Mineralogy and Geochemistry of Fenitized Nephelinites of the Amba Dongar Complex, Gujarat

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Abstract: In the Amba Dongar sub-volcanic complex, nephelinite plugs and dikes of phonolites were emplaced before the carbonatites. The fenitizing fluids released from carbonatite magma caused extensive fenitization in nephelinites with intensity varying from mild carbonatization (CO_2) metasomatism accompanied by hematitization) in the distal outcrops, to a high degree of K-fenitization (feldspathization, phlogopitization) in outcrops closer to the carbonatite bodies. The intensely fenitized rocks are the xenoliths of nephelinites within the sövite. The primary texture of the nephelinites is mostly preserved, but the highly feldspathised nephelinites look more like nepheline syenite with water clear poikilitic K-feldspar in the groundmass. Invariably, nepheline is largely replaced by hydromuscovite and to lesser extent by zeolite (mainly natrolite and phillipsite). Cancrinite is also noticed in some thin sections. Pyroxene has been partially or totally replaced by phlogopite while the groundmass has been feldspathised with formation of poikilitic Kfeldspar (Or>90%). On the basis of mineralogical study, back scattered electron images and elemental mapping on microprobe, three processes of fenitization, namely, K-metasomatism (formation of hydromuscovite, phlogopite and Kfeldspar), zeolitization and CO2-metasomatism along with hematitization are identified. K-feldspar in the norms of fenitized nephelinite varies from 9% to 36%. Fenitized nephelinites show enrichment in trace and rare earth elements over the unfenitized nephelinites.

Keywords: Nephelinite, Carbonatite, Nepheline, K-feldspar, Hydromuscovite, Gujarat.

INTRODUCTION

Previous studies on the fenitization of rocks in Amba Dongar deal mainly with the protolith sandstone (Deans et al., 1972, Sukheswala and Viladkar, 1981, Viladkar, 1986, 1996). The mineralogy of fenitized nephelinites has not been studied in detailed earlier although some aspects were given in earlier publication (see Viladkar, 1996). The major bulk of alkaline rocks in Amba Dongar and surrounding are made up of nephelinite plugs and few dikes of phonolite. Detailed mapping of nephelinite outcrops and later petrographic studies revealed a metasomatic aureole around the ring dike of sövite which extends up to a distance of 5 km. Intense metasomatic effects are seen in xenoliths of nephelinites in sövite outcrops.

After the initial studies of nephelinites and phonolites ofAmba Dongar by Viladkar (1986) subsequently they were studied by Srivastava (1997) and Ray (1997) while the alkaline rocks of the entire Chhota Udaipur province were investigated by Gwalani et al. (1993).

Fenitization results in extensive replacement of nepheline by hydromuscovite, and lesser by cancrinite and calcite. Discrete grains of analcime, natrolite and phillipsite are found in the vicinity of altered nepheline crystals. In intensely K-fenitized nephelinites, K-feldspar (Or_{α} to Or_{72}), forms water clear poikilitic areas in the matrix while phenocrysts of pyroxene are partially replaced by phlogopite.

The author did suspect fenitization of nephelinites much earlier (Viladkar, 1986) as he identified poikilitic feldspar in groundmass and alteration of nepheline to some micaceous mineral. He then used the term "phonolitic nephelinites" for such rocks. He further writes: "...... The petrographic descriptions reveal that majority of these rocks are nephelinite with no trace of feldspar in them but the same rocks when analyzed chemically show considerable amount of potash. — Phenocrystal nepheline, either rectangular or hexagonal in outline, is invariably highly altered either to natrolite or some micaceous mineral— such nepheline crystals when analyzed after separation, showed considerable amount of potassium content (8.50%). This could be attributed to the alteration of nepheline to some micaceous mineral...."

Plotting of all analyzed nephelinites on TAS (Cox et al. 1979) brings out random spread of fenitized nephelinites (Fig. 9) and this perhaps was the reason for different nomenclature of these rocks by later workers.

