

## Alkali Amphiboles and Pyroxenes from Siwana Granite and the Associated Acid Volcanics, Rajasthan

RAMANATHAN BASKAR and NARESH KOCHHAR<sup>1</sup>

Department of Environmental Sciences & Engineering, Guru Jambheshwar University, Hisar - 125 001

<sup>1</sup>Department of Geology, Panjab University, Chandigarh - 160 014

Email: rbaskargjuhisar@yahoo.com

**Abstract:** Compositional characteristics and substitutional schemes of the amphiboles and pyroxenes of the alkali granites and the associated volcanics around Goliya Bhaylan area are studied. In the alkali granite, the amphiboles evolve from richterite to arfvedsonite, in trachytes from winchite to riebeckite and in the case of rhyolites from richterite through arfvedsonite to riebeckite with dominant substitution of the type  $\text{Na}^{\text{M}} + \text{R}^{3+}$  for  $\text{Ca} + \text{R}^{2+}$ . The pyroxenes in alkali granite evolve from hedenbergite to aegirine through aegirine-augite representing the acmitic hedenbergite trend with dominant  $\text{NaFe}^{3+} = \text{Ca} (\text{Mg}, \text{Fe})^{2+}$  substitution and a minor amount of  $\text{NaAl} = \text{CaFe}^{2+}$  substitution, whereas the pyroxenes in the acid volcanics are aegirine representing the acmitic trend, with the same substitution characteristics as those found in the alkali granites. The occurrence of Ti-aegirine and aenigmatite is also reported. The chemical trends of the pyroxenes and amphiboles indicate that they are formed from a highly evolved peralkaline residual melt.

**Keywords:** Pyroxenes, Amphiboles, Peralkaline, Alkali granite, Siwana, Rajasthan.

### INTRODUCTION

The present study deals with the mineral chemistry of the amphiboles and pyroxenes from Siwana ring structure and attempts to discuss some mineralogical aspects in relation to magma composition and evolution. A review of literature on the Malani igneous suite shows that many researchers have studied the petrology and geochemistry on parts of the suite but the work on the mineral chemistry of the suite is relatively few. Mukherjee and Roy (1981) had first presented the chemical analyses of arfvedsonite and aegirine in the Siwana granite. Bhushan (1989) had studied the mineral chemistry of the Malani volcanics to discuss the petrogenetic aspects. Dhar and Kochhar (1997) discussed mineral chemistry of amphiboles from Jalor ring structure and Vallinayagam (1997) presented the mineral chemistry of Siwana ring complex. A review of the attributes and significance of the A-type Malani magmatism was done by Kochhar (2000).

### GEOLOGICAL SETTING AND PETROGRAPHY

The Trans-Aravalli block (TAB) is unique in the geological evolution of the western Indian shield as it is characterized by a major period of anorogenic (A-type),

"Within Plate" magmatism represented by the Malani Igneous Suite (MIS) of rocks (general coverage of 55,000 km<sup>2</sup>) (Fig.1). This Neoproterozoic (750 Ma) suite comprises Siwana (peralkaline), Jalor (metaluminous to mildly peralkaline) and Tusham (peraluminous) granites with cogenetic carapace of acid volcanics (welded tuff, rhyolite, trachyte, explosion breccia) and displays distinctive ring structures and radial dykes. The Siwana ring structure is 30 km in E-W and 25 km in N-S directions. Representatives of the MIS also occur in Kirana Hills, Pakistan. The Malani acid volcanics and the contemporaneous granites are much younger than the Aravalli and Delhi supergroups with which they are associated at places. No direct relationship of the MIS with the Aravalli-Delhi orogenic cycles are observed in the field. This A-type magmatism is bimodal in nature and is of high heat producing type (Kochhar, 1989; Eby and Kochhar, 1990). Based on detailed geological mapping and position of xenoliths in Siwana, it is established that extrusive phase (trachyte, rhyolite, welded tuff, basalt) was followed by the intrusive phase (alkali granite), and the magmatic activity was culminated by the dyke phase (trachyte, trachyandesite, trachydacite, rhyolite, microgranite).

The alkali granites are hypersolvus (Tuttle and Bowen,

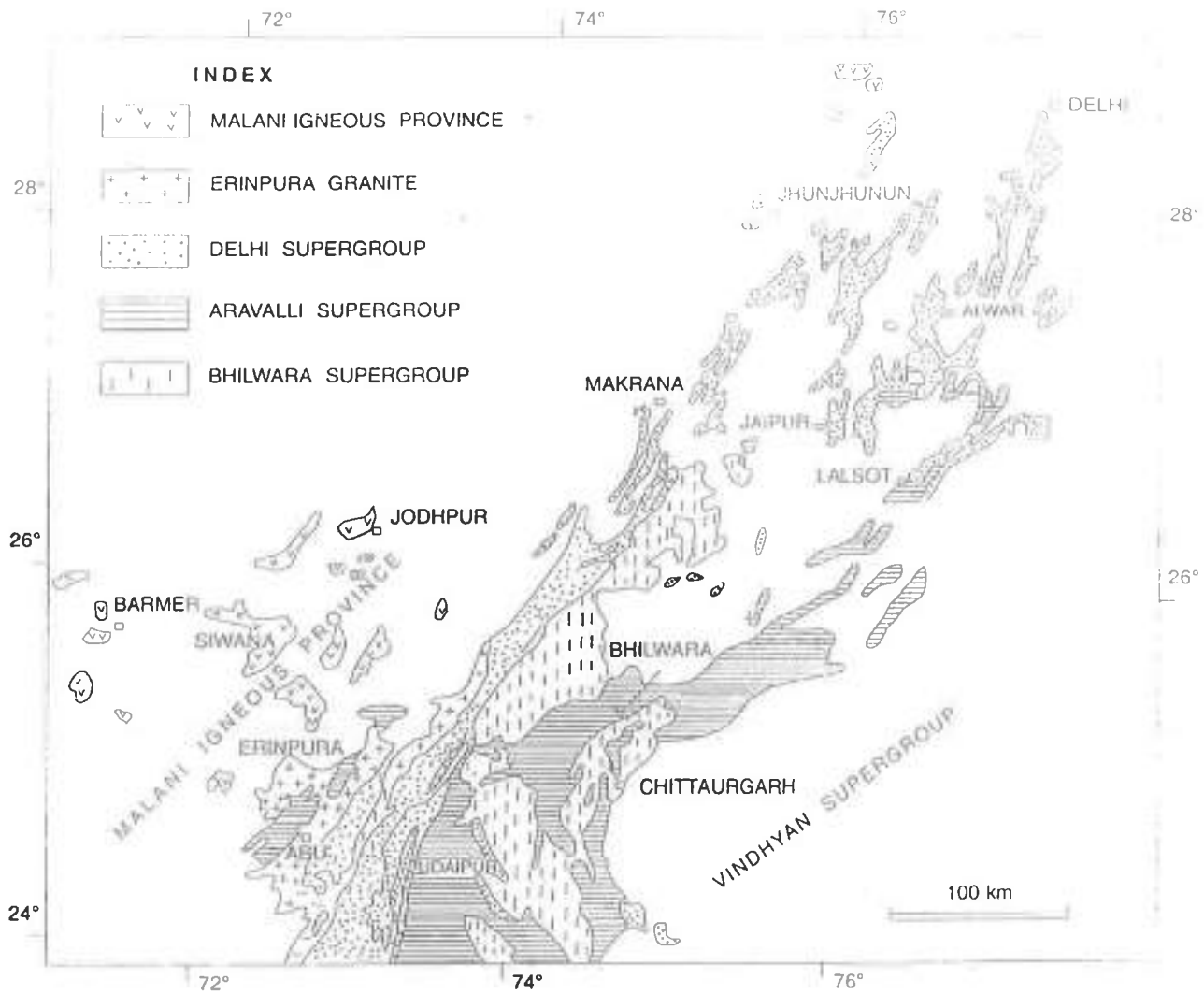


Fig. 1. Regional geological map of part of Rajasthan (modified after Heron, 1953; in Bhushan and Chandrasekaran, 2002).

