Sodic amphiboles in fenites from the Loe Shilman carbonatite complex, NW Pakistan

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ABSTRACT. The carbonatites at Loe Shilman, near Khyber in NW Pakistan, fenitize their country rocks to form a metasomatic zone c.100 m wide of alternate dark blue (mafic) and pale grey (felsic) banded fenites which grade into unfenitized bedded slates and phyllites. The Na-amphiboles in the banded fenites form a complete solid solution series between magnesio-arfvedsonite and magnesio-riebeckite which coexist with varying proportions of aegirine, albite, and K-feldspar, with or without phlogopite or biotite.

The amphiboles show a gradual decrease in Na_2O, K_2O, Mg ratio $[100Mg/(Mg+Fe^T+Mn)]$ and iron oxidation ratio, and an increase in total iron away from the carbonatite contact. The pleochroism correlates with the chemistry and distance from the carbonatite contact.

The Mg ratio decreases from 74 to 35 away from the carbonatite contact. The iron oxidation ratio $[100Fe^{3+}/(Fe^{3+}+Fe^{2+})]$ decreases in the magnesio-arfvedsonite for the first 30 metres from the carbonatite contact, and then increases in the magnesio-riebeckite from 40 to 60 metres from the carbonatite contact. K relative to Na decreases away from the contact in the amphibole, and the decrease in K causes an increase in vacancy in the A site. The main variation in the chemistry in this solid solution series is due to $(K,Na)_A + (Mg,Fe^{2+})_C \rightleftharpoons \square + (Fe^{3+})_C$ substitution.

KEYWORDS: amphiboles, fenites, carbonatites, Loe Shilman, Pakistan.

CARBONATITES are typically associated with anorogenic alkaline magmatism, and are usually surrounded by a fenitic aureole of metasomatized country rocks, commonly granites and gneisses.

Although many authors (McKie, 1966; Currie and Ferguson, 1971; Le Bas, 1977; Vartiainen, 1980; Viladkar, 1980; Woolley, 1982; and Rubie and Gunter, 1983) have made extensive studies of

fenitization by carbonatites, the process is still not well understood. This is partly because of the uncertainties of the nature of fenitizing fluids, but also because of the variation in mineralogical composition, texture, chemical reactivity, the state of oxidation, and particularly, permeability of the country rocks during their formation. Mehnert (1969) stated that if the reactivity of the country rocks is high and permeability is low, then a metasomatic front will result and may consist of parallel zones of varying mineraology. Normally, fenitizing fluids from carbonatites penetrate along joints and fractures, and from these pathways fenitize the country rocks to varying degrees. However, at Loe Shilman in NW Pakistan, a carbonatite intrusion has produced a wide metasomatic zone of alternately banded mafic and felsic fenites in low-grade slates and phyllites of low permeability (fig. 1).

To understand the processes of fenitization in general and behaviour of Na-amphiboles in particular, samples were collected from three traverses across the banded fenites at different intervals from the carbonatite contact. This paper presents the regular variation in mineralogy and chemistry of the sodic amphiboles across the fenite zones from Loe Shilman. They form a complete solid solution series between magnesio-arfvedsonite and magnesio-riebeckite not previously reported. The chemistry of other minerals present in these fenites together with the whole-rock geochemistry are the subject of another contribution (Mian, in prep.). The regular chemical variation in this series and the regular changes in the pleochroic scheme correlate with their distance from the carbonatite contact.
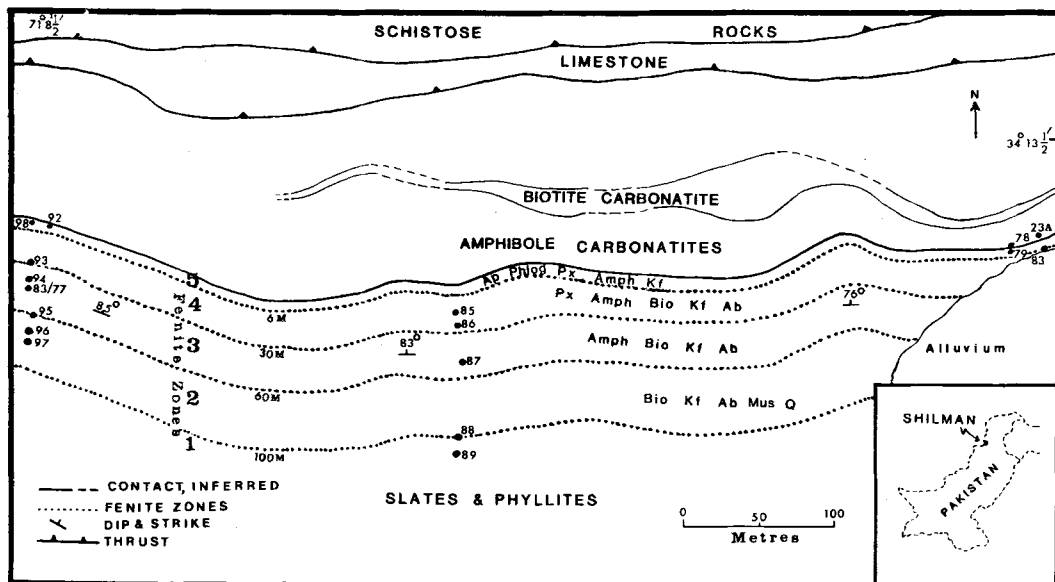
FIG. 1. Geological map of western part of the Loe Shilman Carbonatite complex and its fenitized zones (1–5). The positions of analysed samples are shown. Insert: key map of Pakistan.