Very few outcrops have, as such, escaped fenitization and it is hard to find totally unfenitized nephelinite. Out of large collection, 29 samples which include 2 unfenitized nephelinites and remaining fenitized ones were selected for geochemical analytical work. On the basis of petrography, mineralogy and geochemical investigations, following fenitizing processes, have been identified. These are: Kmetasomatism (feldspathization and phlogopitisation), zeolitization, $CO₂$ -metasomatism (carbonatization), and hematitization and silicification. Among these, Kmetasomatism and zeolitization result in two distinct mineral assemblages, while CO_2 -metasomatism, hematitization and silicification only replace the silicate minerals in nephelinites. Here major emphasis is given to mineralogy and elemental mapping on electron microprobe of altered or replaced minerals rather than geochemistry of these rocks.

GENERAL GEOLOGY OF AMBA DONGAR

The Amba Dongar carbonatite-nephelinite ring complex is situated on the western periphery of the Deccan volcanic province within the rift zone of the Narmada valley (Fig.1). It intrudes the Bagh sandstone-Deccan basalt sequence. Nephelinite occurs as plugs in the immediate outer periphery of the carbonatite ring structure forming prominent conical hills rising to 70 to 100 m high amidst plains at Khandla, Kharvi and Mongra in the west of Amba Dongar and at Kadipani and Moti Chikli in the eastern part of Amba Dongar.A generalized geological map showing distribution of nephelinite plugs in relation to the sövite ring dike is given in Fig.1.

A large number of nephelinite xenoliths in sövite were exposed during continuous mining operations for fluorite in the northern part of the sövite ring dike. The largest xenolith which suffered extensive phlogopitization with transformation to a "glimmerite rock" was collected at the contact between xenolith and the host sövite in an adit driven (in 1972) in sövite. All xenoliths, in general, show intense effects of phlogopitization and feldspathization whereas the effects of zeolitization carbonatization and hematitization are usually seen only in the distal outcrops of nephelinites. Core samples of some drill holes that went through nephelinite outcrops at deeper level clearly show phlogopitization of nephelinite at the contact between nephelinite and alvikite II which intrudes the former (Fig. 2)

Textural Changes during Fenitization

Nephelinites of Amba Dongar are highly porphyritic rocks with phenocrysts of nepheline, pyroxene and melanite.

Fig.1. Geological map of the sub-volcanic diatreme at Amba Dongar. Arrows point to fenitized and carbonatized nephelinites. (**1**) Adit, driven in sövite outcrop in 1971, had huge block of nephelinite which was extensively phlogopitized. Though adit was closed later, the phlogopized nephelinite samples can still be obtained from a dump east of adit.(**2**) Plug of nephelinite with phenocrysts of highly altered nepheline. (**3**) Dike of nephelinite in Khandala which is completely carbonatized and zeolitized.

Fig.2. Formation of phlogopite along intrusive contact of alvikite II in nephelinite.

Brown volcanic glass in groundmass is not uncommon in some sections. An average modal composition (in vol %) of relatively fresh and unfenitized nephelinite shows : nepheline (25), pyroxene (18) melanite (5), apatite (2.5) and sphene (2). The groundmass constitutes about 48%.

In the majority of the samples of fenitized nephelinite, original texture of nephelinite was preserved, except in the highly feldspathised samples, where the texture resembles that of syenite (sp. no. 1274 and 47 in Table 7). In most cases, the shape of all the original minerals is well preserved. Worth mentioning in this respect is a dikes of nephelinite (sp. no. 1266 and 308) in Khandla, west of Amba Dongar where the dikes are completely carbonatized, but the textural outlines of all primary minerals are well preserved. Phenocrysts of nepheline, pyroxene and melanite are replaced by carbonatitic calcite and are set in a fine-grained calcitic groundmass. Apatite, however, show no replacement by calcite and possibly it was introduced from the fenitizing fluids emanating from sövite. Carbonatized minerals are rimmed by cryptocrystalline silica, released during replacement of original silicate minerals by calcite. In some samples replacement by iron oxide is not uncommon.

