The biotite–phlogopite series in fenites from the Loe Shilman carbonatite complex, NW Pakistan

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Abstract

The Loe Shilman carbonatite sheet complex comprises an extensive amphibole sovite which is intruded by minor biotite sovite and amphibole ankeritic carbonatite. The carbonatites have fenitized the country rocks to form a metasomatic zone *c.* 100 m wide of alternating mafic and felsic mica-bearing banded fenites which grade into slates and phyllites. Phlogopite-rich micas occur nearest to the carbonatite contact. The biotites occur in K-feldspar + albite ± Na-amphibole ± aegirine and ± phengite fenites produced by the intrusion of the early amphibole sovite. Aegirine buffered the iron distribution and the biotites became more magnesian. Veins cross-cutting the fenites consist of biotite and/or Ba-bearing K-feldspar, and are interpreted to result from solutions emanating from the biotite sovite. The ankeritic carbonatite is responsible for the formation of phlogopite in the fenites in a *c.* 3 m wide zone adjacent to the carbonatite, and evidently are the result of fenitizing fluids rich in Mg. Chemical equations calculated to balance the reactions interpreted to have taken place in the fenites suggest that about 10% of the Al and Si in the protolith was mobilized and moved towards the carbonatites during fenitization, and that the fenitizing solutions were strongly alkaline and oxidizing.

KEYWORDS: biotite, phlogopite, fenite, carbonatite, Loe Shilman, Pakistan.

Introduction

CARBONATITES are typically surrounded by aureoles of metasomatized country rocks. The country rocks are commonly granites and gneisses which show various stages of fenitization by the development of different metasomatic minerals, usually K and Na feldspars, and the destruction of original textures. Extensive data are available on fenitization of granitic rocks (McKie, 1966; Currie and Ferguson, 1971; Le Bas, 1977; Vartiainen, 1980; Vartiainen and Woolley, 1976; Rubie and Gunter, 1983; and Kresten and Morogan, 1986). Fenitization of basic rocks and schist has been described by Verwoerd (1966); Gittins *et al.* (1975); Cooper (1971); Robins and Tysseland (1983) and Gittins and McKie (1980). However, little is known about the fenitization of the argillaceous rocks, the fluid intruded and particularly the metasomatic formation of biotite–phlogopite solid solutions in fenites.

In most previous studies of fenites, minerals such as micas, feldspars, pyroxenes and amphiboles existed in the protolith before fenitization and the changes induced were mainly in the chemistry and structure of the individual minerals. However, at the Loe Shilman carbonatite in NW Pakistan, the trioctahedral micas grown as a result of the fenitization of the slates and phyllites are new phases.

Around the Loe Shilman carbonatites, fenitizing fluids penetrated along crystal boundaries and minor fractures through metasedimentary pelitic country rocks of low permeability and metasomatized them to varying degrees forming new minerals in a zone of banded fenites *c.* 100 m wide (Mian and Le Bas, 1986). We have previously shown that a series of Na-amphiboles between magnesio-arfvedsonite and magnesio-riebeckite occurs in the fenites with increasing distance from the carbonatite contact and concluded that the low permeability of the country rocks was responsible for the smooth variation in the amphibole composition which resulted from a broad front of Na-rich fenitic fluids penetrating the slates and phyllites.

In this paper, we discuss the regular changes in mineralogy and chemistry of trioctahedral micas across the fenite zones at Loe Shilman. They form a solid solution series between biotite and phlogopite. The chemical variation in this series correlates well with that of both the solid-solution series in Na-amphiboles and distance from the carbonatite contact.

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Geological setting

The Loe Shilman carbonatite complex lies near the Kabul River, 20 km north of the Khyber Pass and lies astride the Afghanistan-Pakistan frontier. It occurs at the western end of the Peshawar alkaline igneous province (Kempe and Jan, 1970; and Jan *et al*., 1981). The carbonatite complex is 170 m wide, at least 3 km long and strikes E-W. The carbonatites are emplaced along a northward-dipping thrust plane, the Warsak thrust, between (?)Palaeozoic metasediments and dolerites to the north and (?)Precambrian slates and phyllites to the south. The southern contact of the carbonatites with country rocks, shown in Fig. 1, is sharp and marked by numerous veins of both amphibole sovite and amphibole ankeritic carbonatite indicative of an intrusive igneous contact. The early and more extensive amphibole sovite is intruded by sheets of biotite sovite, and by an amphibole ankeritic carbonatite along the southern contact with slates and phyllites (Fig. 1). The biotite sovite has yielded a K-Ar biotite average age of 31 ± 2 Ma and the subsequent movement of the thrust has reset the argon content in some biotites which now give an age of 24 ± 2 Ma (Le Bas *et al*., in press).

The fenites south of the carbonatite complex and less than half a kilometre from the Afghanistan border are only slightly affected by movements along the thrust, whereas to the north of the complex the fenites have been completely excised except in the east where they are folded and sheared.

The banded fenites are syenitic and grade into unfenitized slates and phyllites. The fenites are composed of hard, massive, alternate dark blue and pale grey bands of varying thicknesses which are parallel to the E-W contact of the carbonatite and dip 76-85° N. The width of dark (mafic) bands in general decreases gradually from 1.5 m close to the carbonatite to 5 mm up to 60 m from the contact, beyond which no mafic bands are seen in the least and unfenitized slates and phyllites. The pale grey felsic bands become wider away from the carbonatite contact and grade into the unfenitized country rocks.

Petrography and mineralogy

The detailed petrography and mineralogy of the fenite zones has been given in a previous paper by Mian and Le Bas (1986). However a brief description of the petrography and mineralogy is presented here with more emphasis on the behaviour and occurrence of the biotite-phlogopite solid solution series. The fenites are divided into five zones (Fig. 1):