Geological setting

The Loe Shilman carbonatite complex, by the Kabul River, 20 km north of Khyber Pass and 50 km NW of Peshawar, occurs in the extreme west of the NW Pakistan alkaline province (Kempe and Jan, 1970; Jan et al., 1981). The carbonatite intrusion is 170 m wide and at least 3 km long striking E.-W., and lies astride the Afghanistan–Pakistan frontier. It is 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. An early amphibole carbonatite, mainly responsible for the fenitization, is intruded by biotite carbonatite (fig. 1). The biotite carbonatite has yielded an average K–Ar biotite age of 31 ± 2 Ma (Le Bas et al., in prep.).

The fenites south of the carbonatite complex and less than half a kilometre from the Afghanistan border, are only slightly affected by subsequent movements of the thrust, whereas those in the north have been completely displaced, except in the east where they occur folded and tectonically emplaced.

The banded fenites are syenitic in bulk composition and mineralogy, and grade into unfenitized slates and phyllites. The fenites are composed of hard massive alternating dark blue and pale grey bands of varying thicknesses which are parallel to the E.-W. carbonatite contact 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 in zone 3 up to 60 m from the contact, beyond which no mafic bands are seen in the less fenitized 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

Five zones are distinguished in the banded fenites at Loe Shilman on the basis of mineral assemblages and each zone is marked by the appearance or disappearance of metasomatic minerals, or the presence of relict quartz and muscovite (fig. 1).

Both felsic and mafic minerals in the banded fenites are very fine-grained and are distributed in varying proportions from band to band, making optical determination of the modal compositions difficult, particularly of the felsic minerals. Therefore, a least squares mixing program has been employed (Bryan et al., 1969), using the mineral compositions determined by microprobe analysis and rock compositions by X-ray fluorescence analysis. The modal compositions deduced for the fenites are given in Table I. The sum of squares of residuals is less than 0.1, apart from two samples (SM92 and SM98) in the inner zone 5 where it is 0.8 and 0.3 respectively.

Zone 1. The least fenitized slates and phyllites (SM89 and SM88), some 110 and 100 m respectively from the carbonatite contact, are very fine-grained, thinly bedded and composed of light and dark grey laminites showing graded bedding and some disturbed bedding, interpreted as a dewatering structure and/or bioturbation. A weak cleavage is developed across the bedding and is marked by elongated parallel wisps of fine-grained almost isotropic material and by coarser biotite-rich strips. The major constituents of the lower silty and pale portions of the graded beds are quartz, muscovite, biotite, albite, and K-feldspar. The quartz, which forms 32 % of the sediments, occurs as detrital grains and, where recrystallized by a low-grade metamorphism, shows marginal replacement by feldspars. The upper dark and almost isotropic portion of the beds is composed of a turbid interlocking mass of small K-feldspar and albite grains (identified by microprobe) which are interpreted as having replaced argillaceous material and fine detrital quartz during fenitization. Magnetite and calcite are minor components, with traces of tourmaline. Of these minerals, the fresh albite and fresh K-feldspar are interpreted as metasomatically formed by fenitizing fluids.

Zone 2. The banded fenites in this zone (SM97 and SM96) are still very fine-grained, cleaved and show good graded bedding. They are composed of more pronounced parallel alternating dark and pale grey beds. The dark grey beds are composed of fresh albite, fresh and dusty K-feldspar, biotite, and muscovite as major constituents with minor magnetite and ilmenite, and are equivalent to argillaceous beds of zone 1. There is an increase in

K-feldspar at the expense of the muscovite, and likewise relict quartz now forms only 9 to 12 % of the rock (Table I). The frequency and thickness of the pale grey silty beds relative to the darker beds is greater than in zone 1, and they consist of more fresh albite and K-feldspar and less quartz.

The beds are cut by veins of fresh K-feldspar and biotite formed by a later K-fenitization related to the biotite carbonatite. Amphibole is not present in this zone, and this was confirmed by XRD analysis.

Zone 3. This fenite zone is marked by the incoming of Na-amphibole. The banded fenites (SM83/77, SM95, SM87, and SM94) are again very fine-grained and composed of alternating mafic and felsic (light brown) bands and have, in places, sharp rather than gradational contacts. The original bedding is still apparent, even some graded bedding is locally preserved. The felsic bands appear in the field to be equivalent to the dark grey and argillaceous bands in zone 2 and zone 1 respectively. The mafic bands, equivalent to the pale grey beds of zone 2 and silty beds of zone 1, are different. Their intensity and width increases from 0.5 mm to 8 mm on approaching the next zone 4. Muscovite and quartz are absent, apart from sample SM95 which contains 8 % relict quartz and in which Na-amphibole first appears. The felsic bands decrease from 10 mm to 0.5 mm in width towards the carbonatite contact, and are red–brown and composed of interlocking elongate small crystals of brown-stained K-feldspar, fresh colourless albite, flakes of brown pleochroic biotite and minor blue pleochroic Na-amphibole, in this order of abundance. The average grain size is 5 to 20 μm.

The mafic bands are amphibole-rich, comprising

Table I. Modal Composition of Fenites at Loe Shilman
determined by a least squares mixing programme (Bryan et al. 1969)

Sample No. SM	Zone-5				Zone-4			Zone-3			Zone-2		Zone-1	
	92	98	79	83	85	86	93	94	87	95	96	97	88	89
Amphibole	20	30	31	13	2	2	–	12	11	Trace	–	–	–	–
Aegirine	45	61	6	7	8	6	7	–	–	–	–	–	–	–
Apatite	1	1	–	–	–	–	–	–	–	–	–	–	–	–
Albite	–	–	11	50	47	49	23	49	47	48	50	47	15	14
K-feldspar	32	5	20	26	27	28	58	32	31	25	15	13	5	3
Phlogopite	–	–	15	–	–	–	–	–	–	–	–	–	–	–
Biotite	–	–	–	1	12	12	12	5	8	16	15	15	14	26
Calcite	3	1	17	2	6	2	1	1	2	2	–	–	1	1
Ilmenite	1	–	–	1	1	–	–	1	1	–	1	1	–	–
Magnetite	–	2	1	–	–	1	1	–	–	1	1	1	1	1
Quartz	–	–	–	–	–	–	–	–	–	8	9	12	32	28
Muscovite	–	–	–	–	–	–	–	–	–	–	10	12	34	28
Distance from the carbonatite contact.	0.03m	0.4m	0.6m	6m	15m	25m	30m	40m	50m	60m	75m	80m	100m	110m

All distances are with 10% error.

