CHAPTER THREE

GEOCHEMISTRY
Sampling And Analytical Techniques

During the field study a number of samples of the volcanic rocks of Bayana basin and amphibolites of Khetri belt were collected both along and across the strike of the exposures. In Bayana area the volcanics were sampled systematically in Ker-Jahaj section (Figure 2) where the sequence is best developed. The samples of amphibolites of Khetri belt were collected from Kolihan and Madhan-Kudhan areas (Figure 3). Special care was taken in the collection of the samples and the weathered outcrops were outrightly rejected. The samples have been collected only from most fresh looking outcrops. After petrographic studies, unaltered, fresh looking samples were finally selected for geochemical analyses. After separation of weathered crust the clean samples were crushed in a steel mortar. The fragments containing amygdules, vesicles, veins and iron strains were removed. The crushed samples were powdered to about -200 mesh size in an agate mill.

The major and trace element analyses were performed at geochemical laboratories of Wadia Institute of Himalayan Geology, Dehradun by using Energy Dispersive X-Ray Fluorescence (EDXRF) model EDAX EXAM Six – Phillips PV9 100. The operating conditions for major oxides determination were Anode-Ag-X-Ray-12 KV path vacuum and filter nil. For trace
elements. Anode-Ag-λ-Ray tube, voltage was 40 kV and Ag filter was used to reduce the background in spectrum. For XRF analyses the pressed pellets of the samples were prepared by using 3 gms of rock powder in a collapsible aluminium cup with a backing of boric acid and a pressure of 20 tons using a hydraulic press. Whereas the fused pellets were made by employing the method after Norrish and Hutton (1969). The precision coefficient of variation and detection limits for various elements are same as given in Bhat and Ahmad (1990) and Rathi et al. (1991).

All the analysed samples were standardised against the internationally recognised rock standards BR, BE-N, BHVO-1, BIR, GSR-3, JBl1a, MRG, W2, UBN, AGV-1, JA2, GSR-2, GSP-1, Mica-Fe and Mica-Mg. To avoid any error double and triple runs were made taking different samples from the same specimen powder. The precision limits of analysed major and trace elements calculated from international reference rock samples are given in tables 4 and 7.

Rare earth elements (REE) analyses for the representative samples were carried out by ICP-MS techniques at National Geophysical Research Institute, Hyderabad following the procedures described in Balaram (1991a and b) and Balaram et al. (1992). The instrument used is ICP-MS (Plasma Quad) of VG, Elemental, Winsford, Cheshire, Uk. The accuracy of these determinations and other details are given
Results

37 mafic samples from Bayana basin referred herein as Bayana volcanics and 17 mafic samples from Khetri belt referred to as Khetri amphibolites have been analysed for major and trace elements. Six representative samples of Bayana volcanics and four representative samples of Khetri amphibolites have been analysed for their REE.

The major element compositions of Bayana volcanics and Khetri amphibolites are given in tables 3 and 4. The CIPW normative compositions of Bayana volcanics have been calculated and given in table 5. Normative compositions of Khetri amphibolites are not calculated due to their altered mineralogy. The trace element data along with important ratios are presented in tables 6 and 7. REE abundances and important ratios of the two suites are presented in table 8.

Major Element Distribution

Among many petrochemical indices, $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{FeO}$, $\text{MgO}$, $\text{CaO}$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{P}_2\text{O}_5$ and $\text{MnO}$ are commonly referred to as major elements because they constitute almost 99 percent of earth's crust and upper mantle. In igneous suites, the major elements show systematic variation which in turn produce igneous spectrum. Thus, they play an important role in
identification of magmatic rocks and in deducing their general chemical composition.

The geochemical behaviour of various major elements and their inter-element relationship serve as important parameters for the determination of the evolutionary trends of magma (Kuno 1960, 1968; Murata 1960; Poldervaart 1964; Miyashiro 1974, 1975), tectonic settings (Pearce et al. 1977; Rogers 1982; Mullen 1983), crustal thickness (Condie and Potts 1969; Naqvi and Hussain 1973 a,b; Dickinson 1975; Pearce et al. 1975) and the degree of partial melting as well as physico-chemical conditions during partial melting (Hanson and Langmuir, 1978; Sun et al. 1979; Langmuir and Hanson 1980; Francis et al. 1983). The relative concentrations of the major oxides of igneous rocks are also used in deduction of their magma type and the tectonic environment, which existed at the time of their formation (Gilluly 1971; Pearce et al. 1975, 1977; Mullen 1983; Condie 1985, 1986; Watters and Pearce 1987; Wilson 1989; Smith 1992; Tarney 1992). The important aspects of major element chemistry of Bayana volcanics and Khetri amphibolites are discussed in the following paragraphs:

Among major element oxides, silica which plays an important role in the determination of various rock types, show large variation from 43.61 percent to 58.34 percent (average 50.53 percent) in Bayana volcanics. In
Khetri amphibolites the $SiO_2$ contents show a range of variation from 38.62 percent to 50.60 percent (average 44.73 percent). There are some samples of Khetri amphibolites which have $SiO_2$ concentrations less than those expected for normal basalts (i.e. 45 percent : Le Bas et al. 1986). The concentrations of $SiO_2$ in these samples (table 4) appear to have been modified during the processes of alteration and metamorphism during post igneous period.