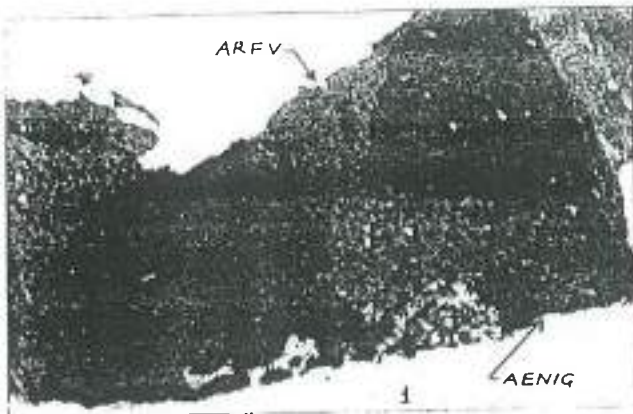
1958) and consist of alkali feldspar, quartz, arfvedsonite, riebeckite and aegirine. In some sections of the alkali granite, aenigmatite is noted. Accessory phases include apatite, titanite, magnetite and fluorite. Srivastava (1989) has reported the occurrence of accessory fayalite and monazite in the Siwana granites.

The sodic pyroxenes range from 5.41 to 8.14 vol % of the alkali granite. Aegirine occurs as short, prismatic crystals; euhedral to subhedral in shape (length 2.5 mm and width 0.5 mm), pleochroic (X=dark green, Y=light green, Z=yellowish green) and the extinction angle varies between 4° to 7°. It is enclosed by arfvedsonite and texturally appears to have formed before the alkali amphiboles.

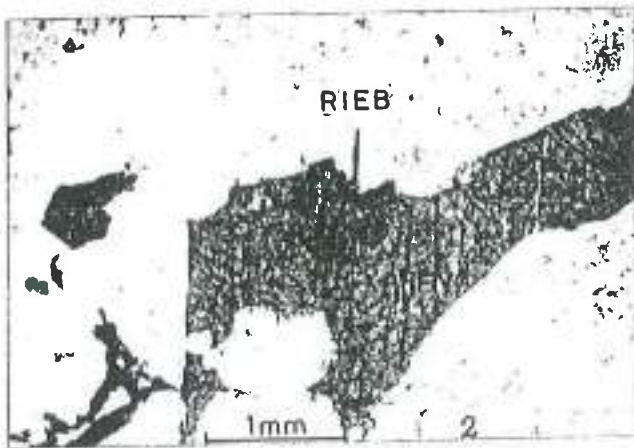
The alkali amphiboles constitute 5.77 to 6.55 vol % of the alkali granite. Arfvedsonite occurs as short, prismatic crystals, euhedral to subhedral in shape (length 0.2 mm to

2.5 mm), pleochroic (X= dark bluish green, light blue, Y= bluish green, blue, Z= yellowish green, dark blue) and the extinction angle varies between 13° to 15°. In the alkali granites, arfvedsonite co-exists with aenigmatite and from the textural relations the latter appears to have formed after arfvedsonite. Aenigmatite is an accessory mineral constituting 0.3 volume percentage and exhibits pleochroism (X=brownish red, Y=reddish brown, Z=deep reddish brown) (Photograph 1). Riebeckite occurs as needles in perthite and as overgrowths along margins of arfvedsonite (Photograph 2). It appears texturally to have formed later than arfvedsonite. It is pleochroic (X=light blue, Y=blue, Z= dark blue) and the extinction angle varies between 3° and 5°. The acid volcanics have the same mineralogy as the alkali granites, but show textural variations.

Chemically, the Siwana granites are characterized by low



Photograph 1. Aenigmatite associated with arfvedsonite in the Siwana alkali granite; magnification X18, PPL.



Photograph 2. The intergrowth of riebeckite and arfvedsonite in alkali granite; magnification X18, PPL.

CaO and Al<sub>2</sub>O<sub>3</sub>, high Fe/Mg, high K<sub>2</sub>O and high absolute alkali abundances, high REE (except Eu), Zr, Nb and Ta trace element abundances and low Co, Sc, Sr, Ni, Ba, Sr and Eu trace element abundances (Eby and Kochhar, 1990). The rocks are peralkaline with agpaite index (molecular proportion Na<sub>2</sub>O+K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>) ranging from 0.95 to 1.37.

**MINERAL CHEMISTRY**

The mineral chemical analysis was carried out on CAMEBAX electron microprobe at the Laboratory of Orsay, France (accelerating potential: 15 kv, sample current: 12 na, count interval: 5s) using natural silicates and oxides as standards and following ZAF correction procedure. A total of 48 pyroxene analyses in 6 samples (3 alkali granites, 2 rhyolites, 1 basalt) and a total of 35 amphibole analyses in 6 samples (3 alkali granites, 2 trachytes, 1 rhyolite) were obtained (Tables 1 to 2). Analyses of aenigmatite along with associated amphibole and pyroxene (one of which is

Ti-aegirine) were obtained (Table 3). The amphibole and pyroxene terminology used in this work are after Leake (1978) and Morimoto (1989) respectively. The mineral formula for amphiboles and pyroxenes are calculated on the basis of 13 cations and 4 cations respectively according to the method of Neumann (1976) and of aenigmatite on the basis of 14 cations and 20 oxygens.

**Amphiboles**

**Compositional Characteristics**

In the sodic and calcic amphiboles of the alkali granites, there are sufficient Si+Al to fill the tetrahedral sites except in case of sodic-calcic amphiboles where Fe<sup>3+</sup> (IV) are indicated. In most cases of amphiboles from acid volcanics, there is insufficient Si+Al to fill the tetrahedral sites and Fe<sup>3+</sup> (IV). During the evolution of the amphiboles in the alkali granite and the associated acid volcanics, the total Al and Al<sup>IV</sup> contents typically decrease. In the alkali granites, the Al<sup>VI</sup> content is vacant in the sodic and sodic-calcic amphiboles and can amount to 0.11 in the case of calcic amphiboles. In the case of acid volcanics, the Al<sup>VI</sup> content is generally vacant except in the case of two riebeckite (A19, A17) and one ferro-richterite (A40) analyses. The A-sites of the sodic amphiboles of the alkali granites are completely filled, contrasting with the sodic-calcic (av. 0.774) and calcic amphiboles (av. 0.114). Contrastingly, the A-sites of the acid volcanics are not completely filled and range from 0.073 to a maximum of 0.717.