Sample No. SM	Zone-5		Zone-4		Zone-3		
	92,98,79	83	85	86	94	87	95
α	Bluish green (124)	Bluish green (123)	Greenish blue (121)	Greenish blue (120)	Greenish blue (118)	Blue (111)	Deep blue (109)
β	Violet (91)	Violet indigo (92)	Bluish indigo (94)	Bluish indigo (97)	Bluish indigo (98)	Bluish indigo (104)	Indigo blue (107)
γ	Greenish yellow (1)	Greenish yellow (2)	Greenish yellow (6)	Orange yellow (19)	Orange yellow (23)	Yellowish orange (24)	Yellowish orange to orange (26)

Figures in parentheses indicate the number of the standard colours according
to The Royal Horticulture Society of London (1966)

the same mineralogy and texture as the felsic bands but the minerals in order of decreasing abundance are albite, K-feldspar, Na-amphibole, and biotite. Na-amphiboles also occur in veins cutting the bands. These Na-amphiboles are coarser (up to 50 μm), subhedral and unzoned. Bordering the veins are narrow zones of albite and colourless K-feldspar growing in the host rock. These Na-amphiboles in the host rock and the Na-amphiboles in veins are interpreted as resulting from a single metasomatic episode of fenitization whereby sodic solutions not only permeated through the sediments, but also permeated along small fractures. The Na-amphiboles have strong absorption. The pleochroic scheme is: α = deep blue to greenish blue; β = indigo blue to bluish indigo, and γ = yellowish orange to orange yellow (Table II). In addition there are later 1 mm veins cutting the bands and the early Na-amphibole veins. Sometimes these veins follow the path of the early Na-amphibole veins when biotite is seen replacing the early Na-amphiboles. These later veins consist of K-feldspar, biotite, and rare calcite, and are thought to be the distal effect of a fenitization related to the later biotite carbonatite (fig. 1).

Zone 4. This zone of the banded fenites is characterized by coexisting Na-amphibole and aegirine. The bands are fine-grained and alternately mafic and felsic. The bedding is still recognizable and even some graded bedding is preserved in places. The mafic bands are less than 2 mm thick whilst the felsic bands increase to 10 mm, in contrast with the previous zone 3, where the mafic bands were wider.

The felsic bands, the equivalent of the dark brown, dark grey, and argillaceous beds of zones 3, 2, and 1 respectively, have an almost schistose appearance with aligned flakes of golden brown phlogopitic biotite and feldspathic elongate tabular patches with rounded ends. These patches are up to

0.1 mm long and are now composed of a mosaic of a few grains of clear albite and K-feldspar which are interpreted to have formed from single crystals of feldspar, analogous to the texture seen in the pseudo-trachytes of East Africa (Le Bas, 1977, p. 117). Small porphyroblasts of rectangular non-pleochroic green crystals of aegirine are scattered throughout the bands, sometimes disturbing the alignment of the phlogopitic biotite and feldspar crystals. A few of the aegirine crystals even show a rotation texture, indicative of later shear movement. There is also minor Na-amphibole developed, which sometimes follows the planar fabric.

The mafic bands, the equivalent of the light brown, light grey, and silty beds of zones 3, 2, and 1 respectively, are composed of the same minerals, but slightly coarser, as the felsic bands in the following order of abundance: aegirine, Na-amphibole, albite, K-feldspar, and phlogopitic biotite. Apart from grain size, the texture relations are the same as for the felsic bands. One sample (SM93 Table I) contains no Na-amphibole, but is cut by veins consisting of aegirine only. These veins have clear margins composed of K-feldspar and albite. As in zone 3 the differences in the modal proportions between the bands reflect changes in the original chemistry of the sediments rather than the effects of fenitization. The Na-amphiboles are unzoned and have strong absorption. The pleochroism is mostly the same as in zone 3, apart from α which is orange-yellow to greenish yellow (Table III).

Cutting these bands are thin, 0.1 mm, veins composed of K-feldspar, biotite, and a little calcite. Where earlier Na-amphibole and aegirine occur near these veins, they are wholly or partly replaced by the brown pleochroic biotite, suggesting that these later veins were the carrier of a later K-metasomatic fluid which we interpret to be associated with the later biotite carbonatite. Plain calcite veins are also common.

Table III. Chemical analyses of Na-amphiboles from carbonatite and fenite at Loe Shilman
(Localities shown on Fig. 1)