$Al_2O_3$, which is an essential structural constituent of many pyrogenetic minerals, widely varies from 9.42 percent to 17.23 percent (average 12.84 percent) in Bayana volcanics. In general the $Al_2O_3$ concentrations are higher in upper flows occurring in Jahaj area than those of lower flows from Ker village. In the Khetri amphibolites also the variation in $Al_2O_3$ contents is large, ranging between 5.34 percent to 14.85 percent (average 10.51 percent).

In Bayana volcanics, the $FeO^+$ contents show small range of variation i.e. from 11.15 percent to 15.81 percent (average 13.00 percent). However, in Khetri amphibolites the $FeO^+$ contents show considerably large range of variation from 6.89 percent to 21.16 percent (average 15.01 percent).

Since alkalis exhibit different geochemical behaviour during different geochemical processes, the
abundances of K and Na are considered to be an important petrogenetic indicator (Engel et al. 1974) and thus they have been variously used in identification of magma types of basaltic rocks and also in identification of the tectonic setting of mafic magmas (Miyashiro 1974; Sugisaki 1976; Cox et al. 1979; Le Bas et al. 1986). However, there is a general consensus that these elements are quite mobile during the post igneous processes (Coish 1977; Humphris and Thompson 1978; Ludden and Gelas 1982).

In Bayana volcanics the Na$_2$O contents do not show very large range of variation as it varies from 1.18 percent to 4.46 percent (average 2.48 percent), except one sample which has abnormally high Na$_2$O content 7.64 percent. Khetri amphibolites also show the similar variation in Na$_2$O contents ranging from 1.41 percent to 3.77 percent (average 2.80 percent).

K$_2$O contents in some of the samples of Bayana volcanics is very high (upto 4.71 percent). However, in most of the samples the K$_2$O content is 1 percent. The high K$_2$O samples are common in Jahai section particularly in the flows comprising the middle part of the volcanic sequence. High-K character of some of the flows from Jahai section has also been identified earlier (Singh 1985). Since no igneous intrusion is present in Bayana basin and no biotite is observed in thin section study of these samples, the high-K
character of some of the flows may be an original characteristic. Since high-K mafic rocks are generally found in rift related mafic sequence (e.g. East African Rift, Thompson et al. 1984; Davies and lloyd 1988) the occurrence of high-K mafic rocks in Bayana basin may be due to their occurrence in a rift related volcano-sedimentary sequence. The $K_2O$ concentration of Khetri amphibolites are low (<1 percent). However, few samples have very low $K_2O$ contents which may have been resulted due to alteration.

MgO contents of Bayana volcanics vary from 5.25 percent to 13.20 percent (average 8.21 percent), only two samples (No. 20 and 31) contain low amounts of MgO i.e. 2.06 percent and 3.17 percent respectively. However, the $SiO_2$ contents of these samples are high (58.34 percent and 55.27 percent respectively). In Khetri amphibolites the range of variation in MgO content is from 8.33 percent to 13.14 percent (average 10.24 percent). Glikson (1983) has used MgO content and MgO/$Al_2O_3$ ratio to distinguish the high-Mg basalts and tholeiitic basalts and placed the boundary between these two at about 10 percent MgO or above 8 percent MgO if MgO/$Al_2O_3$ ratio is $\geq 0.60$. According to this criteria, 43 percent samples of Bayana volcanics and all the samples of Khetri amphibolites are found to be high-Mg basalts while rest of the samples of Bayana volcanics are considered as tholeiitic basalts. The
abundance of CaO in volcanic rocks of Bayana show large range of variation from 1.42 percent to 10.47 percent (average 7.02 percent). In the Khetri amphibolites CaO content shows a range of variation from 8.97 percent to 14.44 percent (average 11.76 percent).

The minor elements viz. TiO₂, P₂O₅ and MnO are considered to be more resistant to the alteration processes and thus are of great petrogenetic importance (Chayes 1964; Winchester and Floyd 1976; Mullen 1983). In Bayana volcanics the TiO₂ abundances varies from 0.68 percent to 2.31 percent (average 1.42 percent) with most of the samples containing TiO₂ content ranging between 1 to 2 percent. In the samples of Khetri amphibolites TiO₂ concentration ranges from 0.12 percent to 2.54 percent (average 0.81 percent). In some of the samples of these amphibolites, particularly those from Madhan-kudhan area, the TiO₂ concentrations are very low (up to 0.12 percent).

