} in excess of that required for $Na^{M(4)}Fe^{+3} \rightarrow CaFe^{+2}$. This is confirmed in Figure 4D. Only pair 11-12 does not conform to this relationship; the pair was collected across the strike of the layered unit and may not have been derived from antecedents with identical Fe^{+3} contents.

The trace-element values possess considerable scatter and rarely show a linear relationship to variations in Na. In the hastingsites from the leucocratic alkaline gneiss Rb, Li and Zr seem to increase, Sr seems to decrease, and Ga and Ba are unchanged or too variable to display a trend. In the magnesian hastingsites from the calc-silicate gneisses Cr, V and Zr seem to increase, Sr, Ba and Rb seem to decrease, and Li, Ga, Co and Ni are uncertain.

DERIVATION OF THE AMPHIBOLES

The gneisses from which these amphiboles are derived are believed on geological grounds described previously (Appleyard 1963, 1967, 1969, 1974; Appleyard & Stott 1975) to have

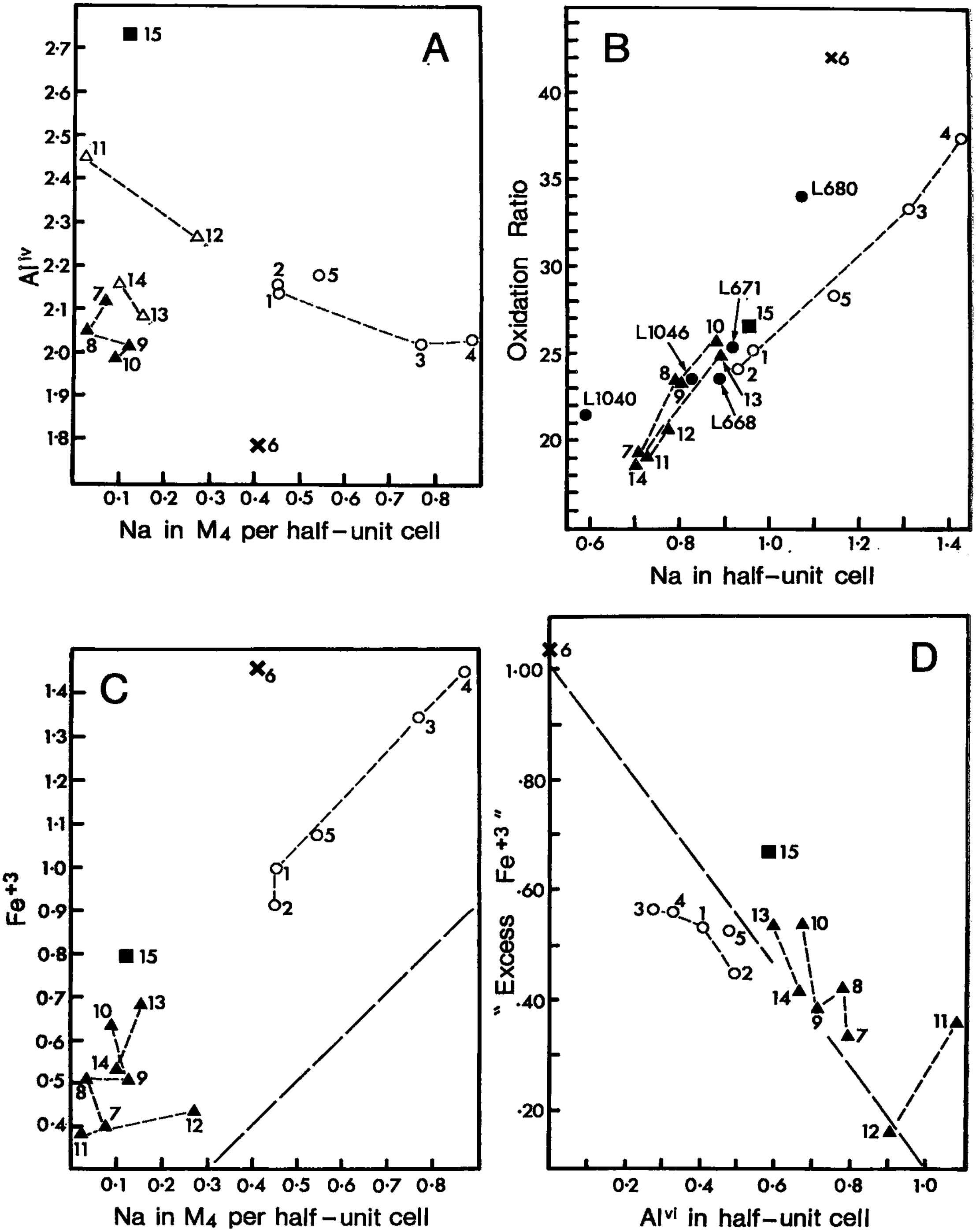

FIG. 4. Some compositional relationships in the Wolfe amphiboles. (A) relationship between Na in the *M*(4) site and tetrahedrally coordinated Al. $Na^{M(4)}$ calculated as described in text; (B) relationship between the total Na content of amphiboles from eastern Ontario alkaline gneisses and their oxidation ratios. Oxidation Ratio = mol. prop. $2\,Fe_2O_3 \times 100/2Fe_2O_3 + FeO$. Wolfe amphibole symbols as in Figure 1. L—numbers refer to amphiboles in Leake's (1968) catalogue; (C) relationship between Na in the M_4 site and ferric iron showing positive correlation paralleling 1:1 ratio; (D) relationship between octahedrally coordinated Al and Fe^{+3} in excess of that required for the substitution $Na^{M(4)}Fe^{+3} \rightarrow CaFe^{+2}$.

comprised several types of metasediments subsequently affected by an episode of plutonic sodium metasomatism. The probable parent lithologies include quartzo-feldspathic paragneisses or leptites, non-alkaline calc-silicate gneisses, amphibolites, and metamorphic pyroxenites, all of which are common within the same stratigraphic interval throughout the area. Evidence from other parts of the Haliburton-Renfrew Alkaline Gneiss Belt (S. L. Mitchell, pers. comm.) demonstrates that the parent gneisses had amphibolite-facies metamorphic parageneses before the emplacement of the igneous alkaline rocks which provided the source of the metasomatising fluids (Appleyard 1969, 1974). The Wolfe Belt amphiboles thus have evolved compositionally from "normal" amphiboles of the antecedent gneisses. The present paragenetic assemblage appears to have equilibrated (Appleyard 1963) during the peak of metamorphic conditions which occurred some time subsequent to the emplacement of the alkaline rocks. The evolution of the amphiboles was therefore influenced both by metamorphic and metasomatic factors. However, an approximation of the net metasomatic effect can be obtained through a comparison of the present compositions of the Wolfe amphiboles with those of amphiboles from similar antecedent lithologies with a similar metamorphic history.