Sample No. SM		Carbonatite		Zone-5				Zone-4		Zone-3				
		23A	78	92	98	79	83	85	86	94	83/77	87	95	95
	SiO_2	55.92	55.04	55.71	54.64	55.55	54.74	53.53	53.23	52.97	53.04	53.08	52.58	53.61
	TiO_2	0.18	0.08	0.21	0.44	0.31	0.74	0.64	0.41	0.49	0.32	0.43	0.21	0.16
	Al_2O_3	0.30	0.33	0.22	0.13	0.99	0.87	1.04	1.31	0.86	0.96	0.92	1.16	0.63
	Cr_2O_3	0.01	0.08	0.00	0.00	0.00	0.04	0.00	0.19	0.06	0.00	0.00	0.14	0.15
	Fe_2O_3	8.86	8.39	9.37	8.62	9.30	9.33	9.69	11.43	11.73	13.18	13.17	14.95	15.41
	FeO	2.95	5.27	4.20	5.82	5.48	7.26	10.00	9.95	11.34	11.13	12.98	12.23	11.43
	MnO	0.09	0.04	0.24	0.35	0.10	0.38	0.25	0.54	0.23	0.38	0.42	0.16	0.00
	MgO	17.00	15.68	16.11	15.00	14.87	14.02	11.72	10.60	9.92	9.27	8.02	7.65	7.94
	CaO	0.69	0.98	0.47	0.47	0.38	0.85	0.70	0.82	0.87	0.68	0.85	0.63	0.31
	Na_2O	7.82	8.27	8.51	8.35	8.48	8.18	8.12	7.60	7.47	7.50	7.11	7.00	6.95
	K_2O	3.27	2.25	2.59	2.36	2.10	2.32	1.95	1.69	1.57	1.13	1.03	0.85	0.54
	Total	97.09	96.41	97.63	96.18	97.56	98.73	97.64	97.77	97.51	97.60	98.01	97.56	97.13
$T = 8.00$	Si	7.991	7.978	7.967	7.978	7.955	7.853	7.856	7.826	7.852	7.855	7.880	7.835	7.957
	Al	0.009	0.022	0.033	0.022	0.045	0.147	0.144	0.174	0.148	0.145	0.120	0.165	0.043
	Al^{vi}	0.042	0.035	0.004	0.000	0.122	0.000	0.036	0.053	0.003	0.022	0.041	0.039	0.067
	Ti	0.019	0.009	0.023	0.048	0.033	0.080	0.071	0.045	0.055	0.036	0.048	0.024	0.018
	Fe^{3+}	0.953	0.916	1.009	0.947	1.003	1.008	1.071	1.266	1.309	1.470	1.472	1.678	1.722
$C = 5.00$	Fe^{2+}	0.352	0.638	0.501	0.711	0.656	0.870	1.227	1.224	1.405	1.378	1.611	1.524	1.418
	Mn	0.011	0.005	0.029	0.029	0.012	0.039	0.031	0.067	0.029	0.048	0.053	0.020	0.000
	Mg	3.622	3.388	3.434	3.265	3.174	2.998	2.564	2.323	2.192	2.046	1.775	1.699	1.757
	Cr	0.001	0.009	0.000	0.000	0.000	0.005	0.000	0.022	0.007	0.000	0.000	0.016	0.018
	Mn	0.000	0.000	0.000	0.014	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$B = 2.00$	Ca	0.106	0.152	0.072	0.074	0.058	0.131	0.110	0.129	0.138	0.108	0.135	0.101	0.049
	Na	1.894	1.848	1.928	1.912	1.942	1.862	1.890	1.871	1.862	1.892	1.865	1.899	1.951
$A = 0-1$	Na	0.273	0.477	0.432	0.452	0.413	0.413	0.421	0.296	0.285	0.261	0.182	0.123	0.049
	K	0.596	0.416	0.473	0.440	0.383	0.425	0.365	0.317	0.297	0.213	0.195	0.162	0.102
Mg ratio = $100\frac{Mg}{(Mg+Fe^{T}+Mn)}$		73.3	68.5	69.1	65.7	65.7	60.9	52.4	47.7	44.4	41.4	36.1	34.5	35.9
Vacancy in A site		0.131	0.107	0.095	0.108	0.203	0.162	0.214	0.387	0.418	0.525	0.623	0.715	0.849
Oxydation ratio = $100\frac{Fe^{3+}}{(Fe^{3+}+Fe^{2+})}$		73.0	58.9	66.8	57.1	60.5	48.4	46.6	50.8	48.2	51.6	47.7	52.4	54.8
XCa = $100\frac{Ca}{(Ca+Na+K)}$		3.69	5.26	2.48	2.57	2.07	4.23	3.95	4.94	5.34	4.40	5.68	4.42	2.28
Distance from the carbonatite contact. All distances are within 10% error.				30 mm	0.4 m	0.6 m	6 m	15 m	25 m	40 m	45 m	50 m	60 m	60 m

Zone 5. This 6 m wide zone is characterized by the presence of a higher proportion of Na-amphibole and aegirine to feldspar, plus some apatite and phlogopite. Albite is not seen in the 3 m adjacent to the carbonatite although its presence in small quantities in SM79 is indicated from the petrological mixing calculation, but is present in the 3 m of zone 5 adjacent to zone 4.

The zone 5 fenites are composed of mafic and felsic bands but no traces of the original sedimentary features can be seen, the whole zone being recrystallized. The mafic bands vary from 1 to 15 mm in width, and are composed of aegirine, Na-amphibole, K-feldspar, and sometimes phlogopite (Table I). Phlogopite-rich bands up to 5 mm wide (in SM79) occur parallel to the mafic bands.

Amphibole and some aegirine are replaced by phlogopite in these phlogopite-rich bands.

The felsic bands, up to 2 mm wide, are almost wholly composed of fresh feldspars and only occasional mafic crystals. These bands may be compared with the argillaceous beds of previous zones.

The aegirine in both bands is usually a fine-grained granular aggregate of crystals, but is medium to coarse grained in the cross-cutting aegirine-rich veins which have well-developed albite and K-feldspar margins. Amphiboles are medium grained and unzoned, and grow interstitially in the matrix of the aegirine. They have strong absorption with pleochroism the same as in zone 4 but β is now violet-indigo to violet (Table II).

The K-feldspar is medium to coarse grained with microcline twinning. A common feature in the metasomatic aureoles around carbonatite in NW Pakistan is the fact that K-feldspar is coarser grained than albite.