A plot of Ca+ Al<sup>IV</sup> against Si+Na+K (Fig. 2) shows that the amphiboles of the alkali granite and the acid volcanics follow a well-defined evolutionary trend (Giret et al. 1980 and Strong and Taylor, 1984). Following the distinction made by Strong and Taylor (1984), the evolutionary path for the amphiboles of the alkali granite can be characterized as magmatic-subsolidus (richterite to arfvedsonite), rather than oxidizing, where as for the amphiboles of the rhyolites,

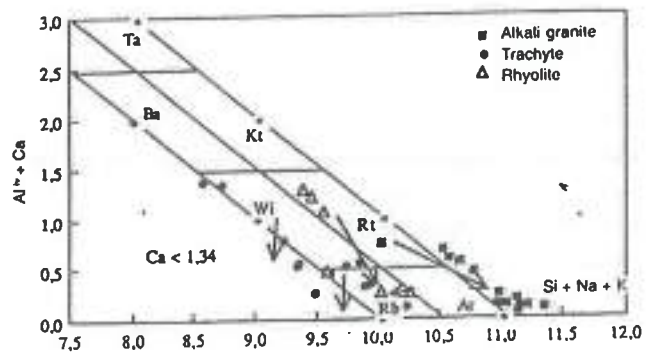


Fig.2. Fields are from Giret et al. (1980) after classification of Leake (1978).



Table 1. Amphiboles

Rock Anal. No.	M-1 2 core	M-1 3 rim	G-98 47 core	G-24 38 rim	M-30 2 core	M-30 12 core	M-30 13 core	G-91 55 sin city	GR-98 48 sin city
SiO <sub>2</sub>	49.56	48.84	51.47	50.08	50.8	50.07	50.98	51.33	50.31
TiO <sub>2</sub>	1.18	1.31	0.04	0.95	0.17	0.74	0.74	0.13	0.42
Al <sub>2</sub> O <sub>3</sub>	0.32	0.40	2.14	0.55	1.27	0.44	0.32	0.38	1.42
FeO <sub>t</sub>	34.88	35.13	23.93	34.43	34.64	35.22	37.01	36.53	28.24
MnO	0.75	0.20	0.42	0.81	1.62	0.94	0.94	0.96	1.31
MgO	0.09	0.08	8.18	1.06	1.54	1.53	1.53	0.69	5.29
CaO	2.90	2.99	12.23	3.82	3.29	2.84	2.84	0.69	5.87
Na <sub>2</sub> O	7.72	7.27	0.1	6.97	4.42	5.85	5.85	6.36	5.37
K <sub>2</sub> O	1.63	1.84	0.23	nd	0.84	1.63	1.63	0.38	0.82
Total	99.03	98.06	98.74	98.67	98.59	99.26	101.84	97.45	99.05
Si	7.94	7.924	7.728	7.891	7.764	7.779	7.712	7.919	7.703
Al <sup>(iv)</sup>	0.06	0.076	0.272	0.102	0.229	0.081	0.057	0.069	0.256
Fe <sup>(iv)</sup>	0	0	0	0.007	0.007	0.14	0.231	0.012	0.041
Z	8	8	8	8	8	8	8	8	8
Al <sup>(vi)</sup>	0	0	0.107	0	0	0	0	0	0
Ti	0.142	0.16	0.005	0.113	0.02	0.086	0.084	0.015	0.048
Fe <sup>t</sup>	4.672	4.766	2.735	4.53	4.42	4.436	4.451	4.881	3.575
Mn	0.102	0.027	0.053	0.108	0.21	0.124	0.12	0.125	0.17
Mg	0.021	0.019	1.831	0.249	0.351	0.354	0.345	0.159	1.207
Y	4.937	4.972	5	5	5	5	5	5	5
Ca	0.498	0.52	1.967	0.645	0.539	0.473	0.46	0.255	0.963
Na (B)	1.502	1.48	0.029	1.355	1.31	1.527	1.54	1.745	1.037
Ca+Na (B)	2	2	1.996	2	1.849	2	2	2	2
Na (A)	0.895	0.806	0	0.774	0	0.235	0.176	0.157	0.557
K	0.333	0.381	0.044	0	0.164	0.323	0.315	0.075	0.16
A	1.228	1.187	0.044	0.774	0.164	0.558	0.49	0.232	0.717
Total	16.17	16.16	15.04	15.77	15.01	15.56	15.49	15.23	15.72
Min.	Arfv.	Calc Arfv.	Ferro Act.	Ritch.	Ferro Win.	Arfv.	Rieb.	Rieb.	Ferro Ritch.
M-1, G-98, G-24:		Alkali granite		M-30, G-91:	Trachyte	GR-98	Rhyolite		

\*These are representative analyses only. Complete analytical data can be obtained from the author.

they can be characterized as magmatic-subsolidus to oxidizing (richterite through arfvedsonite to riebeckite) and for the amphiboles of the trachytes as oxidizing trend (winchite to riebeckite). This is, as demonstrated by the classic work of Ernst (1962); in sodic amphiboles, the A-site is more completely filled under low oxygen fugacities and/or high temperatures than under high oxygen fugacities and/or low temperatures.

#### Substitution Schemes

Within the amphibole structure, in addition to simple substitutions such as Fe<sup>2+</sup> for Mg, there are at least six possible schemes of coupled substitution which involve charge balancing, and lead to idealized end members (Czamanske and Wones, 1973).

The simplest clino-amphibole formula can be written as A<sub>0-1</sub>X<sub>2</sub>Y<sub>5</sub>O<sub>22</sub>(OH, F)<sub>2</sub>, substitutions involving ions of lesser or greater charge are balanced in diverse ways. Charges can be decreased by replacement of Ca by Na in the M<sub>4</sub> site or

Si by Al or Fe<sup>3+</sup>. Conversely, charges are increased by addition of Na or K to the A-site and Al, Fe<sup>3+</sup> or Ti<sup>4+</sup> to the octahedral strip. Figure 3 shows that in the sodic amphiboles of rhyolites and trachytes unlike the calcic and sodic-calcic amphiboles of the granite, these substitutions follow an offsetting relationship. This plot indicates that the charge-reducing substitutions are overcompensated and vacancies must exist in the octahedral strip. Because the average values of A-site occupancy, Al<sup>VI</sup> and Ti cations are relatively constant, the generation of these vacancies must relate principally to the presence of Fe<sup>3+</sup>. As seen from the figure, the charge reducing substitutions are balanced for the acid volcanics and the octahedral strip must be complete. This relationship is further explored in Fig.4, in which the octahedral strip vacancy is plotted against Fe (t).