Zone 1. The biotites, in the least fenitized slaty

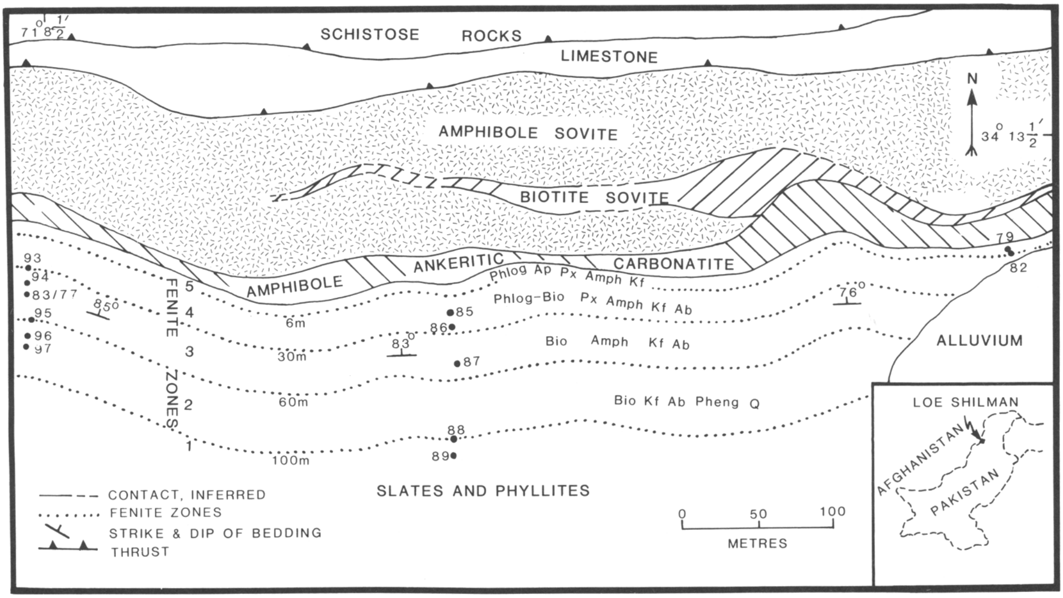

FIG. 1. Geological map of the western part of the Loe Shilman carbonatite complex and its fenitized zones (1-5). The position of analysed samples are shown. Phlog = phlogopite; Ap = apatite; Px = pyroxene; Amph = amphibole; Kf = K-feldspar; Bio = biotite; Ab = Albite; Pheng = phengite; and Q = quartz. Inset: Key map of Pakistan.

and phyllitic laminites, occur as randomly oriented flakes in small clusters along the weak rock cleavage, and under crossed polars show a decussate texture. The biotite neoblasts are seen clearly along the top of the argillaceous portion of the graded beds and are less well developed in the silty portion. The biotites have medium absorption with the pleochroic scheme α = greenish yellow and β = yellowish brown. They appear to have grown at the expense of argillaceous material and phengite. Their first appearance is taken to be the result of the thermal effect of fenitizing fluids emanating from the amphibole sovite.

Zone 2. The biotites in this zone have medium to strong absorption, with the same pleochroic scheme as in zone 1. They are slightly more elongated than in zone 1, are mostly parallel to the bedding and equally distributed between different beds. In this zone, biotite is fine-grained but also occurs in small glomeroblastic lenses, and shows parallel growth. The lenses do not disturb any alignment in the rest of the minerals.

Biotites are also present in later cross-cutting veins along with fresh K-feldspar (containing $> 1\%$ BaO) and in some cases calcite. The mineralogy of these veins changes along their length. They are rich in K-feldspar where they cut the silty beds, and rich in biotite where they cross argillaceous beds (Fig. 2). The mineralogical changes along the length of the veins thus appears to depend mainly on the difference in composition of the original host beds traversed by the fenitizing fluids. The veins were formed during later K-metasomatism related to the biotite sovite, but the biotite in both veins and host rock have the same optical properties and chemical composition. Similar veins occur in zones 3 and 4, but in zone 4 the biotites are phlogopitic.

Zone 3. This zone is marked by the appearance of magnesio-riebeckite and the absence of phengite and quartz. The biotites are beginning to show the typical platy crystal shape in contrast to zones 2 and 1, and again the flakes lie parallel to the bedding. The pleochroic scheme of the biotites in bands and veins is α = golden yellow brown and β = reddish brown.

Zone 4. This zone is characterized by the incoming of aegirine. Fine-grained phlogopitic biotite occurs both in the matrix and as glomeroblastic blebs. These glomeroblasts do not disturb the alignment of other minerals, in contrast to the porphyroblasts of aegirine. The phlogopitic biotites have strong absorption with α = golden yellow and β = golden brown.

Zone 5. This 6 m thick zone is characterized by the presence of a higher proportion of Na-amphibole and aegirine to feldspar, plus some apatite and phlogopite. The phlogopites are coarse-grained relative to the previous zones and present in both matrix and veins, and have strong absorption with α = golden yellow and β = golden brown.

Composition of biotite-phlogopite

The trioctahedral micas from the Loe Shilman banded fenites form a solid-solution series between

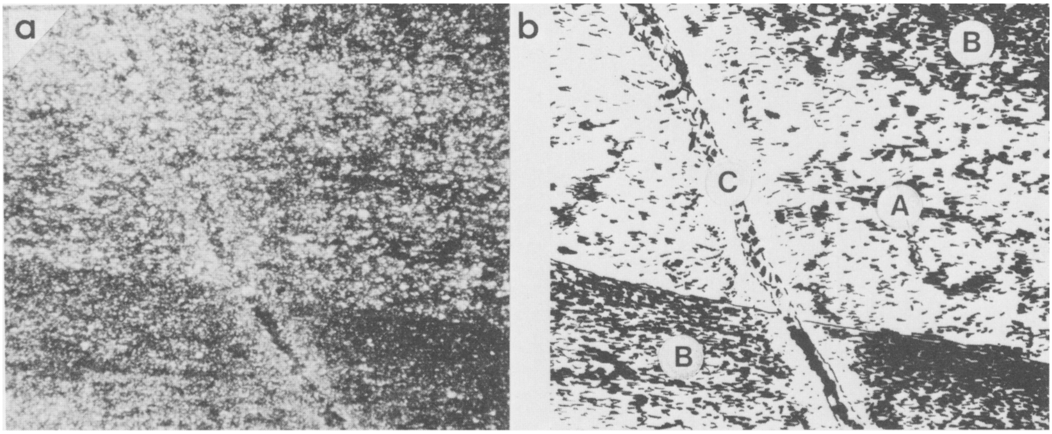

FIG. 2. Biotite–K-feldspar vein traversing zone 2 fenites showing graded bedding with paler coloured silty material (A) passing up into darker argillaceous material (B). The vein (C) is biotite-rich where it traverses the argillaceous layer and K-feldspar-rich in the silty portion of the bed. On each side of the vein the fenite is enriched in feldspar but, while the feldspar in the vein is all potassic and Ba-rich ($> 1\%$ BaO), leucocratic zones on each side contain both K-feldspar (Ba-poor) and albite as elsewhere in the fenite. (*a*) Photomicrograph with field of view 4 mm across; (*b*) sketch of same.