Composition of the Na-amphiboles

The amphiboles from Loe Shilman carbonatites and fenites form a solid solution series between magnesio-arfvedsonite and magnesio-riebeckite (IMA nomenclature; Leake, 1978). Energy dispersive microprobe analyses, at 15 kV on a Cambridge microscan Mark 5, of Na-amphiboles from 10 fenites and 2 from carbonatite were made measuring three or four crystals per sample and two or more spots per crystal. The amphibole analyses from any one sample are remarkably constant, in keeping with lack of zoning or other variations visible under the microscope. Table III gives one representative amphibole analysis from each sample, apart from SM95 where two are given because the small difference in K is considered significant. The data are recalculated assuming maximum Fe_2O_3 using the Papike et al. (1974) amphibole recalculation scheme on the basis of 23 oxygens and 13 cations. This recalculation was favoured because it is appropriate to the co-existence of the amphibole with almost pure acmite. An alternative recalculation, which assumes the Fe_2O_3 content as the midpoint between maximum and minimum Fe_2O_3, would extend this solid-solution series to riebeckite according to the IMA nomenclature.

The amphiboles show a smooth variation, both optically (Table II) and chemically (Table III and fig. 2) across the fenite zones and constitute a solid-solution series. The magnesio-arfvedsonite end member of the solid-solution series occurs in the carbonatite whilst in zones 5 and 4 the amphibole is part-way along the solid-solution series between magnesio-arfvedsonite and
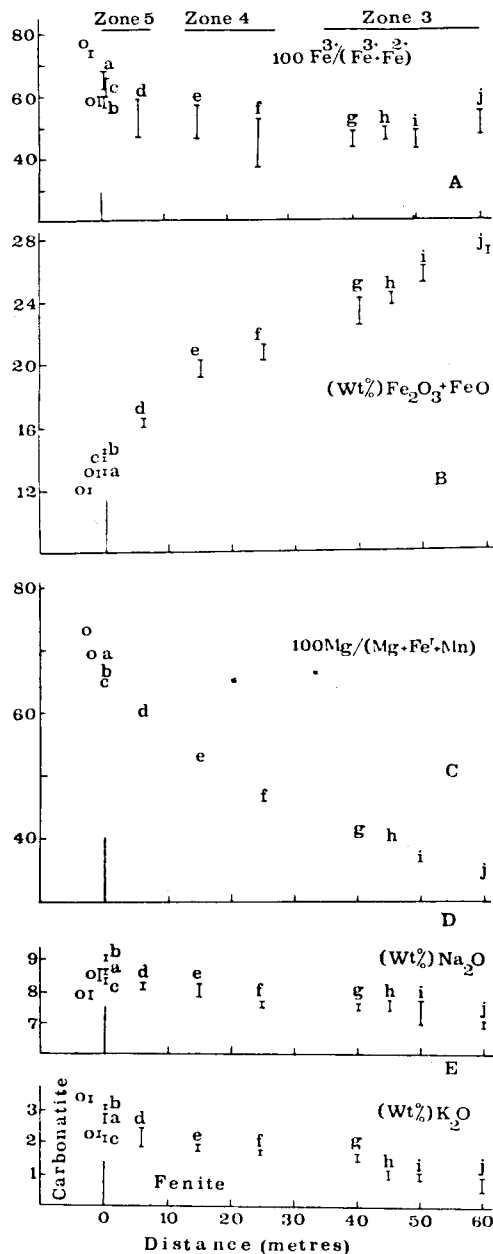

FIG. 2. K_2O, Na_2O, $Fe_2O_3 + FeO$, Mg ratio $= 100Mg/(Mg + Fe^T + Mn)$, and $100Fe^{3+}/(Fe^{3+} + Fe^{2+})$ against distance from carbonatite contact showing the smooth variation. $o = $ SM78 and SM23A (amphiboles within the carbonatite); $a = $ SM92 (0.03 m from the carbonatite contact); $b = $ SM98 (0.4 m); $c = $ SM79 (0.6 m); $d = $ SM83 (6 metres); $e = $ SM85 (15 metres); $f = $ SM86 (25 metres); $g = $ SM94 (40 metres); $h = $ SM83/77 (45 metres); $i = $ SM87 (50 metres); $j = $ SM95 (60 metres from the carbonatite contact). All distances are $\pm 10\%$.
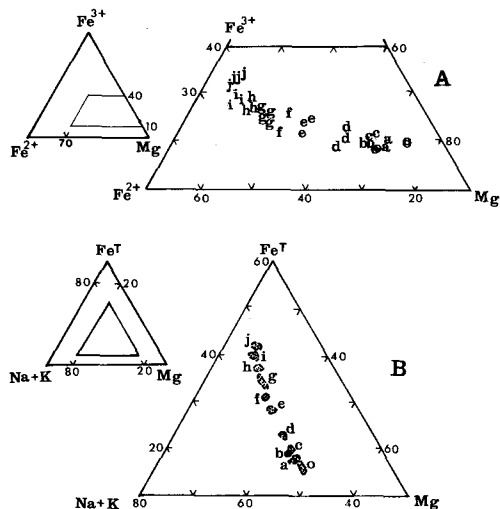
FIG. 3. Plots of Loe Shilman Na-amphibole in terms of (A) $Fe^{2+}-Fe^{3+}-Mg$ and (B) $Na+K-Fe^T-Mg$ showing the regular trend from magnesio-arfvedsonite (*o*) to magnesio-riebeckite (*j*). Symbols as for fig. 2.

magnesio-riebeckite, and in zone 3 the amphibole becomes the magnesio-riebeckite end member of the series.