The P₂O₅ content of Bayana volcanics varies from 0.11 percent to 0.34 percent (average 0.19 percent), only one sample of these volcanics have a high P₂O₅ concentration i.e. 0.42 percent. In Khetri amphibolites the P₂O₅ content varies from 0.12 percent to 0.22 percent (average 0.19 percent). However, few samples of these amphibolites have very low P₂O₅ concentration (upto 0.02 percent) and one sample shows a higher P₂O₅ concentration
(0.40 percent). The low TiO$_2$ (mostly 0.12 to 1.50 percent) and P$_2$O$_5$ (<0.3 percent) contents of these amphibolites are similar to many Proterozoic low-Ti tholeiites found in many Proterozoic mobile belts of the world (Pharaoh and Pearce 1984; Condie 1986; Pharaoh and Brewer 1990; Halden 1991) and Indian subcontinent (Raza et al. 1993).

**Trace Element Distribution**

The trace elements have several distinct advantages over major elements. In petrogenetic studies these elements act as powerful tools for tracing and modelling the igneous fractionation processes. The trace elements are partitioned more strongly than major elements into either crystalline or liquid phase thus making them more sensitive indicator of both degree and mechanism of differentiation. The abundance of trace element in basaltic rocks depends on several parameters such as its initial abundance in mantle source, the degree and extent of partial melting of that source, the nature of residual mineralogy and extent of equilibrium between residual minerals and its liquid, the P-T conditions at the site of melting and the extent of fractional crystallization in the melt during magma ascent (Nesbitt and Sun 1976). The trace element abundances of Bayana volcanics and Khetri amphibolites are discussed as follows:
Ferromagnesian elements

Ni, Cr, Co, V and Sc have been referred to as ferromagnesian trace elements or transitional elements. The crystal-liquid data indicate that these elements are preferentially partitioned into ferromagnesian minerals during partial melting and fractional crystallization processes. Thus the abundances of these elements are very useful indicator of petrogenetic processes particularly which operate in magma chambers or conduits.

Among the ferromagnesian elements Ni is considered to be a sensitive element to crystallization in the early stage of magmatic differentiation. In basaltic rocks the general behaviour of Ni is such that the element along with Cr preferentially enters into the octahedral coordination sites because of ligand field effect (Burns and Fyfe 1964). The concentration of Ni in basaltic rocks is generally controlled by ferromagnesian minerals like olivine and partly by pyroxene. When olivine and pyroxene of same rocks are compared, it is observed that the olivine are more enriched in Ni than pyroxenes.

In Bayana volcanics the Ni concentrations are low and range from 21 ppm to 187 ppm (average 88 ppm). In Khetri amphibolites the concentrations of Ni are much lower than those in Bayana volcanics (4 ppm to 71 ppm, average 27 ppm), only one sample (No 86) displays a higher
value (234 ppm).

Cr is another sensitive element which is considered to be useful indicator of petrogenetic processes in basaltic rocks, because Cr has a tendency to enter preferentially into the early formed pyroxenes. Due to valency difficulties, it prefers pyroxene and enters olivine only in limited amount (MacDougall and Lovering 1963; Turekian 1963; Burns and Fyfe 1964; Prinz 1967).

Cr ranges from 67 ppm to 397 ppm (average 249 ppm) in the rocks of Bayana volcanics. However, Khetri amphibolites are generally depleted in Cr showing range of variation from 24 ppm to 192 ppm (average 80 ppm).

The Co content shows range of variation from 23 ppm to 58 ppm (average 47 ppm) in Bayana volcanics. Whereas in the samples of Khetri amphibolites it varies from 7 ppm to 97 ppm (average 36 ppm). It has been suggested that Co, like Ni and Cr also occupies the octahedral coordination sites (Burns and Fyfe 1964) in basic magma and also that it enters the same mineral as Ni but comparatively in less amount (Turekian and Carr 1963; Burns and Fyfe 1964).

The concentration of V in the samples of Bayana volcanics ranges from 230 ppm to 284 ppm (average 252 ppm) except in sample No. 20 where it is 68 ppm. In Khetri amphibolites V concentrations are low showing a range of variation from 23 ppm to 136 ppm (average 58 ppm). The lower
V content in low-Ti samples of Khetri amphibolites suggests that Ti and V behaved quite similarly during most of magma differentiation history.