Table 1. Chemical analyses of Micas from fenites at Loe Shilman carbonatite-complex (Localities shown on Fig. 1)

	Zone 5 Phlogopite		**Zone 4** Phlogopitic biotite				**Zone 3** Low-Al biotite					**Zone 2** High-Al biotite			**Zone 1** High-Al biotite		Phengite
Sample No.	79B	82B	85B	86B	93B	93V	94B	83/77B	83/77V	87B	95B	96B	97B	97V	88B	89B	
SiO_2	39.74	38.68	38.29	37.56	38.22	38.87	38.01	38.06	37.66	37.38	36.01	35.96	35.53	35.75	35.65	35.17	46.31
Al_2O_3	10.88	11.17	10.85	10.72	10.99	11.16	10.26	10.67	10.40	10.65	10.04	14.17	14.69	15.71	15.35	15.27	30.69
TiO_2	1.99	2.21	2.91	3.29	2.75	3.16	3.14	2.42	2.33	3.28	3.46	2.59	2.55	2.77	2.71	2.39	0.77
*FeO	12.10	12.24	18.27	19.13	16.88	17.50	22.28	21.02	20.69	22.55	23.07	21.12	19.58	20.60	20.73	20.92	2.53
MnO	0.16	0.34	0.16	0.44	0.12	0.21	0.21	0.28	0.20	0.22	0.00	0.49	0.45	0.32	0.37	0.47	0.04
MgO	17.90	18.15	13.99	12.37	14.58	14.84	11.56	11.76	11.93	10.46	11.30	9.85	8.41	8.86	9.74	10.66	1.66
CaO	0.80	0.69	0.48	0.35	0.15	0.15	0.22	0.19	0.11	0.28	0.31	0.01	0.29	0.05	0.06	0.65	0.10
Na_2O	0.13	0.74	0.40	0.43	0.14	0.07	0.48	0.00	0.10	0.44	0.51	0.38	0.51	0.68	0.50	0.21	0.15
K_2O	7.60	7.68	6.50	7.12	9.58	9.09	9.34	9.16	9.18	8.06	6.53	9.42	9.88	9.34	7.53	6.23	11.37
F	0.80	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	90.21	91.90	91.98	91.41	93.41	95.05	95.50	93.56	92.60	93.22	91.23	93.99	91.89	94.08	92.64	91.95	93.62
							No. of ions on the basis of 22 oxygens										
Si	6.055	5.895	5.954	5.938	5.906	5.889	5.906	5.980	5.980	5.915	5.821	5.650	5.695	5.585	5.601	5.543	6.347
Al^{IV}	1.945	2.007	1.989	1.998	2.002	1.993	1.880	1.976	1.947	1.987	1.913	2.350	2.305	2.415	2.399	2.457	1.653
Al^{VI}	0.009	-	-	-	-	-	-	-	-	-	-	0.275	0.471	0.477	0.444	0.38	3.306
Ti	0.218	0.253	0.340	0.391	0.319	0.36	0.367	0.286	0.278	0.390	0.421	0.306	0.307	0.325	0.320	0.283	0.079
Fe	1.542	1.560	2.376	2.529	2.181	2.218	2.895	2.763	2.748	2.984	3.119	2.775	2.624	2.692	2.723	2.758	0.290
Mn	0.021	0.044	0.024	0.059	0.016	0.027	0.028	0.037	0.027	0.029	0.000	0.065	0.061	0.042	0.049	0.063	0.005
Mg	4.065	4.122	3.242	2.914	3.358	3.351	2.677	2.754	2.823	2.467	2.723	2.307	2.009	2.064	2.280	2.504	0.339
Ca	0.131	0.133	0.080	0.059	0.025	0.024	0.036	0.032	0.019	0.048	0.053	0.002	0.050	0.009	0.010	0.110	0.014
Na	0.038	0.218	0.121	0.131	0.043	0.024	0.144	0.000	0.031	0.135	0.159	0.115	0.158	0.205	0.152	0.064	0.039
K	1.477	1.493	1.291	1.436	1.889	1.757	1.852	1.835	1.861	1.628	1.346	1.888	2.020	1.861	1.509	1.252	1.989
Mg ratio	.72	.72	.57	.53	.60	.60	.48	.50	.50	.45	.47	.45	.43	.43	.45	.47	
Distance	0.6m	3m	15m	25m	30m	30m	40m	45m	45m	50m	60m	75m	80m	80m	100m	110m	75-110m

*Total iron as FeO. B - analyses from bed. V - analyses from vein. n.d. - not determined.

biotite and phlogopite. Energy-dispersive electron microprobe analyses of the micas were carried out on two or three crystals per sample in the banded fenites and at least one from the cross-cutting veins. The analyses of micas from the bands and cross-cutting veins in any one sample are indistinguishable. Table 1 gives one representative analysis of mica from each sample. The cationic data are calculated on the basis of 22 oxygens, assuming total iron as FeO.

Biotite occurs in the outer zones 1, 2 and 3, while phlogopitic biotite is present in zone 4 and more Mg-rich phlogopites occur in zone 5 as shown in Fig. 3. Biotite in the outer zones 1 and 2 occurs in association with phengite and is more aluminous (Al_2O_3 = 14–15 wt.%) than that in zone 3 where phengite is absent (Al_2O_3 = 10–11 wt.%), and this is independent of whether the biotite occurs in the beds or in the veins. Al_2O_3 remains roughly constant (at 10–11 wt.%) in the rest of the biotite–phlogopite series of zones 4 and 5 as shown in Fig. 4A. Whilst Al is distributed into these two distinct populations, Si shows a uniform increase from the outer to inner zones (Fig. 4B), and there is an apparent deficiency of cations in the tetrahedral site particularly in the case of biotite SM95 (Table 1) where $Si + Al^{VI} = 7.734$. Since the octahedral site in this biotite is overfilled by 0.263, it would appear that either Fe or Ti, probably Fe^{3+}, fills the remaining tetrahedral site (Guidotti, 1984, p. 432).

Nockolds (1947) distinguished three fields for biotites in igneous rocks on the basis of Al_2O_3, and he correlated high Al in biotite with different mineral assemblages. According to him, biotites in igneous rocks which are associated with muscovite have higher Al_2O_3 content than those biotites which are unaccompanied by any other mafic mineral or accompanied by hornblende, pyroxene, and/or olivine. He concluded that the amount of Al_2O_3 with respect to MgO and total iron as FeO depends on the nature of the other mafic minerals associated with biotites and does not depend on the Mg/Fe ratio. Fig. 5 is a plot of $MgO : FeO^T : Al_2O_3$ in which Nockolds's fields I, II and III are given and