#### Substitution Characteristics

Much of the data are based on plots that do not involve Fe<sup>2+</sup>, Fe<sup>3+</sup> or the octahedral site occupancy. The simplest

Table 2. Pyroxenes

Rock	G-98	G-24	M-1	M-1	G-86	M-12
Anal. No	3	35	4	26	17	36
	rim	core	core	core	sin.cry	sin.cry
SiO <sub>2</sub>	53.79	52.84	51.02	48.74	53.26	52.57
TiO <sub>2</sub>	2.07	1.43	0.35	0.9	0.09	0.39
Al <sub>2</sub> O <sub>3</sub>	0.23	0.22	0.14	0.67	0.28	0.31
FeOt	28.02	30.39	29.14	26.06	30.69	31.06
MnO	0.60	0.15	0.24	1.28	0.86	0.48
MgO	0.06	0.02	0.09	1.72	0.07	0
CaO	0.61	2.18	12.25	18.66	1.15	0.13
Na <sub>2</sub> O	14.52	13.51	6.78	1.61	14.30	14.39
<b>Total</b>	<b>99.90</b>	<b>100.74</b>	<b>100.01</b>	<b>99.64</b>	<b>100.70</b>	<b>99.33</b>
Si	1.997	1.958	1.991	1.969	1.980	1.984
Al <sup>(iv)</sup>	0.003	0.010	0.006	0.031	0.012	0.014
Fe <sup>3+</sup> (iv)	0.000	0.032	0.003	0.000	0.008	0.002
T	2	1.999	2	2	2	2
Al <sup>(vi)</sup>	0.007	0	0	0.001	0	0
Fe <sup>3</sup> (vi)	0.870	0.910	0.510	0.092	0.946	0.973
Ti	0.058	0.040	0.010	0.027	0.003	0.011
Fe <sup>2</sup>	0	0	0.438	0.760	0	0
Mn	0.019	0.005	0.008	0.044	0.027	0.015
Mg	0.003	0.001	0.005	0.104	0.004	0
M1	0.958	0.955	0.971	1.028	0.98	0.999
Ca	0.024	0.087	0.513	0.810	0.046	0.005
Na	1.045	0.970	0.513	0.126	1.018	1.048
M2	1.070	1.057	1.026	0.936	1.064	1.053
<b>Total</b>	<b>4.027</b>	<b>4.011</b>	<b>3.986</b>	<b>3.964</b>	<b>4.044</b>	<b>4.052</b>
Min.	Aeg.	Acg.	Aeg	Heden.	Aeg.	Aeg.

G-98, G-24, M-1: Alkali granite; G-86, M-12: Rhyolite

\*These are representative analyses only. Complete analytical data can be obtained from the author.

substitutions involving M<sub>1</sub>-M<sub>3</sub> sites is that between Mg and Fe<sup>2+</sup>+Mn (Fig.5). For the alkali granites, as the amphibole crystallization evolves, there is no change in Mg for increase in Fe<sup>2+</sup>+Mn. For the trachytes, there is a decrease in the value of Mg as Fe<sup>2+</sup>+Mn value increases, whereas for rhyolites as Fe<sup>2+</sup>+Mn increases, correspondingly the value of Mg also rises.

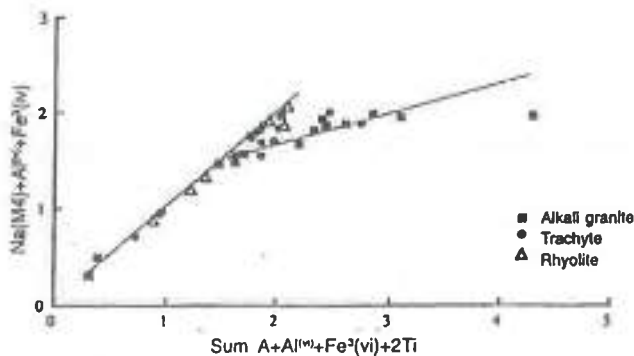


Fig.3. Total A-site occupancy+Al<sup>(vi)</sup>+Fe<sup>3</sup>(vi)+2Ti against Na(M4)+Al<sup>(iv)</sup>+Fe<sup>3</sup>(iv).

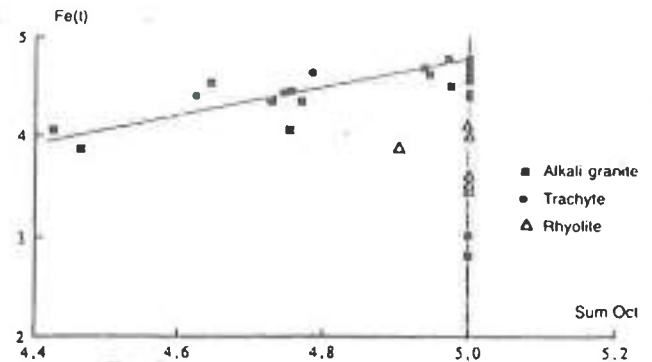


Fig.4. Total octahedral-site occupancy against total Fe (cations).

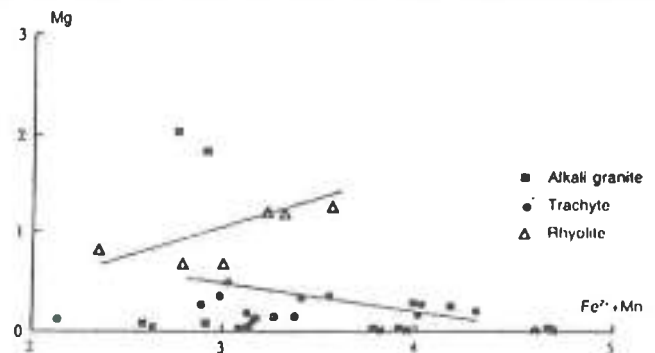


Fig.5. Fe<sup>2+</sup>+Mn against Mg (cations).

There is a diminution in the A-site occupancy with the increase in Fe(t) for the amphiboles of the rhyolites and granites whereas the trachytes show large diminution in A-site occupancy with increase in Fe(t) (Fig. 6). This could probably be due to the Ca + Fe<sup>3+</sup> for Na (A) + Fe<sup>2+</sup> (riebeckitic) substitution.

As shown in Fig. 7, the dominant substitution in the alkali amphiboles is Na (M4) +Fe for Ca+Mg. The slope of the data set for the amphiboles from the alkali granites indicates that the loss of Ca+Mg is not totally compensated by Na (M4)+Fe, a fact which could imply the creation of vacancies in the M<sub>1</sub>-M<sub>3</sub> octahedral sites, whereas the slope of the data

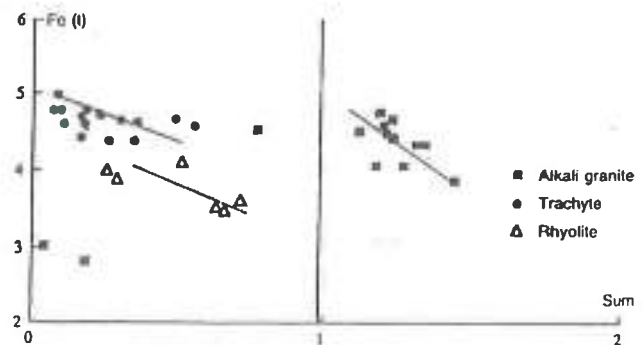


Fig.6. Total A-site occupancy against total Fe (cations).