Large ion lithophile elements (LILE)

Rb, Sr, Ba, K and Th are included in the category of LILE. The concentrations as well as inter-element relationships of these elements are of great significance in petrogenetic processes (Lessing et al. 1963; Oxburgh 1964; Heir and Compston 1966; Brooks 1968; Drake and Weill 1975). However in basaltic rocks of older ages these elements except Th do not show their original contents as they are normally mobile during metamorphism and alteration and may provide some uncertainty or ambiguity. Thus they are not generally used for petrogenetic and tectonic interpretations. However, the mean values of large number of samples from an individual succession of given age can be used because in such cases the losses and gains of these elements are averaged out. Since a small number of samples of Khetri amphibolites are analysed for LILE, the concentrations of these elements are not discussed herein.

The concentrations of Rb, Sr and Ba in Bayana volcanics show ranges of variation i.e. Rb: 4 to 159 ppm (average 49 ppm) Sr: 63 to 323 ppm (average 185 ppm) Ba: 83 to 1106 ppm (average 374 ppm).

Th which remains immobile during post igneous
processes, (Pharaoh et al. 1987) is generally low in Bayana volcanics (~2 ppm). However, the abundances are significantly high in high-K samples and goes up to a maximum of 16.00 ppm at 4.32 percent K$_2$O (sample 18). An increasing trend of K$_2$O with increasing Th concentrations suggests original K abundances. Despite depleted in K$_2$O, the Th contents in Khetri amphibolites are relatively high (>3 ppm) except sample 98 which contains Th = 1.60 ppm. Low contents of K$_2$O in Khetri amphibolites are probably a consequence of their mobilization through post magmatic processes.

High field strength elements (HFSE)

The elements having small ionic radii and low radius/charge ratios are classified as high field strength elements (HFSE). Zr, Y, Nb, Hf and Ta are the trace elements which have been grouped in this category. Other than these elements the minor elements Ti and P are also grouped with them. In basaltic melts these elements tend to be strongly incompatible, having very small bulk partition coefficient, are considered immobile during low temperature alteration (Pearce and Norry 1979; Saunders et al. 1980; Shervais 1982). The concentrations, particularly their inter-element ratios remain unaffected by the process of fractionation of olivine, clinopyroxene and plagioclase (Cox et al. 1979). This property together with their systematic variation in fresh lavas, has made them sensitive indicators of their
source region (Erlank and Kable 1976; Pearce and Norry 1979; Sun et al. 1979; Pearce 1982). In the study of basaltic rocks, these elements have several advantages over other elements due to their distinct geochemical behaviour. First and most important characteristic is that they are generally immobile during weathering, hydrothermal alteration and metamorphism (Pearce and Cann 1973; Winchester and Floyd 1976; Pearce and Norry 1979; Pearce 1982). Secondly, in the crust these elements are held in refractory minerals such as zircon, sphene and epidote, due to which small degree of crustal melting is unable to partition these elements strongly into the melt (Watson and Copobiano 1981; Watson and Harrison 1984). Due to this property even selective assimilation of crustal material into basic magmas does not affect their primary abundances.

Zr contents of Bayana volcanics vary from 50 ppm to 182 ppm with an average of 99 ppm. In comparison to Bayana volcanics the Khetri amphibolites are depleted in Zr as indicated in table 10 where Zr varies between 11 ppm to 85 ppm with an average of 52 ppm.

The Y content shows range of variation from 17 ppm to 34 ppm (average 23 ppm) in Bayana volcanics and from 7 ppm to 29 ppm (average 17 ppm) in Khetri amphibolites. Despite similar ranges of variation in both rock suites the Bayana volcanics are more enriched.
23 ppm) as compared to Khetri amphibolites (average 17 ppm).

Nb content in Bayana volcanics ranges from 6 ppm to 19 ppm (average 9.60 ppm). However, two samples (Nos 2 and 16) have low Nb contents i.e. 4 ppm and 3 ppm respectively. In the amphibolites of Khetri belt Nb values are relatively low, except sample 86 (Nb = 13 ppm) other samples have Nb contents less than 9 ppm.

The Nb/Y ratio, which serves as an indicator of alkalinity, is low (< 1) both in Bayana volcanics and Khetri amphibolites, indicating a sub-alkaline nature of both suites (Pearce and Gale 1977). Average Zr/Nb ratio of Bayana volcanics (12.93) and Khetri amphibolites (8.84) are much lower than that of primordial mantle (Zr/Nb=18) indicating an enriched nature of their sources.