MINERALOGICAL CHANGES DURING DIFFERENT METASOMATIC PROCESSES

K-metasomatism

This is the most widespread fenitization in Amba Dongar (Deans et al. (1972, 1973, and Viladkar 1986a, 1991, 1996). The most intense K-metasomatism is observed in the xenoliths of nephelinites in sövites. In general, K-rich fenitizing solutions caused the following mineralogical changes:

- i) Replacement of nepheline by hydromuscovite,
- ii) Replacement of pyroxene by phlogopite and,
- iii) Formation of poikilitic feldspar in the groundmass of fenitized nephelinites.

(i) Replacement of nepheline by hydromuscovite is common in these fenitized nephelinites. In the mildly fenitized nephelinites, relicts of nepheline form isolated patches surrounded by newly formed hydromuscovite (Fig.3 a, b). Similar observation was reported by Drüppel et al (2005) at Swartbooisdrif, NW Namibia, where fenitizing solutions are supplied by ferrocarbonatite magma. Le Bas (2008) reports replacement of nepheline by cancrinite in ijolites of Cape Verde Islands.

Furthermore, newly formed hydromuscovite and relict nepheline can be well distinguished on back-scatteredelectron (BSE) images and elemental mapping images (Figs. 4-5). In some intensely fenitized samples, large scale replacement of nepheline by hydromuscovite is observed preserving only its form (Fig. 4B). The Na released during conversion of nepheline (to hydromuscovite Table 1) is fixed in analcime (Table 2) that is usually found as tiny spots surrounded by hydromuscovite. In the BSE image hydromuscovite shows fibrous nature. The brighter areas of Al and K within the nepheline crystal point to hydromuscovite while very bright spots outside the nepheline grain are newly formed poikilitic K-feldspar in the groundmass (Fig. 4A solid lines). K-rich solutions also carried small amounts of Ba which is fixed in hydromuscovite (Table 1).

(ii) All stages of phlogopitization from incipient to the total replacement of pyroxene by phlogopite and formation of glimmerites can be observed in the fenitized nephelinites. Phlogopitization progresses from margins towards centre of the pyroxene grains. Occasionally it occurs only in patches leaving behind relict pyroxene intact (Fig. 5 and 6). In an advanced stage, the entire pyroxene crystal is replaced by the strongly pleochroic golden yellow coloured phlogopite. Grains of newly formed wollastonite and iron oxide are observed in the close vicinity of phlogopite. It is presumed that Ca that is released during conversion of pyroxene to phlogopite is fixed together with silica in wollastonite. In

Fig.3. (A and B) Alteration of nepheline to hydromuscovite in fenitized nephelinite

Fig.4A. Element mapping (Na, Al and K) showing partial replacement of nepheline by hydromuscovite. Lighter shades point to higher concentrations of that particular element. Solid lines point to poikilitic K-field points outside nepheline while the solid in nepheline crystal point to newly form hydromuscovite in nepheline.

Fig.4B. Major part of nepheline has been replaced hydromuscovite (bright areas of Na and K and dark area in Na)

Table 1. Represnetative analyses of hydromuscovite

Fig.7 euhedral crystal of pyroxene seem to have been unaffected on prismatic side; prismatic borders are sharp and not damaged (bright while area in Na mapping) and fenitizing solutions carrying K, Al and Mg have an easy access only on pyramidal side. Bright areas in K and Mg mapping shows newly formed phlogopite. Le Bas (2008) reports similar process of K-metasomatism wherein pyroxene from ijolite has been rimmed and replaced by biotite on Brava, Cape Verde Island. He also reports phlogopitization between sövite and host rock in the west coast of Fuerteventura, Canary Islands (Ler Bas, 2008).

iii) The third effect of K-metasomatism is seen in the formation of water-clear poikilitic K-feldspar (Or_{98} to Or_{72} see Table 3, Fig. 4A) in the groundmass of fenitized nephelinites. Some of these highly feldspathised nephelinites

exhibit syenitic texture with a poikilitic feldspar plate enclosing altered nepheline and pyroxene.

CO2 -metasomatism, Hematitization (Fe-metasomatism) and Silicification

CO₂ -metasomatism (carbonatization) and hematitization are often associated together. They are more widespread

Fig.5. Elemental (Na, Al, K, Fe and Mg) map showing conversion of pyroxene to phlogopite in the centre of pyroxene crystal. Lighter shades in each element shows the higher concentration of that particular element.