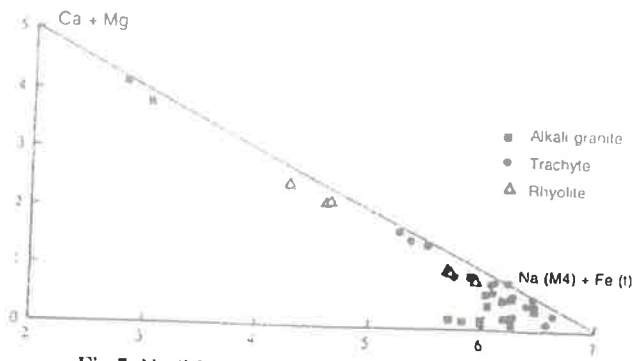


Fig. 7. Na (M4)+total Fe against Ca+Mg (cations).

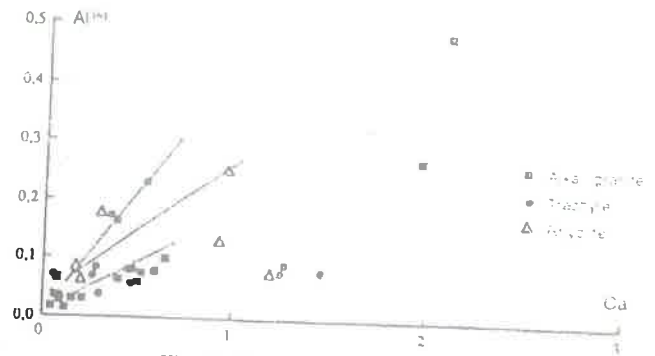


Fig. 10. Ca against Al<sup>IV</sup> (cations)

set for the amphiboles from the acid volcanics indicates the loss of Ca+Mg is totally compensated by Na(M4)+Fe, a fact which could imply the lack of vacancies in the M<sub>1</sub>-M<sub>3</sub> octahedral sites.

Relations between Na and Fe contents are illustrated in Fig. 8. For the amphiboles of the alkali granites Na content increases with decrease in Fe (t) content, for the amphiboles from rhyolites total Na content increases with increase in Fe (t) and for the amphiboles of the trachytes Na and Fe (t) contents show no correlation. Figure 9. Shows the appropriate correlation between Na (M4) and Fe<sup>3+</sup> (VI).

Figure 10 indicates that Al<sup>IV</sup> and Ca obey a relation of 1:2 in the alkali amphiboles of the granite, rhyolite and

trachyte. Fabries (1978) considers a relation of 1:2 ratios between Al<sup>IV</sup> and Ca to be typical of alkali amphibole fractionation trend in the over saturated alkaline rocks. There is no relation between Al<sup>IV</sup> and Na (A) for the rhyolites and trachytes, whereas for granites Al<sup>IV</sup> decreases with increase in Na.

Papiké et al. (1969) suggest that in the richterite lattice, Na<sup>+</sup> substitution for Ca<sup>2+</sup> in the (M4) site is coupled with Na substitution for vacancy in the (A) structural site. A plot of Na (M4) versus Ca (M4) (Fig. 11) supports the idea of Na substitution for Ca in the amphiboles. They exhibit a well-defined linear trend. In fact, Ca approaches zero as Na tends to a maximum of 2.

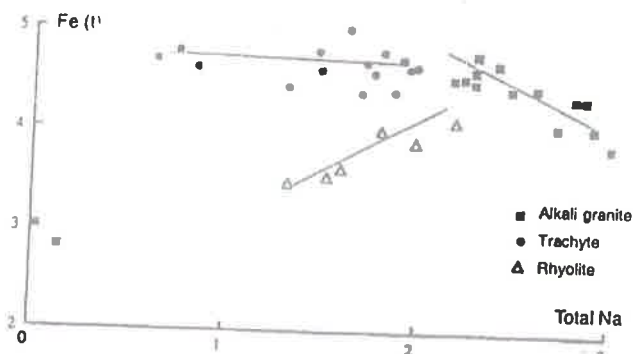


Fig. 8. Total Na against total Fe (cations).

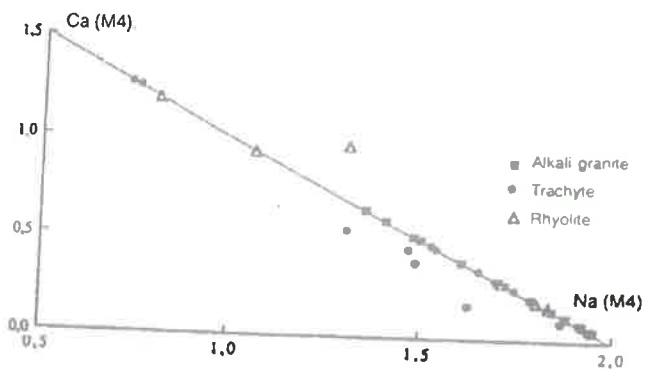


Fig. 11. Na (M4) against Ca (M4).

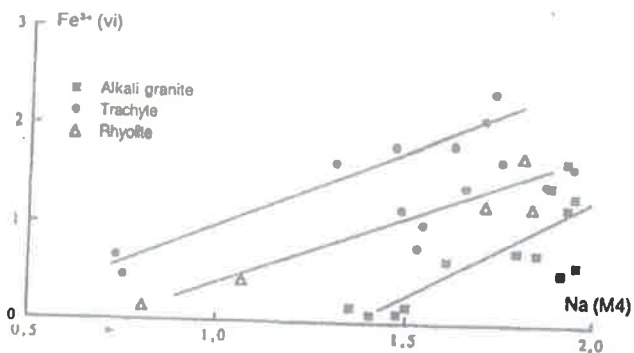


Fig. 9. Na (M4) against Fe<sup>3+</sup> (vi) (cations).

**Pyroxenes**

*Compositional Characteristics*

T- position: The number of Si atoms per formula unit in the aegirines of the rhyolites range from 1.95 to 1.99. In the tetrahedral position, in addition to Si and Al, Fe<sup>3+</sup> is required to complete it. The number of Si atoms per formula unit in the augites of the basalt range from 1.967 to 2.02 as there is enough Si; most of the Al must be placed at the M1 site. In the case alkali granites the number of Si atoms per formula unit in the aegirines range from 1.933 to 2.004. And in most cases, there is enough Si and Al to complete the tetra-