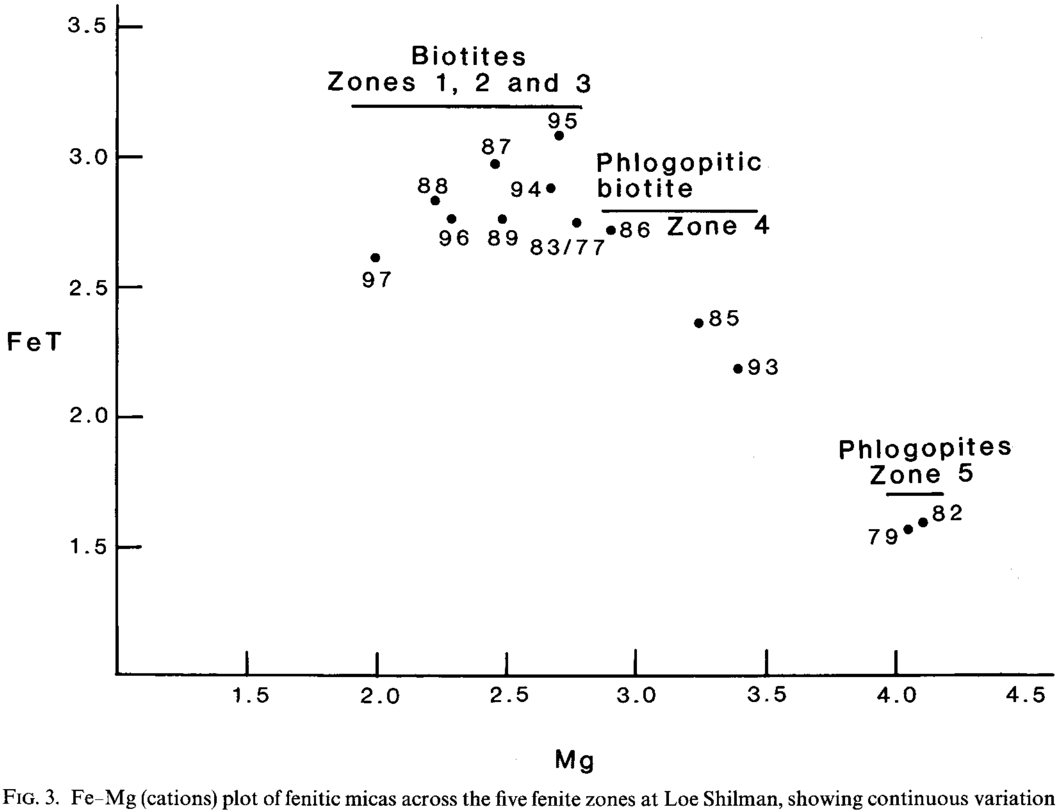

Fig. 3. Fe–Mg (cations) plot of fenitic micas across the five fenite zones at Loe Shilman, showing continuous variation from biotite in the lowest grade zones to phlogopite in the highest grade zones. Numbers indicate analyses presented in Table 1.

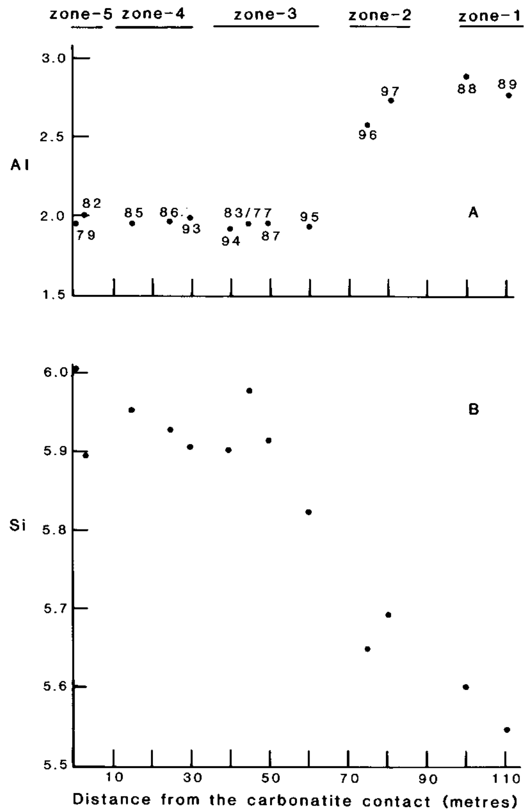

FIG. 4. (A) Variation in total Al in the micas against distance from the carbonatite contact showing the more aluminous biotites coexisting with phengite in zones 1 and 2, and the low-Al micas in zones 3, 4 and 5. (B) Variation in Si against distance showing the continuous increase in Si content in the micas with increasing fenitization.

compared with Loe Shilman data, other metasomatic biotites and phlogopites, and biotites from igneous rocks. The micas from Loe Shilman in zones 3, 4 and 5 and metasomatic biotite from Sokli fenites (Vartiainen and Woolley, 1976) are separated from metamorphic biotites. Only micas in zones 1 and 2 are in the field of igneous biotites and plot close to the metamorphic field. These high-Al biotites in zones 1 and 2 are accompanied by phengite and plot in Nockolds's field II.

Guidotti (1984) distinguished biotites present in muscovite-bearing pelitic schists from those associated with other mafic minerals by higher $\mathrm{Al^{VI}}$ contents (between 0.7 and 1), and $\mathrm{Mg/(Mg+Fe^T)}$ ratios between 0.3 and just under 1. However, at Loe Shilman the micas in zones 5, 4 and 3 have no $\mathrm{Al^{VI}}$ and the $\mathrm{Mg/(Mg+Fe^T)}$ ratio ranges from 0.72 to 0.5 while in zones 2 and 1, $\mathrm{Al^{VI}}$ is between 0.275 and 0.471 and the $\mathrm{Mg/(Mg+Fe^T)}$ ratio between 0.42 and 0.47 (Table 1). Fig. 6 is a plot of $\mathrm{Mg/(Mg+Fe^T)}$ *vs.* $\mathrm{Al^{VI}}$ on which the Loe Shilman data are plotted and compared with the data given by Guidotti (1984). The biotite and phlogopite in zones 5, 4 and 3 are deficient in the octahedral site and even in the tetrahedral site, while high-Al biotite in zones 2 and 1 plot close to biotites occurring in calc-silicates and amphibolites which are sometimes associated with muscovite. Cerny and Burt (1984) have also discussed the high-Al content in phlogopite and biotite associated with muscovite in pegmatites. Speer (1984) has reported that the composition of biotites in granitoids from the Aregos region, Portugal, varies with the $\mathrm{Al^{IV}}$ of coexisting minerals which generally increases in the sequence hornblende ($\mathrm{Al^{IV}} = 2.3$–2.5), muscovite ($\mathrm{Al^{IV}} = 2.6$–2.75), and muscovite plus aluminium silicates ($\mathrm{Al^{IV}} = 2.8$). However at Loe Shilman, the $\mathrm{Al^{IV}}$ in biotites in zones 1 and 2 varies between 2.3 and 2.46 and is less than 2 in the inner zones (Table 2 and Fig. 6). These features of $\mathrm{Al^{VI}}$ and $\mathrm{Al^{IV}}$ occupancies indicate that the biotites in Loe Shilman fenites are neither igneous nor normal metamorphic minerals but are probably metasomatic in origin.