Figure 5 is a synoptic diagram which attempts

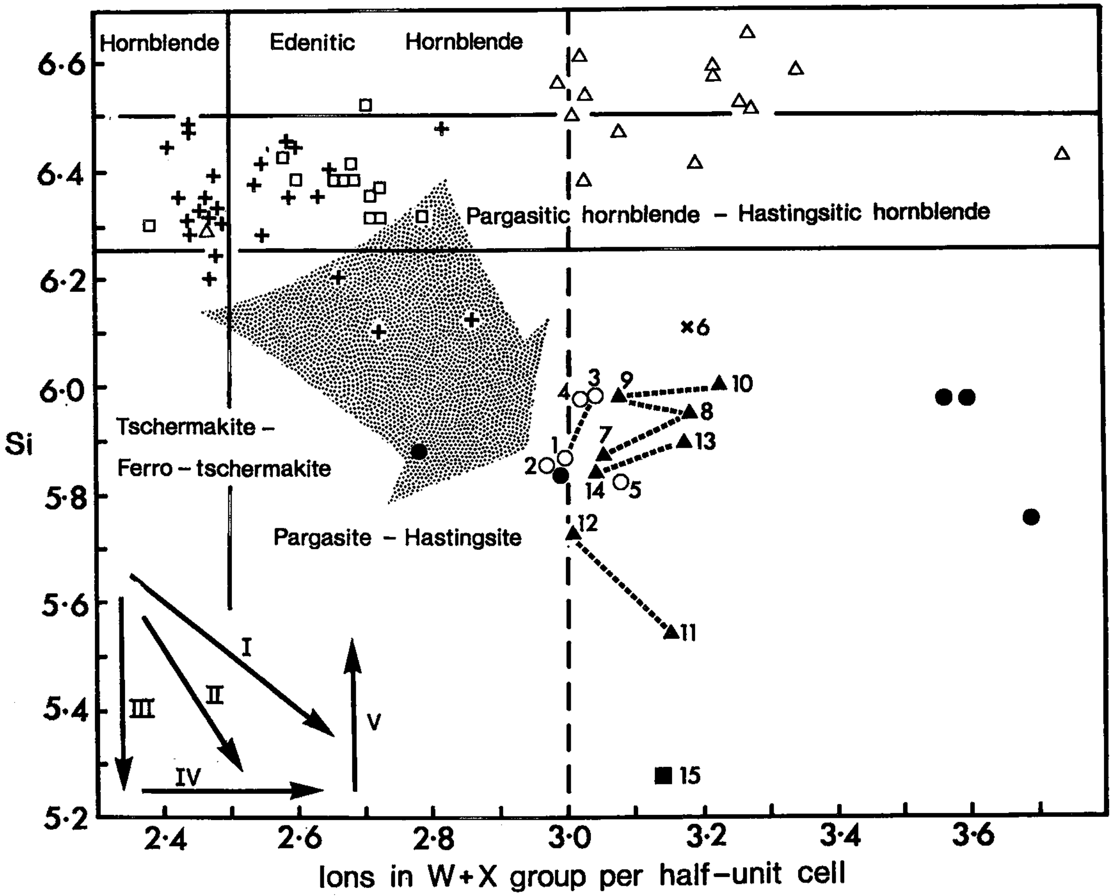

FIG. 5. Synoptic diagram illustrating the possible derivation of Wolfe amphiboles from pre-nephelinization antecedents. Terminology according to Leake's (1968) nomenclature. Symbols of Wolfe amphiboles as in Figure 1. Other symbols: closed circles—amphiboles from other alkaline gneisses in eastern Ontario; open triangles—amphiboles from Grenville carbonate-rich metasediments; open squares —amphiboles from Grenville quartzo-feldspathic and feldspathic paragneisses and leptites; crosses—amphiboles from Grenville amphibolites including para-amphibolites and hornblende-scapolite rocks. Trends of substitution formulae as follows: I — edenite substitution, $Na^{A}Al^{iv} \rightarrow Si$; II pargasite substitution, $Na^{A}2Al^{iv}Al^{vi} \rightarrow R^{+2}2Si$; III tschermakite substitution $Al^{vi}Al^{iv} \rightarrow R^{+2}Si$; IV richterite substitution, $Na^{A}Na^{M(4)} \rightarrow Ca$; V—Wolfe substitution, $Na^{M(4)}Si \rightarrow CaAl^{iv}$.

to make this comparison by relating the $W+X$-group totals to the amount of Si in the Z-group. These factors were chosen since Na-Ca and Si-Al^{iv} involvements both seem to be dominant features in the substitutional paths. The Wolfe amphiboles and others from nepheline gneisses in the Haliburton-Renfrew Alkaline Gneiss Belt are characteristically poor in Si (generally less than 6.0 atoms) and tend to have high $W+X$-group totals (generally greater than 3.0 atoms). Amphiboles from Grenville amphibolites, including some para-amphibolites and calc-silicate gneisses, quartzo-feldspathic gneisses, and carbonate-rich rocks are plotted for comparison. The pargasitic hornblendes of the carbonate-rich rocks, although apparently only requiring desilication to yield the Wolfe hastingsites, differ from them in ways not illustrated on this diagram. Similarly, field relationships demonstrate without doubt that the nepheline gneisses were not developed from rocks of this type (Appleyard 1967), so this source is not considered likely. The geological relationships seem to dictate that tschermakitic and ferroan pargasitic hornblendes constitute the most likely precursors of the Wolfe hastingsites; such compositions characterize the amphibolite, calc-silicate, and quartzo-feldspathic gneisses of the area.