Table 3. Aenigmatite and Ti-Aegirine

Rock Anal. No	MW-7 15	MW-7 18	MW-7 21	MW-7 24
SiO <sub>2</sub>	40.95	49.36	51.82	51.6
TiO <sub>2</sub>	9.64	2.75	0.7	4.31
Al <sub>2</sub> O <sub>3</sub>	0.58	0.07	0.36	0.24
FeO (t)	41.65	33.6	32.9	29.26
MnO	0.8	0.99	0.69	0.24
MgO	0.17	0.15	0.15	0.03
CaO	0.64	0.44	0.71	3.04
Na <sub>2</sub> O	7.01	8.55	13.64	12.3
K <sub>2</sub> O	0.09	2.77	0.02	0.08
<b>Total</b>	<b>101.52</b>	<b>98.18</b>	<b>100.99</b>	<b>101.1</b>
Si	5.789	7.976	1.977	1.952
Al	0.097	0.013	0.016	0.011
Fe <sup>3+</sup>	0.213	0	0.944	0.833
Fe <sup>2+</sup>	4.71	4.54	0	0
Mn	0.096	0.135	0.022	0.008
Mg	0.036	0.036	0.009	0.002
Ca	0.097	0.076	0.029	0.123
Ti	1.025	0.334	0.02	0.123
Na	1.921	2.678	1.009	0.902
K	0.016	0.468	0.001	0.004
	Aenigmatite	Arfvedsonite	Aegirine	Ti-Aegirine

MW-7 Alkali granite

hedraI sites, except a few cases where Fe<sup>3+</sup> is required. Consequently, most of the Al at the M1 site is generally present in very small amounts. In the case of the aegirine-augites of the alkali granite, the number of Si atoms per formula unit ranges from 1.954 to 1.991 and in addition to Si and Al, Fe<sup>3+</sup> is required to complete it. Consequently, there is no Al at M1 position. In the case of hedenbergite of the alkali granite the Si value is 1.969 and a small amount of Al is required to complete it.

*M1 position:* This involves the largest number of elements i.e. Mg, Mn, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Al and Ti. The octahedral site occupancies of the aegirine of the rhyolite range from 1.997 to 2.052, the augites of basalt range from 1.894 to 1.996. In the aegirines of the alkali granite, the octahedral site occupancies range from 1.923 to 2.074, in the aegirine-augites they range from 1.986 to 2.001 and in the hedenbergite it is 1.964.

*M2 position:* Ca+Na=1.007-1.064 in the aegirines of rhyolites and 0.521-0.561 in the augites of the basalt. The deficiency of these elements in the augites indicates the presence of large amounts of Na and Ca-poor pyroxene in solid solution. Ca+Na=0.827-1.163 in the aegirines of the alkali granites, 1.018-1.043 in the aegirine-augites of the alkali granite and 0.936 in the hedenbergites.

In the Na enriched pyroxenes, Ca+Na approximately closely to 1.00, which seems to be a normal feature for the alkali pyroxenes (Tyler and King, 1967). In the Ca and Ca-

Na pyroxenes, the amount of Ca is matched by an equal amount of Mg+Fe<sup>2+</sup>+Mn in M1, indicating that these four elements are present as diopside and hedenbergite components in minor amounts.

#### Substitution Schemes

Starting from the most common pyroxene formula, M2 (R<sup>2+</sup>) M1R<sup>2+</sup>T<sub>2</sub>(2R<sup>4+</sup>)O<sub>6</sub>, four coupled substitutions are possible, if one assumes more than one R<sup>4+</sup> in the T site (Morimoto, 1989). The calculated amounts of various end members (in mol percent) in the pyroxene series are given in Table 4.

A perusal of the Table 2 when considered along with the mol percent of the various end members (Table 4) indicate a dominant NaFe<sup>3+</sup>=Ca (Mg, Fe)<sup>2+</sup> substitution with up to 93.96 mol% NaFe<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub> component in the aegirine of acid volcanics and up to 93.95 mol% NaFe<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub> component in the aegirine of the alkali granite. In the case of aegirine-augite, this component ranges up to 51.49 mol % and in the case of hedenbergite it is 12.12 mol%, hence it implies a minor substitution of the type NaFe<sup>3+</sup>=Ca (Mg, Fe)<sup>2+</sup> as compared to the alkali granites and the acid volcanics. They also indicate significant amounts of the NaAl=CaFe<sup>2+</sup> coupled substitution in the M-site as the NaAlSi<sub>2</sub>O<sub>6</sub> component ranges from 0-10.41 mol% in the aegirine of the acid volcanics and 0.42-16.83 mol% in the aegirine of the alkali granite. This could be due to the fact that aegirine forms a nearly ideal solution series with jadeite as shown by Newton and Smith (1967). The Ca and Ca-Na pyroxenes do not seem to show these types of substitutions. It is observed that where the Al<sup>VI</sup> component of the pyroxenes is practically nil, no NaAl=CaFe<sup>2+</sup> substitution is noted. The basalts show that the augite is the solid solution of Ca<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> and Fe<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> molecules. It is further noted up to 6.53 mol% of Ca "Tsc" molecule is absorbed in the pyroxene as solid solution.

#### Substitution Characteristics

Stephenson's (1972) variation diagram (Na minus Mg) has been chosen as a fractionation index, since this allows the complete pyroxene trend to be represented in one diagram.

A plot of (Na-Mg) versus Si, Mn, Al and Ti shows no correlation. In the alkali granites and the associated acid volcanics a clear decrease in Ca and Fe<sup>2+</sup> contents is observed as Na-Mg content increases (Figs. 12a and b). This curve shows two types of substitution characteristics.

CaFe<sup>2+</sup> for CaMg and NaFe<sup>3+</sup> for (Ca, Mg) Fe<sup>2+</sup>. The point at which NaFe<sup>3+</sup> enrichment becomes dominant (Na-Mg = 0.800) is clearly seen on the Ca plot (Fig. 12a)

Table 4. Calculated amounts of various end members (in mol percent) in the pyroxenes

	Basalt Augite	Acid volcanics Aegirine	Alkali granite Hedenbergite	Alkali granite Aeg. augite	Alkali granite Aeg.
Jadeite	0.82-4.62	0-10.41	0.61	0	0.42-16.83
Acmite	0	88.36-93.96	12.12	48.20-51.49	81.07-93.95
CaFeTs	0	0-0.56	0	0-3.30	0
CaCrTs	0.22-0.48	0-0.44	0	0-3.30	0
CaTiTs	0-0.34	0-1.31	1.3	0.32-0.44	0-0.44
CaTsc	3.13-6.53	0-0.50	0	0	0
Wollastonite	24.95-25.64	0.25-6.08	40.13	23.97-26.23	0.09-10.12
Enstatite	25.79-27.54	0-0.84	5.23	0.24-0.26	0-2.15
Ferrosilite	39.41-43.04	0.60-1.47	40.6	21.70-21.94	0.02-13.93

Similarly, Fe<sup>2+</sup> contents also show an abrupt decrease after Na-Mg = 0.800 (Fig. 12b).

Plots based on pyroxene structural formulae of the granites show no relation between Mg and Ti, Ca and Ti, where as the total Fe contents seem to increase with decrease in Ti contents, it is also noted that there is no relation between Al and Ca for the sodic pyroxenes, where as the case of Ca and Ca-Na pyroxenes there is increase of Al with Ca (Fig. 13a). In the case of acid volcanics, they show no relation between Mg and Ti, Al and Ca, but show an increase in Fe contents with decrease in Ti contents (Fig. 13b). This indicates the presence of simple substitution of the

type Fe = Ti in the pyroxenes of the alkali granites and the acid volcanics.