**Rare Earth Elements (REE)**

The rare earth elements (REE) form a group of fifteen elements from Lanthanum (La) to Lutetium (Lu) with atomic numbers ranging from 57 (La) to 71 (Lu). Despite similarity in their chemical behaviour, they can be partially fractionated, one from another, by several magmatic processes. All the REE except for Eu and Ce, are trivalent under most geological conditions. Eu is both trivalent and divalent whereas Ce is tetravalent. There is small but steady decrease in the ionic radii for the trivalent REE in octahedral coordination from La to Lu.
Thus, a given REE has geochemical characteristics very similar to those of its nearest atomic neighbour but differs systematically from those of the REE with greater or smaller atomic numbers (Hanson 1980). These are the characteristics which make the REE an important tool in igneous petrogenesis. The measured degree of REE fractionation in a rock can be a pointer to its genesis. The REE abundances normalized against chondritic values prove to be a widely useful way to examine relationship between and within the suites of igneous rocks, particularly in terms of partial melting and fractional crystallization modelling. REE data on Bayana volcanics as well as on Khetri amphibolites are not presently available in literature.

In the present study six representative samples of Bayana volcanics and four samples of Khetri amphibolites have been analysed for REE and data is presented in table 8 and their chondrite normalised patterns are shown in figure 4 A and B respectively. In Bayana volcanics the samples show REE enrichment from about 40 - 70 x chondrite for LREE and about 6 -11 x chondrite for HREE. Sample 20, which represents the high-K sample is more enriched in LREE (about 177x chondrite) but its HREE are similar to those of other samples (about 12x chondrite). In general the LREE enrichment in Bayana volcanics is moderate to strong with \((\text{Ce}/\text{Yb})_n\) ratio ranging between 4.04 to 5.15.
Figure 4 Chondrite normalized REE patterns for representative samples of Bayana volcanics (A) and Khetri amphibolites (B) illustrating their REE enriched nature. Normalizing values are after Palme et al. (1981).
However, the (Ce/Yb)n ratio of high-K sample (No. 20) is very high (9.71) showing its highly LREE enriched nature. In general the REE patterns of Bayana volcanics are gentle, moderately enriched without having any significant Eu anomaly, implying lack of plagioclase fractionation. On the other hand the REE profile of high-K sample is steep, strongly LREE enriched with almost flat HREE and without any Eu anomaly. The (La/Yb)n ratio, which can not be considerably increased by fractional crystallization (Cf. Bender et al. 1984; Albarede and Tamagnan 1988), is also high in this sample and shows more than 2 fold increase when compared to other samples.

REE patterns of all the samples of Khetri amphibolites are similar in shape to each other except the nature of Eu anomalies. They show strong REE enrichment from about 58-132 X chondrite for LREE and about 3-7 X chondrite for HREE. (La/Lu)n ratio varies from 14.85 to 38.14. Although REE patterns of the samples from each area i.e. Madhan-Kudhan and Kolihan are parallel to each other, the samples of one area have crossing relationship with those of other. While the samples of Madhan-Kudhan area display strong positive Eu anomalies, the samples from Kolihan area have negative Eu anomaly (sample No. 86) or no Eu anomaly at all (sample No. 87).
Effect of Alteration

Most of the Precambrian volcanic rocks have suffered alteration, sometimes up to such an extent that their original compositions are completely obscured. The most common types of alteration observed from the study of older volcanics from different Precambrian areas are albitization, epidotization, silicification, carbonation and chloritization and the mineral assemblages produced by such types of alteration are similar to low grade metamorphic assemblages (Jolly and Smith 1972; Condie et al. 1977; Strong et al. 1979). In some instances the alteration occurs purely in response to progressive low grade regional metamorphism, while in other cases secondary minerals such as carbonate, quartz and sericite may replace low grade assemblages and cross cut foliation indicating post metamorphic alteration (Condie et al. 1977; Condie 1982b).

In geochemical studies of older volcanic rocks it is necessary to verify whether the rock bears magmatic composition or the composition has been modified during post igneous period, and if so, then up to what extent. It is a common observation that the distribution of major and trace elements can be modified during or after the magmatic activity through the processes of alteration (Christlein et al. 1973; Hart et al. 1974; Scott and Hajash 1976; Winchester and Floyd 1976; Ludden and Thompson 1978).
However, there are considerable informations regarding the alteration of basic igneous rocks of various ages (Pearce and Cann 1973; Coish 1977; Ozima et al. 1977; Winchester and Floyd 1977; Humphris and Thompson 1978; Raza 1985) particularly on the rocks of Precambrian volcanic sequences (Jolly and Smith 1972). It is important to investigate whether the concentration of any particular element or group of elements have been modified during alteration and/or metamorphism, so that they can be excluded from the petrogenetic evaluation. Petrographic studies generally give primary clues regarding the effect of alteration. Presence of minerals like chlorite, tremolite, talc etc. indicate alteration and/or metamorphism.