The high-Al content in the outer zones is either because of the presence of less feldspar or the association with phengite or both. However, biotite has been reported from low-grade metasediments near Landikotal some 15 miles south of Loe Shilman carbonatite complex by Shah *et al.* (1980). Therefore the possibility of a metamorphic origin for these high-Al biotite cannot be ruled out as some of them are close to the metamorphic field (Fig. 5), although the texture and similar chemistry with those in veins which are associated with Ba-bearing K-feldspars argue against this origin.

$\mathrm{FeO^T}$ remains roughly constant (19–22 wt.%) in the biotites but drops to 12% in the phlogopite in zone 5. This sudden decrease is correlated with the decrease of $\mathrm{FeO^T}$ in Na-amphibole and with distance from the contact as seen in Fig. 7A where tie-lines are drawn between the coexisting mica and amphibole. In zones 5 and 4 these minerals coexist with almost pure acmite. An upward inflection of $\mathrm{FeO^T}$ and oxidation ratio in Na-amphiboles in the magnesio-riebeckite part of the series in zone 3 (figs. 2 and 4 in Mian and Le Bas, 1986) was interpreted as caused by the absence of acmite in zone 3 and its presence in zones 5 and 4. This interpretation is in accord with the biotite-phlogopite series in which bioite is present in zone 3, and is borne out by reaction 3 in Table 3.

In Fig. 7B, tielines are drawn between the coexisting mica and amphibole. Both are well correlated with the distance from the carbonatite

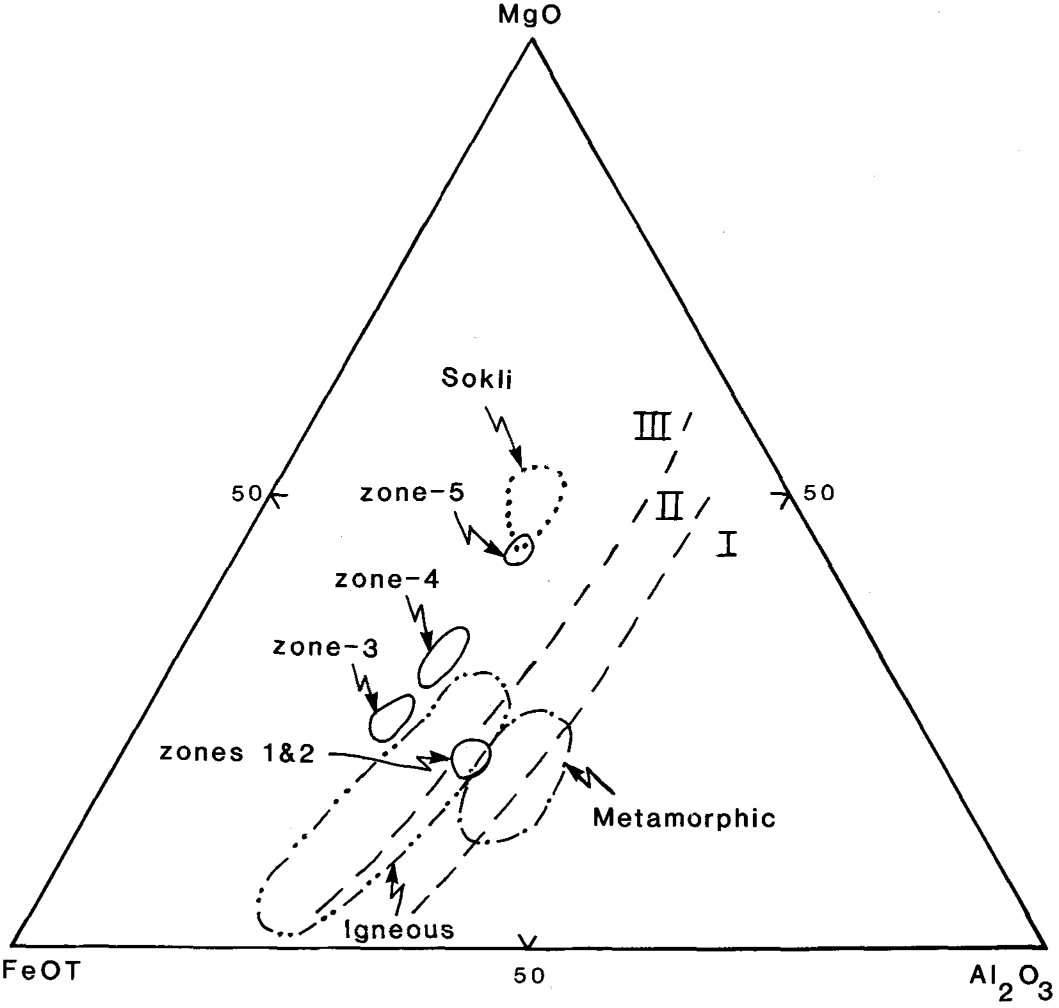

Fig. 5. MgO-Al_2O_3-FeO^T plot showing the smooth Fe–Mg range of the fenitic micas across the zones 3, 4 and 5 at Loe Shilman, and the higher Al content of those in zones 1 and 2 and compared with the data from the phlogopites of the Sokli carbonatite complex in Finland (Vartiainen and Woolley, 1976). Metamorphic and igneous data are taken from Deer *et al.* (1963). Field I = biotites associated with muscovite, II = biotite unaccompanied by other mafic minerals and III = biotite associated with amphibole, pyroxene or olivine (after Nockolds, 1947).

contact. Coexisting acmites have a MgO content below the detection limit in zone 4, while in zone 5 MgO increases to approximately 1 wt.%. Therefore the Mg ratio in acmite increases towards the carbonatite contact and also correlates with the series of micas and Na-amphiboles.

Discussion

Whilst the biotite and phlogopite developed in acid, basic igneous and regional metamorphic rocks have compositions related to their host rocks (Speer, 1984, fig. 30; Guidotti, 1984, p. 438), those developed during fentitization depend not only on host rock composition but also on the composition of the fenitizing fluids. The main compositional distinction is that most fenitic biotites and phlogopites in rocks without phengite have $Si+Al^{IV} < 8$, and $Al^T < 2$ (on the basis of 22 oxygens per unit cell) as shown in Figs. 5 and 6.

The main features controlling the composition of the biotite or phlogopite formed during fenitization

Table 2. Average modal composition of the fenite zones at Loe Shilman.