Figure 14 illustrates the Na-Fe<sup>3+</sup> balance for the pyroxenes. In the Na and Ca-Na pyroxenes, there is excess Na over Fe<sup>3+</sup> which accounts for minor amount of jadeite component in addition to the dominant aegirine component, as to form jadeite only small amounts of Al<sup>VI</sup> is needed. In the augites, there is also a small excess Na, which combines with Al to form a minor jadeite component (up to 4.62 mol %).

The range of pyroxene compositions in terms of acmite and "other components" is shown in Fig. 15. As seen from

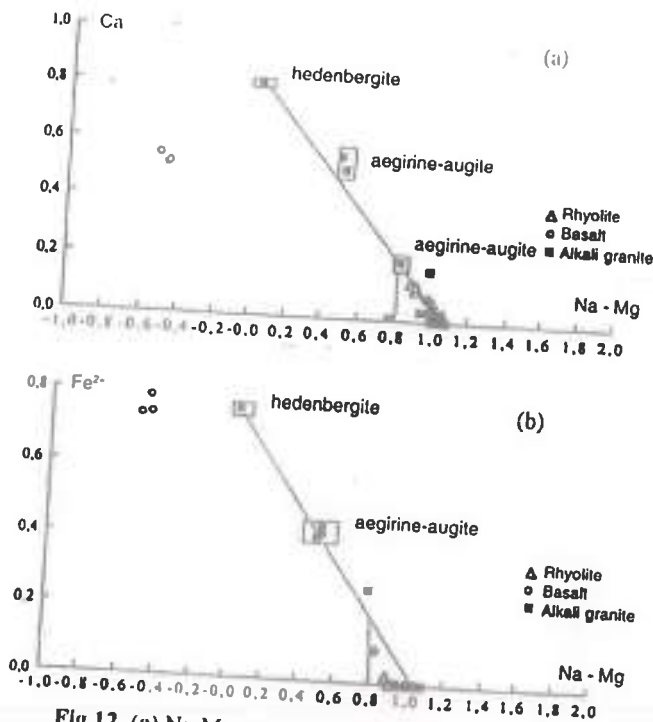


Fig. 12. (a) Na-Mg versus Ca. (b) Na-Mg versus Fe<sup>2+</sup>

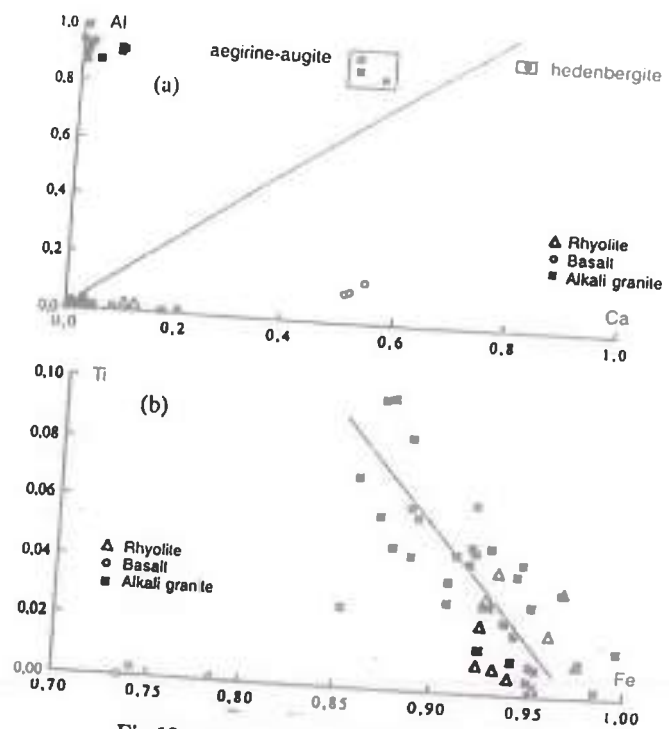


Fig. 13. (a) Al versus Ca. (b) Fe versus Ti.



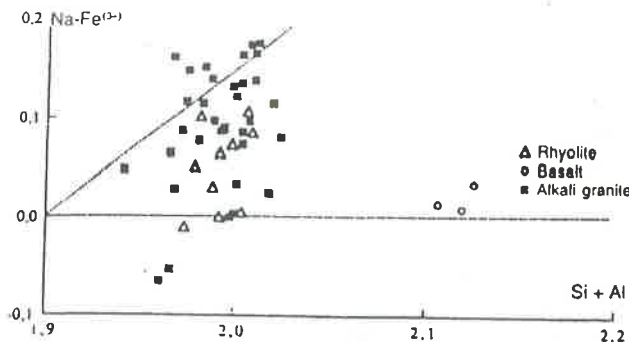


Fig.14. Diagram illustrating the Na-Fe<sup>(3+)</sup> balance for the pyroxenes.

the figure the sodic pyroxenes have a dominant acmite component and cluster towards  $\text{Na} + \text{Fe}^{3+} = 2.00$ , whereas the position of Ca-Na and Ca pyroxenes are distinct.

In the alkali granites, the pyroxenes evolve from hedenbergite to aegirine through aegirine-augite representing the acmitic hedenbergite trend. In the rhyolite, the pyroxenes are aegirines representing the acmitic trend. (Figs.16 a, b, c).

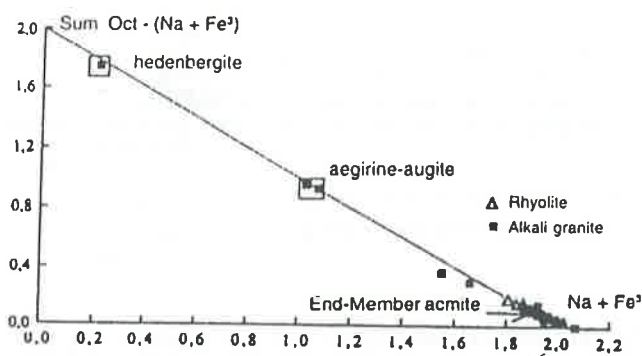


Fig.15. Range of compositions for pyroxene in terms of acmite and "other components".

### SOME MAGMATIC ASPECTS

The amphibole and pyroxene chemistry of the peralkaline Siwana rocks conforms to the mineralogical profile of the mafic mineral assemblage in the alkaline silica oversaturated series and is entirely compatible with the experimental studies on the alkali amphiboles and pyroxenes (Black and Bowden, 1985; Pla Cid et al. 2001; Njonfang and Moreau, 2003).

It has been established that the pyroxenes in the peralkaline rocks define a trend from the augite field to acmite corner. The sodic pyroxene could crystallize under high oxygen fugacities (Yagi, 1966) or under  $f\text{O}_2$  conditions much lower than required for QFM buffer at temperature below 780°C (Bailey, 1969). Factors more important than

oxygen fugacity in restricting the crystallization of sodic pyroxenes must exist. Acmite only crystallizes from liquids with a molecular excess of alkalis over aluminium and iron oxide (Bailey, 1969). Late stage sodic pyroxenes show through their chemistry the composition of the magma during the final stages. During the final stages the magma has very high contents of sodium and iron and is strongly depleted in  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$ .