In this solid-solution series, the principal substitution is ferrous iron for magnesium but in the magnesio-riebeckite portion of the series the substitution $(K,Na)_A + Fe_C^{2+} \rightleftharpoons \square_A + Fe_C^{+3}$ attains equal significance. Co-existing with the magnesio-arfvedsonite is almost pure aegirine ($Na_2O = 13\%$)
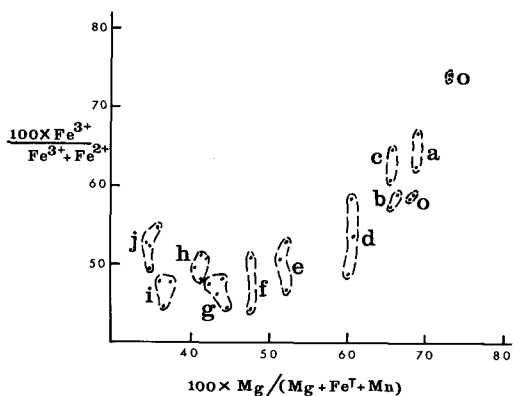
and its presence apparently buffers the Fe^{3+} available for the magnesio-arfvedsonite structure. This is shown by fig. 2A in which the oxidation ratio $[100Fe^{3+}/(Fe^{3+}+Fe^{2+})]$ decreases regularly in the magnesio-arfvedsonite up to *c*.30 m from the carbonatite contact, and then increases in the magnesio-riebeckite in the absence of aegirine up to 60 m from the carbonatite contact. The total iron content of the amphibole against distance (fig. 2B) shows an upward inflection at about 30 m with Fe^{2+} steadily increasing throughout the series, but with Fe^{3+} being constant up to 30 m from the contact and increasing beyond it in zone 3 (Table III). When combined with the evidence for increase in oxidation (fig. 2A), this shows that the Fe^{3+} content of the amphibole, whilst increasing with the falling intensity of fenitization in zones 5 and 4, increases even more steeply when aegirine is absent in zone 3 (fig. 2B). This increase of Fe^{3+} and total Fe can also be seen in fig. 3A and B. Plotting the Mg ratio against oxidation ratio again shows clearly the regular decrease from *a* to *g* and then increases to *j* (fig. 4).

The increasing oxidation trend shown by these fenitic amphiboles contrasts with the magmatic trend for Na-amphiboles (fig. 5). Strong and Taylor (1984) show that with progressive crystallization of peralkaline magmas, the Na-amphiboles progress from barroisite through richterite to arfvedsonite, whereas with falling temperature in the formation
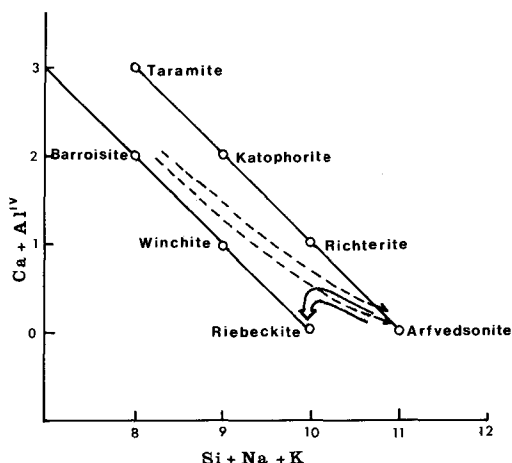

FIG. 5. $(Ca+Al^{IV})$ *vs.* $(Si+Na+K)$ plot after Strong and Taylor (1984), showing the contrast in their magmatic-subsolidus trends for Na-amphibole (dashed arrows) with that for fenitic Na-amphiboles at Loe Shilman (broad arrow) which progressively formed under high oxidizing conditions away from the carbonate contact. All analyses plotted were recalculated using the Papike *et al.* (1974) method.

FIG. 4. Mg ratio against oxidation ratio $100Fe^{3+}/(Fe^{3+}+Fe^{2+})$ for amphiboles from Loe Shilman. Note that the oxidation ratio in magnesio-arfvedsonite decreases from *o* to *f* and increases in magnesio-riebeckite from *g* to *j*. Symbols as for fig. 2.

of the Loe Shilman Na-amphiboles, the trend is
from arfvedsonite to riebeckite with a particularly
sharp increase in the oxidation state in the last zone
(fig. 5).

The Mg ratio [$100Mg/(Mg+Fe^T+Mn)$], K_2O
and to a small extent Na_2O all smoothly decrease
away from the carbonatite contact (fig. 2C, D, and E)
whilst CaO and TiO_2 remain almost constant and
Al_2O_3 rises slightly (Table III).

The slope of the straight line given by plotting
the Mg ratio against MgO (fig. 6) for the fenitic
amphiboles from Loe Shilman is steeper than that
for magmatic Na-amphiboles, taking data for rie-
beckite, magnesio-arfvedsonite and pargasite from
Deer et al., 1963, and further data from similar
amphiboles of the Coldwell syenite igneous com-
plex in Ontario, Canada (Mitchell and Platt, 1982;
Fig. 6). This difference in the slope of the metasoma-
tic and igneous amphiboles is a product of differing
oxidation states, with that in the metasomatic rocks
being the higher.

The proportion of K relative to Na decreases
away from the carbonatite contact (Table III)
whilst Na is roughly constant throughout. The
decrease in K within the magnesio-arfvedsonite to
magnesio-riebeckite series corresponds to increas-
ing vacancy in the A site as well as increasing Fe^{3+}.