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in outcrops of nephelinites which are located far from the sövite ring dike at Mongra and Khandla, West of Amba Dongar and Moti Chikli, East of Amba Dongar. The carbonatization process results in total replacement of nepheline, pyroxene and melanite (garnet) by calcite. Some melanite, where the original rhombohedral and trapezohedral forms are preserved, show alternating layers of calcite and oxidized magnetite. Cryptocrystalline granular silica usually marks the outlines of such minerals. Similar type of carbonatization of melilite-bearing dike rocks at Ruri is described by McCall (1963) and by Clarke and Roberts (1986) at the Got Chiewo, western Kenya. Silicification of

Fig 6. Mapping of elements K and Mg show formation of phlogoite within pyroxene crystal.

Fig.7. Phlogopitization of pyroxene crystal, elemental mapping of Na, K, Fe and Mg. Lighter colour shows higher concentration that element.

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some primary minerals in nephelinites at times is very prominent and entire mineral has been replaced by granular quartz. Silica released during carbonatization of primary silicate minerals does not leave the system and is being used in the process of silicification. Low temperature silicification of sövite (along with introduction of fluorite and barite) is common in Amba Dongar. Presence of hydroxides indicates higher oxidizing conditions of fenitizing solutions. Le Bas (1977) described hematitization in feldspathic breccias at North Ruri, Kenya, relating the hematitization to late-stage effects associated with intrusion of ferrocarbonatite, unlike Amba Dongar where it is related to the sövite.

Zeolitization

Associated with hydromuscovite are zeolite; natrolite and phillipsite (Table 5). In some samples cancrinite is also observed. Nepheline is converted to fibrous aggregates of zeolite which show wavy extinction. In some cases nepheline is so extensively replaced by zeolite that only relict patches of original nepheline can be noticed. Such natrolite-rich patches (fan-shaped radiating aggregates) are abundant in some nephelinitic rocks of Mongra, NW of Amba Dongar.

ANALYTICAL TECHNIQUES

Microprobe analyses and elemental mapping were made on the Joel Superprobe JXA-8200 electron microprobe with accelerating voltage of 15kV and beams current 10 nA, at the Max-Planck Institute for Chemistry (MPI), Mainz, Germany. Major and trace elements were determined on XRF at the Mineralogische-Petrographisches Institute of the Albert-Ludwigs University, Freiburg im Br. Germany. Two samples of fenitized nephelinite were analysed at the Department of Earth Sciences, Dartmouth College, Hanover, USA (major elements on XRF and trace and REE on ICP-MS)

Table 5. Natrolite, phillipsite and cancrinite minor alteration products

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SiO ₂	49.36	43.98	39.00	
TiO ₂	0.22	0.20	0.00	
AI ₂ O ₃	22.77	29.01	29.87	
FeO	0.00	1.30	0.10	
MgO	0.00	1.02	0.00	
CaO	0.78	1.71	4.10	
Na, O	12.10	4.33	15.00	
K,O	0.61	4.32	0.10	
Total	85.50	84.83	88.17	

MINERAL CHEMISTRY

Micas: Two distinct types of brown micas, phlogopite and phlogopitic biotite, develop during the phlogopitization of nephelinites. All mica analyses show high F which is added from fenitizing solutions out of sövitic melt.

The micas from the phlogopitized rocks differ considerably in different samples which are closer to the sövite contact and farther away from the contact (Table 6). Accordingly those from intensely phlogopitized nephelinites (closer to the sövite contact) are more magnesian (MgO 16% to 22%) with higher Al_2O_3 contents (between 10 and 16%). In contrast, micas from phlogopitized nephelinites which are farther away from the sövite outcrop are phlogopitic biotite or biotite (analyses 1 to 5 in Table 6).

Feldspar: K-rich fenitizing solutions have replaced original groundmass converting it in to K-feldspar which forms poikilitic patches. The compositions of this poikilitic feldspar show slight change in their composition though it's predominantly low temperature K-feldspar (Table 3, Fig. 8).