Various methods are currently used to overcome the problem of alteration. In present study we have tried to select a series of samples containing magmatic textures and original minerals. Such samples are commonly found in Bayana volcanics, because they are unaltered, hard, massive and vesicular with intact igneous minerals and undisturbed textural features. Their magmatic features are well preserved because they are almost unmetamorphosed or metamorphosed only upto lowest grade of greenschist facies metamorphism (Sharma 1988). No intrusions are present in the area which could alter these rocks and they have not been affected by any prominent deformation leaving them virtually
undeformed. In this manner the fresh and unaltered samples are easily available.

On the other hand, the amphibolites of Khetri belt are generally metamorphosed and their host sequence is intruded by a number of granite bodies. Although presence of relict magmatic textures and minerals at places and their chemical characteristics attest their igneous origin, the bulk mineralogy of Khetri amphibolites is dominated by secondary minerals. The occurrence of secondary minerals such as amphibole, quartz, epidote, chlorite and calcite suggests that phenocrysts probably of plagioclase, clinopyroxene and augite have been extensively altered during post igneous processes.

In view of the above discussion it is expected that, under type of alteration that the Bayana volcanics have undergone, the concentration of even major elements are not grossly distributed. However, in case of Khetri amphibolites the major elements particularly K, Na, Ca and probably Si can not be considered reliable (e.g. Beswick and Soucie 1978; Davies et al. 1979) and therefore, can not be used for petrogenetic interpretations. In such a situation the reliance can be placed only on trace elements and REE which are considered immobile or less mobile in various studies made on ancient volcanic suites (Pearce 1970; Pearce and Cann 1973; Wood et al. 1979; Pearce 1982;
Meschede 1986). Although some major elements will be used to identify the magma type of Khetri amphibolites, the result obtained would be confirmed by using immobile trace element before reaching any meaningful conclusion. As a precautionary measure, in case of Bayana volcanics also, the immobile elements would be used to verify the results obtained from major element composition.

To test the degree to which post igneous processes may have affected the whole rock geochemistry, particularly of the Khetri amphibolites, the data is plotted on a MgO/10- CaO/Al₂O₃ - SiO₂/100 triangular diagram devised by Davis et al. (1978) and used by Schweitzer and Kroner (1985). Most of the samples of Khetri amphibolites fall within the "not altered" field and satisfy Davis' criteria for mineral metasomatic alteration (Figure 5). The plot of some of the Bayana volcanics outside the "not altered" field towards MgO apex may be due to their comparatively high Al₂O₃ and MgO contents. Since these samples are mineralogically and texturally unaltered, they can not be considered as chemically altered.

It is generally believed that Ti, like HFSE is immobile during the alteration processes including low grade metamorphism (Pearce and Cann 1973; Pearce et al. 1975; Winchester and Floyd 1976, 1977; Mullen 1983). To assess the validity of MgO and CaO data for Bayana volcanics
Figure 5 CaO/Al$_2$O$_3$-MgO/10-SiO$_2$/100 ternary diagram (after Davis et al. 1978) for Bayana volcanics and Khetri amphibolites. Most of the samples of both rock suites plot inside or close to the field of unaltered rocks, indicating little effect of post igneous processes on the bulk-chemistry.
their MgO/TiO$_2$ and CaO/TiO$_2$ ratios are plotted in figure 6. Despite a scatter, a sympathetic relationship is observed, that does not favour any significant effect of alteration processes on these elements.

The REE patterns of both the Bayana volcanics and Khetri amphibolites are regular and similar for all the samples in each suite. Despite mineralogically altered nature of Khetri amphibolites, together with the fact that samples are from two different areas, the REE patterns of all the samples are almost parallel except the nature of Eu anomalies. Although Eu anomalies in basaltic rocks have been attributed to plagioclase fractionation (Sun et al. 1974; Sun and Nebitt, 1978), they could also be produced by effect of alteration (Sun and Nesbitt 1978). Considering the secondary mineralogy of Khetri amphibolites it appears likely that the observed variation in Eu anomalies of Khetri amphibolites may be due to alteration effects. Furthermore, the ratios of supposedly mobile REE such as La, Ce and Nd (Condie et al. 1977; Sun and Nesbitt 1978; Helleman et al. 1979; Furner 1980) show narrow range of variation e.g. (La/Ce)$_n$ = 1.34 to 1.88, (La/Nd)$_n$ = 1.94 to 3.64, (Ce/Nd)$_n$ = 1.45 to 2.18. In general the parallel and generally similar REE patterns of Khetri amphibolites suggest that concentration of their rare earth elements except Eu, are primary and can be used for the evaluation of petrogenetic processes.
Figure 6 MgO/TiO$_2$ versus CaO/TiO$_2$ diagram for Bayana volcanics showing a slightly scattered but sympathetic relationship, as an indication for little effect of alteration in terms of these major element ratios.
Element Variability

The crystal-liquid fractionation processes related to either partial melting or fractional crystallization have a capability to produce compositional variation in an igneous suite. There are numerous variation diagrams and chemical parameters which account chemical differences and trends shown by a related suite of lavas in which the compositional variation is a consequence of crystal-liquid fractionation processes. Some diagrams have been proved very useful in derivation of models to explain the petrogenesis of a particular igneous assemblage. In the present section the geochemical data of Bayana volcanics and Khetri amphibolites are discussed to assess the chemical variations in these suites. These variations may be proved useful to find out the original and evolutionary history of these rock suites.