Hogarth and Lapointe (1984) gave two separate
evolution trends for amphiboles from fenites at
Cantley, Quebec: magnesio-arfvedsonite from bio-
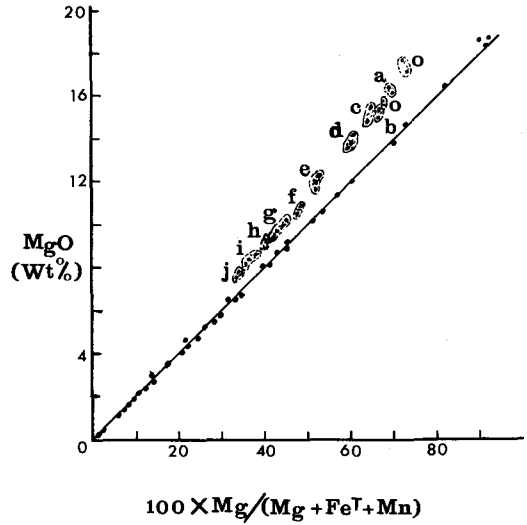tite gneiss; and magnesio-riebeckite from pyroxene

FIG. 6. Trends of Mg ratio against MgO for amphiboles
at Loe Shilman, compared with data for magmatic
Na-amphiboles taken from the Coldwell complex,
Quebec (Mitchell and Platt, 1982), and Deer et al. (1983).

gneiss (MA and MR respectively, fig. 7). They
suggest that magnesio-arfvedsonite and riebeckite
make solid-solution series with winchite as shown
by dotted lines in fig. 7. However the sodic amphi-
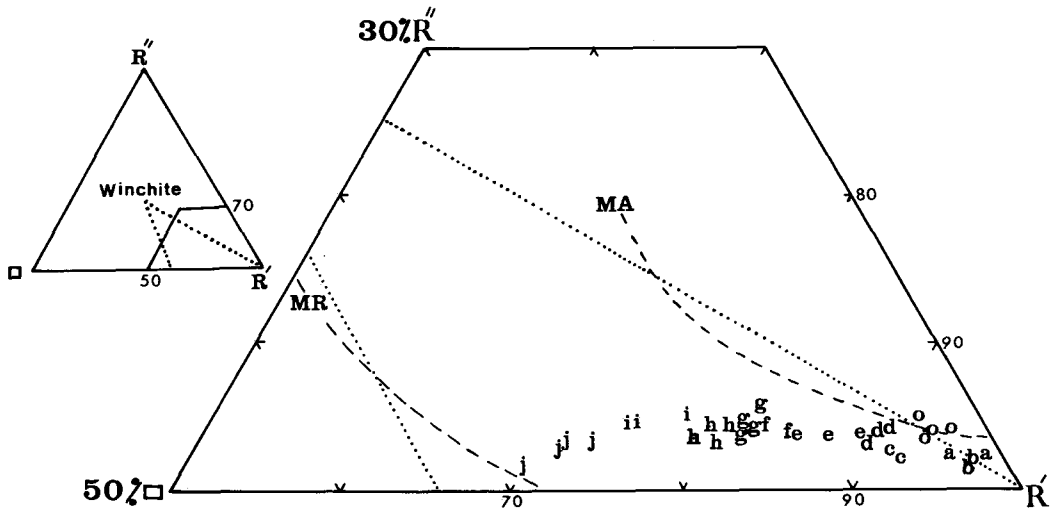boles from Loe Shilman show a single smooth

FIG. 7. The Na-amphiboles (o to j) from Loe Shilman plotted with respect to monovalent cations R', divalent cations in
B site R'', and vacancies (□) in the A site. Also shown (as dashed lines) are the fenitic trends in gneisses and the solid
solution series between magnesio-arfvedsonite (MA) and magnesio-riebeckite (MR) with winchite (dotted lines) as given
by Hogarth and Lapointe (1984). Symbols as for fig. 2.

curve from magnesio-arfvedsonite to magnesio-riebeckite (fig. 7). In the Loe Shilman series the vacancies are progressively filled from magnesio-riebeckite to magnesio-arfvedsonite while Ca roughly remains constant. These vacancies are also correlated with the distance from the carbonatite contact. In contrast, the Na-amphiboles formed in the fenitized granite gneisses around the Sokli carbonatite complex in Finland (Vartiainen and Woolley, 1976) have full A site and hence would plot along the $R'-R''$ line in fig. 7. There is thus no correlation of vacancy with distance.
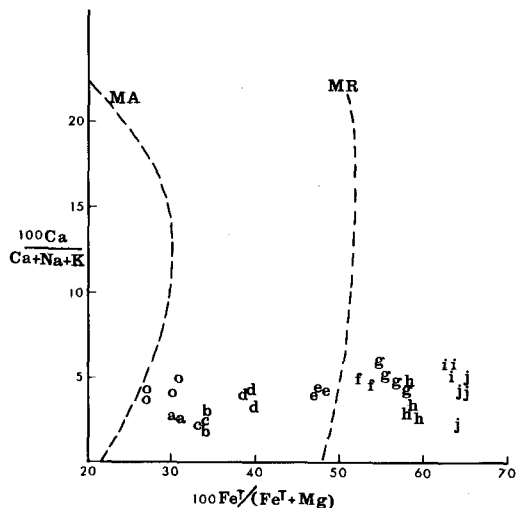
FIG. 8. Plot of $100Fe^T/(Fe^T + Mg)$ vs. $100Ca/(Ca + Na + K)$ for Loe Shilman Na-amphiboles with MA and MR trends from Cantley (Hogarth and Lapointe, 1984). Symbols as for fig. 2.

In fig. 8 $X_{Ca} = [100Ca/(Ca + Na + K)]$ remains roughly constant against $X_{Fe^T} = [100Fe^T/(Fe^T + Mg)]$ in contrast to the two fenitic trends (MA and MR described by Hogarth and Lapointe, 1984). Instead, X_{Fe^T} increases regularly from 26 in the carbonatite outward across the fenites to 65 in zone 3 and correlates well with distance from the contact.