Table 6. Representative analyses of mica from fenitized nephelinite

	1	\overline{c}	3	$\overline{4}$	5	6	7
SiO,	41.26	39.41	39.51	39.79	38.59	39.90	39.18
TiO,	1.01	2.05	2.15	1.87	2.36	0.00	0.82
AI_2O_3	10.16	10.92	10.88	10.25	11.27	16.09	15.91
FeO	12.88	14.42	14.38	15.26	15.14	4.80	6.04
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	17.08	17.01	16.66	15.76	15.92	22.80	21.70
BaO	0.06	0.02	0.07	0.04	0.12	0.00	0.00
Na ₂ O	0.48	0.42	0.31	0.28	0.25	0.00	0.00
K_2O	9.79	9.71	9.75	9.63	9.40	9.00	8.49
F	3.29	2.34	2.48	2.62	2.23	n.a.	n.a.
H ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.01	96.30	96.19	95.50	95.28	92.85	92.46
O F Cl	1.39	0.99	1.04	1.10	0.94		
CTotal	94.62	95.31	95.15	94.40	94.34		
Si	5.69	5.43	5.45	5.56	5.38	5.77	5.71
Ti	0.11	0.21	0.22	0.20	0.25	$\mathbf{0}$	0.09
Al	1.65	1.77	1.77	1.69	1.85	2.74	2.73
Fe ²	1.49	1.66	1.66	1.78	1.77	0.58	0.74
Mn	0.00	0.00	0.00	0.00	0.00	$\mathbf{0}$	$\mathbf{0}$
Mg	3.51	3.49	3.43	3.28	3.31	4.91	4.72
Ba	0.00	0.00	0.00	0.00	0.01		
Na	0.13	0.11	0.08	0.08	0.07	$\mathbf{0}$	$\mathbf{0}$
K	1.72	1.71	1.72	1.72	1.67	1.66	1.58
Cations	14.30	14.38	14.34	14.30	14.31		
O	22.00	22.00	22.00	22.00	22.00	22.00	22.00

Fig.8. Composition K-feldspar in groundmass of fenitized nephelinites

Nepheline and its altered products: Fresh crystals of nepheline are rare in fenitized nephelinites and wherever they occur they are mostly homogeneous. Representative analyses of fresh nepheline from unfenitized nephelinites are given in Table 4. The nepheline geothermometry of Hamilton (1961) yields a temperature range of 700°C to 950°C for fresh nepheline.

Nepheline has been altered to, hydromuscovite, natrolite, cancrinite and phillipsite during different process of fenitization. Their formation is discussed in earlier section.

Whole Rock Chemistry

Representative analyses of unfenitized nephelinite, Kfenitized and carbonatized nephelinites are given Table 7 and all analyses are plotted on the TAS diagram (Cox et al 1979). CIPW norms are listed in Table 8. The random spread seen on TAS diagram (Fig.9) is due to various degree of fenitization of original nephelinites and this spread is the reason for different nomenclature by other researchers on the Amba Dongar alkaline rocks. The most remarkable feature in these analyses and norms is the increase in K_2O resulting in high K-feldspar from unfenitized nephelinite (112) to fenitized nephelinites (570 and 47). K-feldspar increases from 9% to almost 21% and is the highest (36%) where syenitic texture is observed (Sp. No. 1274, Table 8). The norm of phlogopitized nephelinite does not give proper composition as in absence of water, phlogopite cannot be formed in norms and instead olivine and leucite appears in norm due to high content of MgO and K_2O in the analysis.

The chondrite normalized multielemental and REE

UN - Unfenitized nephelinite; FN - Fenitized nephelinite; CFN-Carbonatitzed nephelinite; PN - Phlogopitized nephelinite

patterns are presented in figures 9 and 10. During the process of fenitization Ba, Rb, Th, and Nb appears to have been added in large amount. For Ba highest peak is seen in a syenitic textured fenitized nephelinite and this is true for Rb also. Unfenitized nephelinite shows lower concentration in these elements while all other types of fenitized nephelinites show remarkable increase. Phlogopitized nephelinite shows trough in Sr while highest peak is in Nb. It has been mentioned earlier that phlogopitized nephelinites show high concentrations of Nb (Viladkar and Bismayer, 2010). The chondrite normalized REE distribution (Fig. 10) shows rise in all REE's in both fenitized nephelinite and phlogopitized nephelinite in comparison to unfenitized nephelinite.