One of the most commonly used variation diagram in igneous petrogenesis is the Harker's diagram, in which the weight percent of the constituent oxides are plotted against the weight percent of SiO$_2$ (Harker 1909). SiO$_2$ is generally chosen on abscissa as an index of differentiation. Coherent trends on Harker's diagram are generally interpreted as to represent the course of geochemical evolution of magma and are referred to as liquid lines of descent. When the concentration of various element
oxides of Bayana volcanics and mafic amphibolites of Khetri belt are plotted against their SiO\textsubscript{2} contents (Figures 7 A and B respectively), no meaningful correlation of any oxide with SiO\textsubscript{2} observed except MgO which shows progressive depletion with respect to SiO\textsubscript{2}. Because both SiO\textsubscript{2} and MgO are considered as good indicators of igneous fractionation, their negative correlation suggests that the fractional crystallization has played an important role during the evolution of these rocks. Moreover, the negative correlation between SiO\textsubscript{2} and MgO also indicates the fractionation of olivine. In Bayana volcanics the inconsistent relationships of other oxides with SiO\textsubscript{2} may be attributed to non differentiation related relationship between various flows which might have undergone independent differentiation. However, in case of Khetri amphibolites it may also be due to their altered mineralogy.

To determine the variation in the chemical composition in terms of differentiation from primitive to more evolved composition, Mg numbers (100 Mg/Mg+0.85 Fe, all in cation percent, Sevigny 1988) have been used. The Mg numbers in the Bayana volcanics and Khetri amphibolites show large variation in their values. In the Bayana volcanics the Mg number shows a range of variation from 49 to 71 (average 56) except in samples 20 and 31 which show values of 25 and 37 respectively. Whereas in the Khetri amphibolites Mg
Figure 7A Harker's variation diagram (after Harker 1909) for Bayana volcanics showing insignificant relationship between SiO$_2$ and most of the major oxides.
Figure 7B Harker's variation diagram (after Harker 1909) for Khetri amphibolites showing inconsistent relationship between SiO$_2$ and all the major oxides.
numbers vary from 50 to 76 (average 60). It is generally believed that Mg numbers are insensitive to the degree of partial melting but are highly sensitive to the amount of subsequent fractional crystallization, particularly of olivine. The very low to very high Mg numbers shown by both of these basic rocks indicate their near primitive to highly evolved nature.

$\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{CaO}/\text{TiO}_2$ ratios of basaltic rocks have been variously interpreted (Sun and Nesbitt 1978; Nesbitt et al. 1979; Sun et al. 1979; Hickey and Frey 1982; Rajamani et al. 1985; Ahmad and Bhat 1987). Sun et al. (1979) argued that $\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{CaO}/\text{TiO}_2$ ratios in MORB vary with degree of partial melting and the nature of the source region because CaO and $\text{Al}_2\text{O}_3$ behave compatibly and $\text{TiO}_2$ incompatibly during initial phase of melting. With increasing degrees of partial melting the CaO and $\text{Al}_2\text{O}_3$ bearing phases are exhausted, with further increase in partial melting CaO and $\text{Al}_2\text{O}_3$ also behave incompatibly. In this manner the CaO/TiO$_2$ and Al$_2$O$_3$/TiO$_2$ ratios will continue to increase till they reach the source ratio. Further melting will not change these ratios but the abundances of $\text{Al}_2\text{O}_3$ and CaO will be diluted. $\text{Al}_2\text{O}_3/\text{TiO}_2$ and CaO/TiO$_2$ ratios of Bayana volcanics and Khetri amphibolites are plotted against their TiO$_2$ contents in figures 8 A and B respectively. In these diagrams the samples of Bayana
Figure 8A TiO₂ versus Al₂O₃/TiO₂ and CaO/TiO₂ variation diagrams (after Nesbitt et al. 1979) for Bayana volcanics. Arrows indicate fractionation vectors for olivine (Ol), clinopyroxene (Cpx) and plagioclase (Plag).
Figure 8B TiO\textsubscript{2} versus Al\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} and CaO/TiO\textsubscript{2} variation diagrams (after Nesbitt et al. 1979) for Khetri amphibolites. Note the relatively large variation in TiO\textsubscript{2} contents. Cpx=clinopyroxene, Ol=olivine, Plag=plagioclase.
volcanics plot through almost the whole field of MORB and beyond towards higher TiO₂ contents. CaO/TiO₂ ratios plot slightly below the field of MORB. Moreover, both Al₂O₃/TiO₂ and CaO/TiO₂ ratios of Bayana volcanics are lower than chondritic ratios (20 and 17 respectively). The trends displayed by Bayana volcanics may be interpreted in different ways (Ahmad and Bhat 1987) such as (1) These rocks have been derived from the melts generated through varying degree of partial melting with samples containing high TiO₂ are products of low degree of partial melting. (2) The magma evolved through fractional crystallization of olivine (+ orthopyroxene), clinopyroxene and plagioclase. (3) The rocks have been derived from a heterogeneous source. The relative importance of these processes during the evolution of Bayana volcanics would be discussed under the heading of petrogenesis (chapter Five).