The variation in $(Na + K)$ in the amphibole across the Loe Shilman fenite zones is also in contrast to that of other fenitic amphiboles. At Loe Shilman, the $(Na + K)$ rises smoothly as the Mg ratio increases (fig. 9A). This increase occurs as the carbonatite contact is approached, and corroborates the fact that alkalis fixed during the fenitization emanate from the carbonatite. Apart from the introduction of some Mg into zone 5
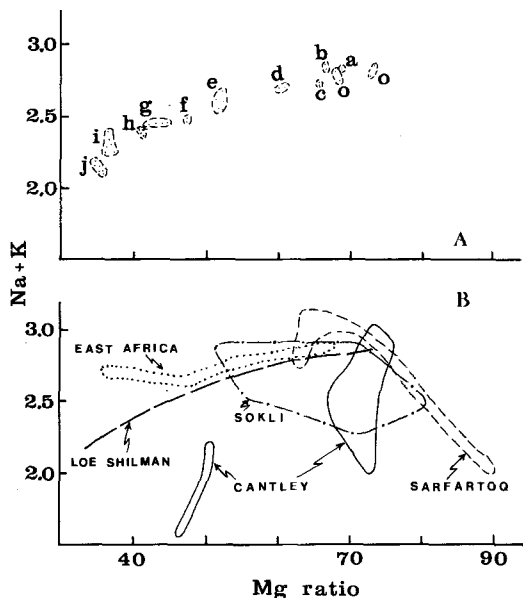

FIG. 9. Plot of Mg ratio against (A) Na + K for amphibole in fenites at Loe Shilman, showing a regular increase in Na + K with increasing Mg ratio; and (B) the trend for amphiboles from Loe Shilman in comparison with fenitic amphibole from Sokli, Finland (Vartiainen and Woolley, 1976); Sarfartoq, West Greenland (Secher and Larsen, 1980); Cantley, Quebec (Hogarth and Lapointe, 1984); and from East Africa (Sutherland, 1969).

during fenitization, the smooth change in Mg ratio appears to be largely controlled by temperature change together with buffering effect of aegirine in zone 4 and its absence in zone 3. The variation in alkali vs. Mg ratio across the fenite zones at Loe Shilman also shows interesting contrasts with amphiboles in fenites from other areas (fig. 9B). The fenitic amphiboles, from Cantley, Quebec, are in two groups corresponding to whether these were formed from biotite gneiss or pyroxene gneiss, again illustrating the dependence on the bulk composition of the host rock. At Sokli, Finland, where carbonatite is emplaced into granite gneiss, the alkali content of the amphibole shows no variation with the distance from the carbonatite contact (Vartiainen and Woolley, 1976; and Vartiainen, 1980) but the Mg ratio varies. Similarly for the East African fenitic amphiboles (Sutherland, 1969) where, apart from one analysis not plotted (Na + K = 2, Mg ratio = 83), the alkalis remain constant over a wide range in Mg ratio, but here the samples analysed were taken from a variety of plutonic and volcanic acid rocks. The amphiboles in Sarfartoq fenites differ. These show a wide range

in both alkali content and Mg ratio, and behave in an opposite sense to those at Loe Shilman (fig. 9B). Therefore the composition of these fenitic amphiboles appear to be more dependent on the host-rock chemistry than on the composition of the fenitizing fluid.

It has already been shown that the amphiboles at Loe Shilman formed at a higher oxidation state than that for Na-amphiboles in most magmatic rocks (fig. 6). Since fenitic amphiboles from other areas also plot with similar but steeper slopes than that for magmatic Na-amphiboles (fig. 10), they also would appear to have been formed at a similarly high oxidation state.
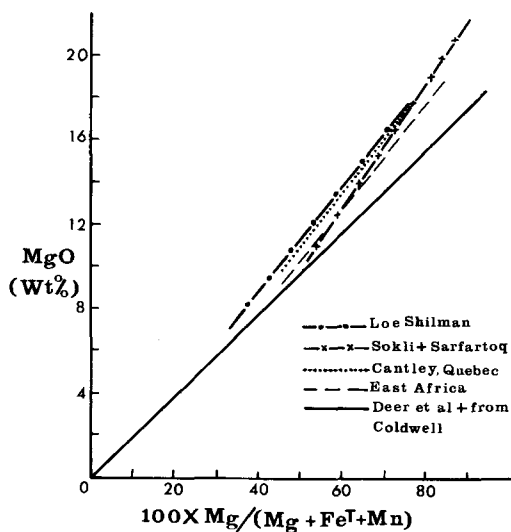

FIG. 10. Plot of MgO vs. Mg ratio for Na-amphiboles from Loe Shilman and compared with Na-amphiboles from Sokli, Finland (Vartiainen and Woolley, 1976); Sarfartoq, West Greenland (Secher and Larsen, 1980); East Africa (Sutherland, 1969); and igneous examples from Coldwell, Quebec (Mitchell and Platt, 1982); and those given in Deer et al. (1963).

However, the Na-amphiboles in the nordmark-ites of the Oslo region of Norway (Andersen, 1984a), if plotted, would coincide with those from Loe Shilman. It is evident that these Oslo Na-amphiboles crystallized at a higher than usual state of oxidation for magmatic rocks, and thus would accord with Andersen's (1984b) interpretation that the nordmarkite was formed from a hydrous magma.

It is suggested that these variations in the chemistry and optical properties of the Na-

amphiboles in the fenites at Loe Shilman are not caused primarily by any variable chemistry of fenitizing fluids but are mainly controlled by the permeability of the rocks being fenitized, and also as the response of the chemistry and mineralogy of these country rocks to the fenitizing solutions permeating through them from the carbonatite. These conditions have produced the uniform variation with distance seen in the amphiboles at Loe Shilman.

Conclusions

The sodic amphibole from Loe Shilman, Khyber Agency in NW Pakistan, form a complete solid-solution series between magnesio-arfvedsonite and magnesio-riebeckite not previously reported. The regular chemical variation and pleochroism of the amphiboles correlate with distance from the carbonatite contact. These smooth variations are the result of fenitizing fluids slowly soaking their way through slates and phyllites of low permeability and, depending on distance and temperature from the carbonatite igneous contact, the reaction under strongly oxidizing condition with the fine-grained sediments.

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