It can be reasonably assumed, due to the presence of fayalitic olivine, magnetite and quartz that the crystallization took place at an oxygen fugacity at or above that of QFM. The assemblage aegirine+arfvedsonite are stable only over a limited range of T- $f\text{O}_2$  conditions between 700° to 780°C and the QFM and the wustite magnetite oxygen buffers (Bailey, 1969). It is therefore concluded that aegirine and arfvedsonite were among the last minerals to crystallize in these rocks, which is consistent with the textural evidence of crystallization sequence as discussed earlier.

In the sodic amphiboles, the A-site is more completely filled under low oxygen fugacities and/or high temperatures than under high oxygen fugacities and/or low temperatures (Ernst, 1962).

Bailey (1969) concluded that arfvedsonitic amphibole is the stable phase under severely reducing conditions and that the mixed assemblage of arfvedsonite-acmite may indicate a lower degree of peralkalinity in the magma or slightly higher  $f\text{O}_2$ . He also noted that fluctuating crystallization of acmite and arfvedsonite ".....may have been controlled by fluctuating oxidation conditions in the magma".

The aenigmatite, relative to the co-existing aegirine and arfvedsonite, is enriched in Ti and depleted in  $\text{Fe}^{3+}$ . It appears that  $f\text{O}_2$  in the residual liquid is buffered initially by arfvedsonite-aegirine and later by arfvedsonite-aenigmatite. Low  $f\text{O}_2$  is also supported by the replacement of aenigmatite by titanian-aegirine (Grapes et al. 1979).

The riebeckites must have formed during subsolidus stages as can be seen from textural relations and can form in the magnetite field at low temperatures (500-550°C) for an oxygen fugacity of  $10^{-18}$  bar. Pure hydroxyl riebeckites are stable at relatively low temperatures and high fugacities of oxygen in rocks of requisite bulk composition (high soda and iron, low  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ ) (Ernst, 1962).

In conclusion, it appears that these magmas provided the precise chemical requirements for the development of aegirine-arfvedsonite-riebeckite bearing alkali granites and the associated acid volcanics, having high alkali, low  $\text{CaO}$ , iron enriched relative to  $\text{MgO}$ . Arfvedsonite-bearing assemblages are presumed to have crystallized at low

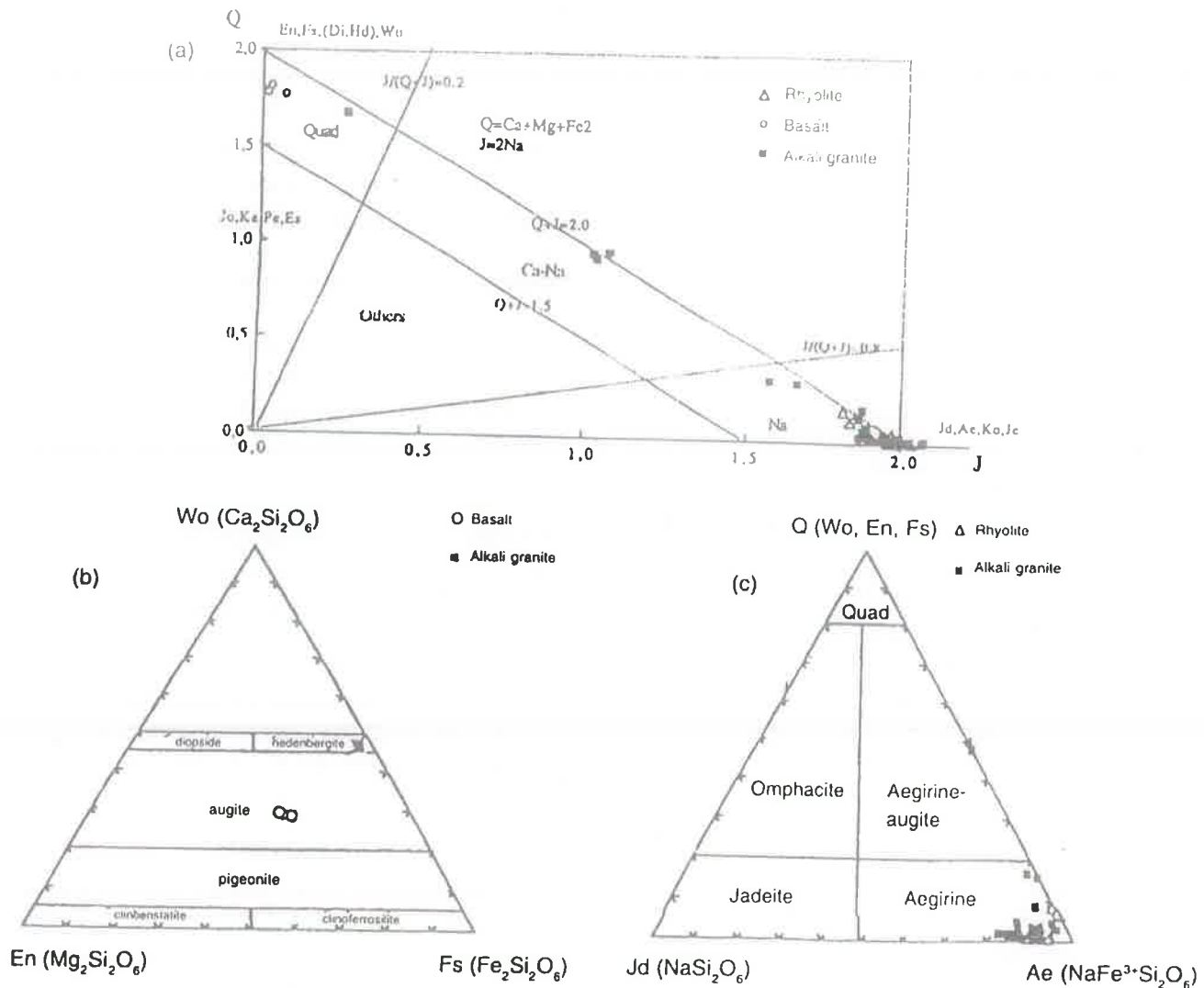


Fig. 16. (a) Q-J diagram for the pyroxenes, on which the positions of the 13 accepted end-members are indicated. (b) Composition range of the Ca-Mg-Fe clinopyroxenes. (c) Ca-Mg-Fe and Na pyroxenes. Quad represents the Ca-Mg-Fe pyroxene area.

oxidation states, where as riebeckite crystallized at high oxidation states at lower temperatures during subsolidus stages. Bulk composition of magma appears to control the presence of amphibole/pyroxene; alkali amphibole/aegirine bearing granites are peralkaline. The lime-soda ratio of the magma may determine whether calcic or sodic amphibole/pyroxene crystallizes. The final temperature of consolidation of the magma is estimated to be between 700°C for an oxygen fugacity of  $10^{-16}$  to  $10^{-20}$  bars. The observed chemical trends of the alkali amphiboles and pyroxenes of the Siwana granites and the associated acid volcanics indicate that

they are formed from a highly evolved peralkaline residual melt.

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