	Zone 5	Zone 4	Zone 3	Zone 2	Zone 1
Amphibole	20	2-3	8	-	-
Pyroxene	25	7	-	-	-
Albite	21	42	48	49	15
K-feldspar	21	31	30	14	4
Phlogopite/Biotite	6	12	10	15	15
Quartz	-	-	2	11	32
Phengite	-	-	-	11	33
Others = il+mt+cal+ap	7	6	1	1	1
Distance from the carbonatite contact	0-6m	15-30m	40-60m	75-80m	100-110m

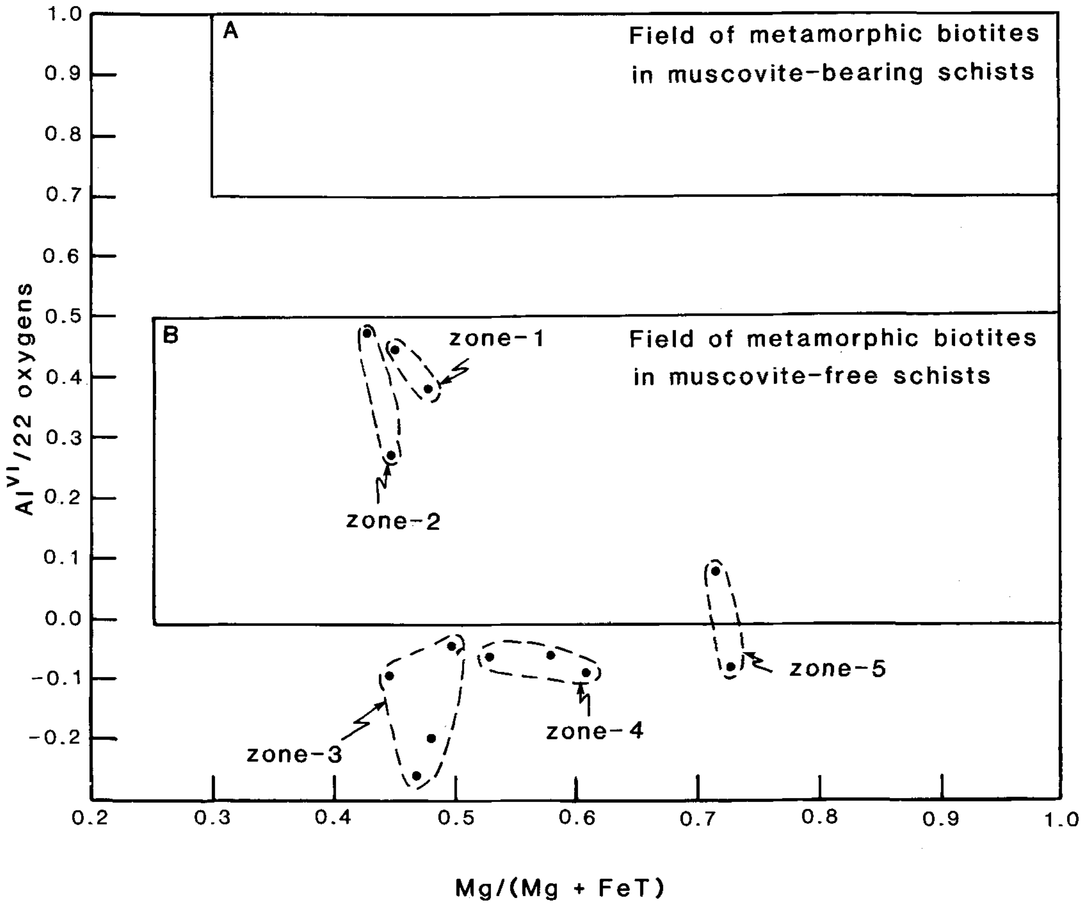

FIG. 6. Mg/(Mg + Fe^T) *vs.* Al^{VI} plots of the Loe Shilman fenitic micas showing that the Al^{VI} content distinguishes the biotites in zones 1 and 2 which coexist with phengite from normal metamorphic biotite in muscovite-bearing schists (field A), and instead plot with metamorphic biotite from muscovite-free pelitic schists (field B). The negative values for Al^{VI} are a measure of the deficiency of Si + Al in filling completely the tetrahedral sites, and this typifies fenitic biotite and phlogopite (the plot is after Guidotti, 1984).

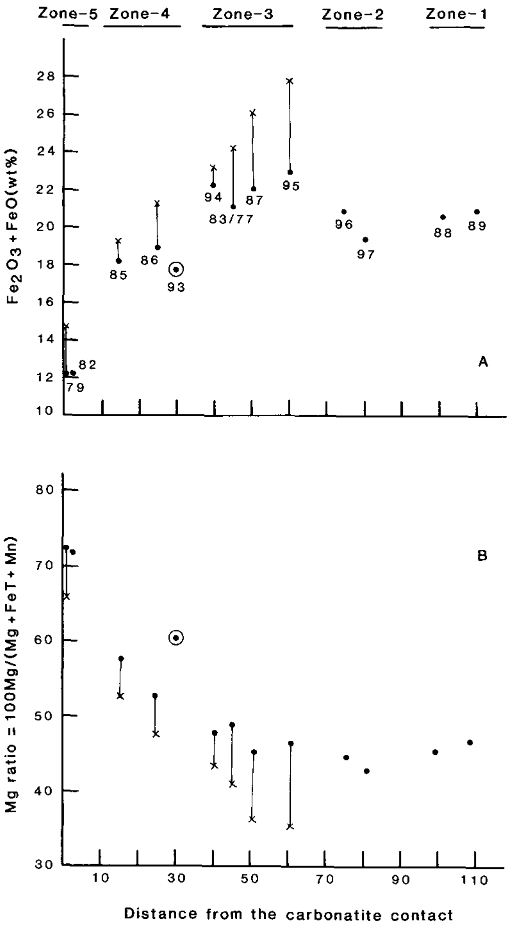

FIG. 7. This plot shows the tie-lines joining coexisting micas (dots) and Na-amphibole (crosses) in zones 1–5 in the Loe Shilman fenites. The circled dot is the anomalous sample SM93 discussed in the text. The micas present in zones more than 30 m from the igneous contact show little variation, but those near the contact coexist with aegirine and decrease sharply in their total iron content (A) and increase sharply in their Mg ratio (B). Amphibole data are taken from Mian and Le Bas (1986).

are: (1) the chemical composition of the host rock; (2) the chemical composition of the fenitizing fluid; and (3) the *PT* conditions prevailing during fenitization. To examine these conditions, chemical reactions between consecutive zones have been calculated using (*a*) the modal proportion of the individual minerals present in each zone and (*b*) the compositions determined by microprobe analysis of the individual minerals observed in each zone.