Composition of Fenitizing Solutions

The very fact that the intense fenitization (phlogo-

pitization of pyroxene and alteration of nepheline to hydromuscovite) is seen in the xenoliths of nephelinites in sövite suggest that fenitizing fluids containing K, Mg, H_2O , $CO₂$, F and Cl were released form sövitic magma. Addition of K_2O during fenitization is the most common process during fenitization in the high level carbonatites (Woolley, 1982; Le Bas, 1981, Le Bas, 1987, Le bas, 2008). Conversion of nepheline to hydromuscovite involves the addition of K and $\mathrm{H}_2\mathrm{O}$ from the fluids to nepheline, releasing Na from it. There seems to be extensive mobility of fluorine from sövitic magma which is reflected in high F in all micas from fenitized nephelinite. The released Na is fixed in analcime, natrolite and cancrinite which occur as discrete grains in these rocks. The following reactions may occur at low temperature and can explain formation of hydromuscovite and analcime:

 $\text{Na}_3 \text{ (Na,K)} \text{ (Al}_4\text{Si}_4\text{O}_{16}\text{) } + \text{K}_2\text{O} + \text{H}_2\text{O} =$ $KAI₄ (SiAlO₂₀) (OH)₄ + NaAlSi₂O₆. H₂O$ Nepheline + K fluids + water = Hydromuscovite + Analcime

It is known that nepheline can be stable even at low temperatures under nonhydrous conditions (Schairer &

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Fig.10. Chondrite normalized multielemental patters for
Fig.9. Plots of all nephelinites on the TAS.
Fig.10. Chondrite normalized multielemental patters for the TAS. unfenitized nephelinites (open square), fenitized nephelinites (open circle), fenitized nephelinite with syenitic texture (cross) and phlohopitized nephelinite (filled triangle).

Yoder, 1960, 1961) while under hydrous conditions it becomes unstable and is converted to analcime and phillipsite (Kim and Burley, 1971; Henderson and Gibb, 1977). Formation of phillipsite requires addition of some amount of Ca which obviously is added from fenitizing solutions released from the sövitic magma.

Phlogopitization of pyroxene requires addition of K, OH and F from the fluids from sövitic magma. Sövite which is the source of fenitizing fluids seems to have had sufficient Mg as documented earlier by presence of periclase (Viladkar and Wimmenauer 1992) in sövites from deeper levels and the presence of magmatic phlogopite, too (Viladkar, 2000). Thus the presence of periclase and magmatic phlogopite indicate the availability of sufficient Mg in carbonatite magma at Amba Dongar. F content ranges

Fig.11. Chondrite normalized REE patterns in unfenitized nephelinie (open square), fenitizied nephelinite (open circle) and phlogopitized nephelinite (filled triangle).

between 2.34 to 3.29 wt % in the newly formed phlogopite during fenitization and its source is sövite magma. Fluid inclusion studies by Veksler and Lentz 2006) clearly indicates that F is available in carbonatite magma in the early stages. Temperatures of fenitization may be around 500-600°C. Bailey (1966) showed that with relative high H2O presssures phlogopite can be formed while at lower H2 O presssures K-feldspar can form.

CONCLUSIONS

1. Petrographic criteria (textures of fenitized nepheli-nites) clearly indicate replacement of nepheline by hydromuscovite and that of pyroxene by phlogopite and BSE images and elemental mapping of these minerals on microprobe clearly support this observation.

- 2. Chondrite normalized multielemental patterns and REE patterns undoubtedly demonstrate that Ba, Rb, Nb, Th and LREE's are added to host rock during fenitization.
- 4. Field, petrography and mineral BSE images on microprobe analyses present indisputable evidence that these nephelinite outcrops have undergone widespread fenitization which is attributed to the sövite and alvikite intrusions in nephelinites.

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