In Al₂O₃/TiO₂ versus TiO₂ and CaO/TiO₂ versus TiO₂ variation diagrams, the Khetri amphibolites display a much larger variation relative to MORB field of Sun et al. (1979), with many samples having the highest Al₂O₃/TiO₂ (upto 82) and CaO/TiO₂ (upto 108) ratios. The high Al₂O₃/TiO₂ and CaO/TiO₂ ratios of these rocks may be either due to their derivation from a more refractory source or fractionation of Ti bearing phase during their evolution.

In CaO/Al₂O₃ versus MgO diagram (figure 9)
Figure 9 MgO versus CaO/Al\textsubscript{2}O\textsubscript{3} variation diagram of Bayana volcanics and Khetri amphibolites showing positive relationships which suggest the dominance of clinopyroxene fractionation.
the positive relationship is displayed by Bayana volcanics as well as Khetri amphibolites. However, the samples of Khetri amphibolites from Kolihan and Madhan-Kudhan areas plot along two different trends. A decrease in CaO/Al2O3 with decreasing contents of MgO suggests the dominance of clinopyroxene fractionation (Zhao 1994).

Several workers have made successful attempts to correlate the trace element abundances with source characteristics and fractionation processes (Allegre et al. 1977; Hanson 1980; Carr and Fardy 1984). The compatible elements Ni, Cr and Co of Bayana volcanics and Khetri amphibolites are plotted against MgO in figure 10. Despite a scatter a positive relationship between MgO and Cr and MgO and Co is observed in the plots of Bayana volcanics. The samples of Khetri amphibolites are subjected to scatter in all these diagrams and those of Bayana volcanics in MgO - Ni diagram.

Ti/V ratio in basaltic melts is considered to be a function of oxygen fugacity, the degree of partial melting and fractional crystallization and therefore is considered to be a diagnostic feature for tectonic setting (Shervais 1982). Ti and V contents of Bayana volcanics and Khetri amphibolites are plotted in figure 11, in which both of these suites display a positive relationship. However, they plot to the right of chondrite line suggesting that V
Figure 10 MgO-Cr, MgO-Ni and MgO-Co variation diagrams for Bayana volcanics and Khetri amphibolites.
Figure 11 Ti versus V diagram (after Shervais 1982) for Bayana volcanics and Khetri amphibolites showing positive relationships.
has been depleted relative to Ti. The depletion of V relative to Ti with respect to chondrite abundances may be an inherited non-chondritic feature in the upper mantle.

In Zr versus Y, Nb and Ce diagrams (Figure 12) both Bayana volcanics and Khetri amphibolites show enrichment of Zr relative to Y, enrichment of Nb relative to Zr and enrichment of Ce relative to Zr, suggesting the derivation of these rocks from an enriched source. In Zr versus TiO$_2$ diagram (Figure 12) the Bayana volcanics show a positive trend and most of the samples falling below the chondritic line. However, the samples of Khetri amphibolites plot well below the chondritic line and roughly follow the Calc-alkaline trend. A positive relationship between Zr and Zr/Y (Figure 12) is also displayed by Bayana volcanics. On the other hand, the Khetri amphibolites do not show any particular trend in this diagram. In Zr versus P$_2$O$_5$ diagram (Figure 12) both Bayana volcanics and Khetri amphibolites are subjected to scatter.
Figure 12 Zr versus various incompatible elements (Y, Nb, Ce, TiO₂ and P₂O₅) and element ratio (Zr/Y) plots for Bayana volcanics and Khetri amphibolites. Arrows indicate fractionation vectors for plagioclase (Plag), olivine (Ol), clinopyroxene (Cpx) and magnetite (Mt) used by James et al. (1987). Primordial mantle ratios are after Sun and McDonough (1989).