The modal data given in Table 2 are the means of the modal compositions calculated, using the least-squares mixing programme of Bryan *et al.* (1969), from the bulk chemistry of the rocks rather than from point counting because of the very fine grain size of the fenitized sediments. The individual modal compositions were given in full in Table 1 by Mian and Le Bas (1986). The chemical composition of the minerals used in the reactions shown in Table 3 are the averages of probe analyses for the individual mineral in each zone. The mica analyses used were obtained by averaging the data given in Table 1. The amphibole compositions are taken from Mian and Le Bas (1986), and the pyroxene and feldspar compositions are taken from as yet unpublished microprobe data. The pyroxene in the fenites is almost pure acmite ($Ac_{>85}$) and likewise the feldspars are almost pure end-member compositions ($Ab_{>99}$ and $Or_{>94}$).

The reactions given in Table 3 are calculated on the basis of balancing the compositions of the minerals between zones in terms of the modal proportions in which they actually occur in the zones. To do this, it was necessary to standardize each mineral to an arbitrary unit volume. Taking the unit volume as *c.* 200 Å^3, the formula unit for mica had to be calculated on 11 oxygens, for amphibole 11.5 oxygens, for feldspar 8 oxygens, for pyroxene 12 oxygens and for quartz 16 oxygens. It is appreciated that these figures do not produce exactly the same unit volume, but they have the merit of keeping the numbers employed fairly rational and recognizable as the minerals they represent. Likewise, the number of formula units in the reactions are given as whole numbers since the equations do not warrant further precision, although the calculations were made to two decimal places. The reactions were also calculated on the basis of introducing only Na^+ *ions* wherever necessary to balance the equations. Justification for doing this comes from a study of the whole-rock geochemistry of the Loe Shilman fenites (in prep.). Trace minerals such as iron oxides and calcite were omitted from the calculation.

Reaction 1 balances the change in mineralogical assemblages from zone 1 to zone 2 in the volumetric proportions of the mineral present as shown in Table 2. The biotite has high Al since it is in equilibrium with phengite. The K-feldspar and albite may be the product of fenitization in this outermost zone or they may be the product of authigenic growth pertaining to the original sediment, but in view of the proximity of these rocks to carbonatite and their similarity in composition to the feldspars next to and undoubtedly formed by the carbonatite, they are interpreted to be fenites. Unfortunately samples were not taken of the sediments further from the carbonatite contact

Table 3. Balanced reactions between mineralogical assemblages within pairs of fenitic zones at Loe Shilman

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Zone 1 **REACTION 1**

$$25[K(Mg,Fe)_{.35}Al_{2.5}Si_{3.15}O_{11}(OH)_2] + 16[K_{.75}(Mg,Fe)_{2.56}Al_{1.4}Si_{2.8}O_{11}(OH)_2] + 6[KAlSi_3O_8] + 17[NaAlSi_3O_8] + 20[Si_8O_{16}] + 24[Na]^+ + 6H^+$$

Phengite High-Al biotite K-feldspar Albite Quartz

$$\Downarrow$$

Zone 2

$$11[K(Mg,Fe)_{.35}Al_{2.5}Si_{3.15}O_{11}(OH)_2] + 18[K_{.95}(Mg,Fe)_{2.56}Al_{1.4}Si_{2.8}O_{11}(OH)_2] + 15[KAlSi_3O_8] + 41[NaAlSi_3O_8] + 13[Si_8O_{16}] + 15H_2O$$

Phengite High-Al biotite K-feldspar Albite Quartz

Zone 2 **REACTION 2**

$$11[K(Mg,Fe)_{.35}Al_{2.5}Si_{3.15}O_{11}(OH)_2] + 18[K_{.95}(Mg,Fe)_{2.56}Al_{1.4}Si_{2.8}O_{11}(OH)_2] + 15[KAlSi_3O_8] + 41[NaAlSi_3O_8] + 13[Si_8O_{16}] + 31[Na]^+$$

Phengite High-Al biotite K-feldspar Albite Quartz

$$\Downarrow$$

Zone 3

$$8[K_{.1}Na_{1.03}(Mg,Fe)_{2.45}Al_{.1}Si_{3.94}O_{11.5}(OH)] + 11[K_{.85}(Mg,Fe)_{2.8}Al_{.97}Si_{2.96}O_{11}(OH)_2] + 33[KAlSi_3O_8] + 64[NaAlSi_3O_8] + 10[H_2O] + 8H^+$$

Amphibole (Mg-riebeckite) Low-Al biotite K-feldspar Albite

Zone 3 **REACTION 3**

$$8[K_{.1}Na_{1.03}Mg_{.95}Fe_{1.5}Al_{.1}Si_{3.94}O_{11.5}(OH)] + 11[K_{.85}Mg_{1.35}Fe_{1.45}Al_{.97}Si_{2.96}O_{11}(OH)_2] + 33[KAlSi_3O_8] + 64[NaAlSi_3O_8] + 6[Na]^+$$

Amphibole (Mg-riebeckite) Low-Al biotite K-feldspar Albite

$$\Downarrow$$

Zone 4

$$3[K_{.17}Na_{1.24}Mg_{1.22}Fe_{1.46}Al_{.07}Si_{3.92}O_{11.5}(OH)] + 12[K_{.95}Mg_{1.61}Fe_{1.22}Al_{.995}Si_{2.98}O_{11}(OH)_2] + 5[Na_{1.92}Fe_{1.8}Al_{.12}Si_4O_{12}] + 32[KAlSi_3O_8]$$

Amphibole (Mg-arfvedsonite) phlogopitic biotite Aegirine K-feldspar

$$+ 65[NaAlSi_3O_8] + 4H^+$$

Albite

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because they looked no different from those in zone 1.

To obtain zone 2 from zone 1 requires the addition of Na as shown in reaction 1. The biotite in zone 2 remains Al-rich since some phengite persists in that zone but more feldspar is formed: K-feldspar from the breakdown of phengite and quartz, and much albite by the introduction of metasomatic Na-bearing fluids.

Reaction 2 shows the mineralogical changes from zone 2 to zone 3 in which the Al content of the biotite is reduced at the same time as phengite is eliminated. Amphibole (magnesio-riebeckite) is formed from the Mg and Fe released by the partial breakdown of the biotite together with that from the complete breakdown of phengite. Feldspar increases in proportion with further K-feldspar developing by the breakdown of the micas, and Na is required to satisfy the incoming amphibole and an increase in albite, although such an increase is not apparent from the modal calculation. The quartz in zone 2 is largely consumed by the formation of amphibole and feldspar.