Sundius (1946) recognized a number of standard types of substitutions in the hornblende group, four of which produce effects that can be portrayed on Figure 5. Using the notation adopted in this account, these are as follows: the edenite substitution, $Na^{A}Al^{iv} \rightarrow Si$ (trend I); the pargasite substitution, $Na^{A}2Al^{iv}Al^{vi} \rightarrow R^{+2}2Si$ (trend II); the tschermakite substitution, $Al^{iv}Al^{vi} \rightarrow R^{+2}Si$ (trend III); and the richterite substitution, $Na^{A}Na^{M(4)} \rightarrow Ca$ (trend IV). A further substitution not recognized by Sundius, $Na^{M(4)}Si \rightarrow CaAl^{iv}$ (trend V) has been demonstrated in the Wolfe amphiboles. Since this substitution does not operate in the derivation of end-member compositions from the basic tremolite structure, it is not a "standard formula" in Sundius' nomenclature. For this account it will be termed the "Wolfe substitution".

As noted previously, the Wolfe amphiboles are believed to represent arrested stages in the progressive nephelinization of the gneisses, and by their sequential changes indicate the trends by which they responded to this process. To derive the Wolfe amphiboles from the tschermakites, tschermakitic hornblendes and pargasitic hornblendes of the Grenville gneisses requires desilicating and alkali-enriching substitutions. During this early stage of metasomatism, it appears that the edenite and pargasite substitutions, possibly combined with the tschermakite and richterite substitutions, were principally responsible for the compositional change. The first two of these involve addition of Na to the vacant site which would eventually become filled and these substitutions would cease. In the later stages, the Wolfe substitution developed with its Si-enriching trend. Minimum Si-values are thus to be expected in cells in which the $W+X$-group is close to 3.00 atoms.

Of particular interest is the unusual subsilicic titaniferous magnesian hastingsite (analysis 15) from the so-called Wolfe Belt "iron-formation" (Appleyard 1967). This is an enigmatic banded unit enriched in titaniferous magnetite (14-20%) and apatite (9-11%). It has skarn-like affinities and in that respect is similar to a rock yielding a ferro-tschermakite amphibole analyzed by Gittins (1961). Both these compositions may have evolved from more Na-poor tschermakites through the edenite and pargasite substitutions. Similarly, the sodic magnesian hastingsite of the nephelinized amphibolite of the Wolfe Belt (analysis 6) can be derived from the more Si-rich ferroan pargasitic hornblendes of the normal amphibolites.

CONCLUSIONS

The silica-poor hastingsites and magnesian hastingsites from the nephelinized supracrustal rocks of the Wolfe Belt evolved from the normal tschermakitic hornblendes, pargasitic hornblendes, and tschermakites of the Grenville Supergroup. The primary amphiboles seem to have accepted Na and suffered simultaneous desilication, initially by the edenite and pargasite substitutions. When the vacant space (A-site) became filled, additional Na was taken into the structure by the substitution $Na^{M(4)}Si \rightarrow CaAl^{iv}$. This reversed the desilication trend, resulting in the negative correlation between $Na^{M(4)}$ and Al^{iv} displayed by the suites of amphiboles described in this study. Such a changing balance of substitutions would result in minimum Si contents as the $W+X$-group total approached 3.00 atoms. The subsilicic magnesian hastingsites (analyses 11, 12 and 15) may have evolved from Na- and Si-poor tschermakites or tschermakitic hornblendes.

A final word of caution is warranted. Speculations such as these are extremely susceptible to error either in the analyses themselves or in the initial sampling and sample preparation. They rest also on the validity of the arbitrary technique of distributing atoms within the structural formula. Relatively small errors in

Ca:Mg, Fe^{+2}:Fe^{+3}, and volatile determinations can have significant effects on the distributions discussed in this paper. The analyses in this paper are presumably not perfect in this regard, but as a group they betray consistent internal relationships as well as group similarities with other amphiboles from similar sources, factors which appear to the author to be more likely real than accidental. In addition, the major-element values of the most extreme analysis (no. 15) were checked by a second analyst and confirmed. It is unfortunate that the large number of microprobe analyses of amphiboles from similar rocks in the area are not adequate for use in such studies because of their deficiencies in iron oxidation state and volatile determination.

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