In reaction 3, the biotite becomes phlogopitic in zone 4 without change in the Al content. Aegirine in which all Fe is Fe^{3+} now appears in the reaction product partly due to the increase in temperature but mainly due to the strongly oxidizing conditions. The magnesio-riebeckite of zone 3 grades with increasing Mg/Fe ratio into magnesio-arfvedsonite of zone 4 as a result of the buffering by aegirine as seen in the reaction 3. Further Na has to be introduced to balance the equation and for the formation of more amphibole and pyroxene. In this reaction 0.03 Si_8O_{16} and 0.06 H_2O, not written in the equation, is needed in zone 3 to maintain balance. The more Mg-rich mica (phlogopite), present in the inner zone 5 adjacent to the ankeritic carbonatite, is believed to be the result of Mg-fenitization by the ankeritic carbonatite, but it could also be related to the buffering effect of the presence of aegirine.

The anomalous fenite SM93 requires further comment. This rock has 10 wt.% K_2O (whereas in the other fenites K_2O normally ranges between 4.9 and 5.9 wt.%) and it contains much aegirine, mainly in veins now showing minor folding but also in the rock. There is also an unusually large amount of K-feldspar (58%) and albite (23%) but no amphibole, and this is unusual for zone 4. The biotite is more magnesian than in the rest of zone 4 (Fig. 7) in both veins cutting the aegirine as well as in the matrix (Table 1). Why this is so is not clear. It is unlikely to be the product of variation in the protolith which appears to have been constant, and the following sequence of events for sample SM93 is envisaged. The first and more widespread and pervasive fenitization by the early amphibole sovite produced the normal Na-amphibole-aegirine (also in veins)-Na-feldspar-K-feldspar-phlogopitic biotite fenite. A second fenitization, probably emanating along small cracks, fissures and minor shear planes from the biotite sovite, produced a potassic fenitization as is known elsewhere, for instance in East Africa (Le Bas, 1977). As the result of the K-fenitization, the early Na-amphibole was destabilized and reacted with the potassic fluids to form more magnesian biotite plus magnetite. At the same time the aegirine in the veins and matrix appears to have recrystallised.

Interpretation

The biotites in zones 1, 2 and 3 were formed at the expense of argillaceous material and phengite by reaction with Na-bearing fluids which emanated from the amphibole sovite. The biotite present in cross-cutting veins which coexists with K-feldspar (BaO = > 1 wt.%), and sometimes calcite, is interpreted as the result of K-metasomatism by the biotite sovite. These K-feldspars with high Ba can be easily distinguished from K-feldspar present in the bands which have low Ba contents. The biotites in zones 1 and 2, both in beds and veins, have similar chemistries with high Al, and as the biotites in veins are undoubtedly metasomatic, the biotites in beds are also considered to be metasomatic.

The biotite in zone 4 became phlogopitic as a result of the preferential partitioning of Fe into aegirine as shown by reaction 3. The more Mg-rich mica (phlogopite) in zone 5 is interpreted as a result of Mg-metasomatism simply on the basis of the sharp increase in Mg in the whole-rock chemistry. However, buffering cannot be ruled out as the aegirine increases in proportion in the innermost zone 5 (Table 2).

In balancing the reactions given in Table 3, the assumption was made that only Na needed to be added. Whilst this enabled the balancing and the production of appropriate modal proportions in reaction 1, the products of reactions 2 and 3 depart from the known modal proportions of the minerals in zones 3 and 4, particularly those for albite contents. In reaction 2, it takes over 30 Na^+ ions to balance the equation, and it produces 65 moles of albite whereas 50 or less would be a better approximation of the modal content (Table 2). Likewise in reaction 3, a further 5 Na^+ are required to balance the equation with the final result of having over 20 moles of albite in excess (65 are shown in reaction 3 but only 42 shown for the mode in Table 2).

Since these reactions imply that too much albite has been created, the remedy for having too much Na introduced is to remove excess Al and Si. It is suggested that over 15 Na^+ ions should be introduced in reaction 2, and over 15 $AlSi_3O_8$ moles removed. In reaction 3, no Na^+ should be added, allowing further $AlSi_3O_8$ to be set free. The figure for Na^+ added is, of course, additional to the *c.* 24 Na^+ ions added in reaction 1, and which remains present throughout in reactions 2 and 3. It is therefore interpreted that, in zones 3 and 4, both Al and Si are lost presumably by fluid transfer. Calculation shows that the amount of Al and Si removed from zone 2 to make zone 3 is about 10%. A more precise figure cannot be given owing to the assumptions made in constructing the reaction in Table 3. The Al and Si in zones 1 and 2 show no increase but remain at values normal for pelitic rocks. Therefore, either the mobilized Al and Si remained in solution and passed from the inner zones out through zones 2 and 1 to be dispersed beyond them, or the mobilized Al and Si moved towards the carbonatite. The latter interpretation is preferred.

Reactions 1 and 2 release water, and the Eh and pH can be estimated. In reaction 1, the requirement of H^+ ions in zone 1 indicates that the reaction to produce the zone 2 assemblage is reducing, as is normal in very low-grade metamorphic reactions in pelitic rocks. But in reactions 2 and 3, the reactions are oxidizing. It was deduced above that some Al and Si were mobilized in zones 3 and 4 considering the known solubilities of Al and Si in aqueous solutions at low temperatures (Stumm and Morgan, 1970), it is suggested that the fenitizing solutions which enabled the Al and Si to move must have been at pH about 10 to 11. Such highly alkaline and oxidizing solutions are considered appropriate for fenitic solutions from the Loe Shilman carbonatites.

Conclusions

The trioctahedral micas in the fenitized slates and phyllites which occur at Loe Shilman in NW Pakistan form a series between biotite and phlogopite not previously reported from these or any other fenites. The regular chemical variation in the micas correlates well with that in the amphiboles (from magnesio-riebeckite to magnesio-arfvedsonite). The biotite–phlogopite series also is correlated with distance from the contact. The biotite and phlogopite are less aluminous (10–11 wt.%) than biotites and phlogopites encountered in ordinary metamorphic rocks, except where phengite or sericite still coexist with the newly formed biotite, in which case the biotite is more aluminous (Al_2O_3 = 14–15%). The biotites in zone 4 became Mg-enriched by the presence of aegirine which buffers Fe in biotite. The more Mg-rich micas (phlogopite in zone 5) are interpreted as the result of Mg-metasomatism by the adjacent ankeritic carbonatite.

Balancing the chemical equations which represent the reactions from zones 1 to 2, 2 to 3 and 3 to 4 incidate at Loe Shilman that Na is added in all the zones, but that in zones 3 and 4 Al and Si are lost. The fluids transporting the Al and Si are interpreted to have been strongly oxidizing and alkaline, with the Al and Si moving back towards the carbonatites.

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