CHAPTER 5

PETROGENESIS

It is important to arrive at an agreement about the nature of the RJY basalts before discussing the petrogenesis in detail.

5.1 PRIMARY NATURE

Earlier, workers like Sukheshwala and Poldervaart (1958) and Subba Rao (1965) were of the view that the tholeiites are parental to picritic basalts. But, the growing evidences strongly support that the tholeiites are not primary in nature but have undergone extensive differentiation from more basic parental melt i.e., picrites which in turn are derived from the upper mantle peridotitic source with extensive partial melting (Green and Ringwood 1967; Cox, 1980).

The conclusion, that the commonly erupted basaltic rocks are derived from picritic magma is based on the following observations.

1. There is geophysical evidence for the existence of significant magma chambers under currently active volcanoes, mid-oceanic ridges i.e., chambers in which crystal fractionation can take place.

2. Low pressure phenocryst assemblages such as, pyroxenes, plagioclases are prevalent in common basalts, indicating the liquid compositions are equilibrated to low pressure crustal conditions rather than that of high pressure mantle conditions (O'Hara et al., 1975).
3. From the experimental petrology studies it is known that the tholeiites with even 9-10 percent MgO are not in equilibrium with olivene at mantle pressures (O'Hara et al., 1975). The commonly accepted values of Mg number for mantle parental melts is 70 to 72, according to the report on "Basaltic volcanism project" (1981).

The RJY basalts with low Mg-number ranging from 38 to 47 and having low values of Ni, Cr, Co therefore indicate their derivation from more basic parental melts with Mg number higher than 60 as suggested by Cox (1980).

5.2 PARTIAL MELTING

5.2.1 Sr/Ca-Ba/Ca (SB) systematics.

The parental melts of RJY tholeiites have undergone large degrees of partial melting before they reached crustal magmatic chambers and were subjected to extensive differentiation-fractionation processes during their evolutionary trend. In order to estimate partial melting percentages, SB systematics as suggested by Onuma et al. (1968) and Matsui (1977) diagram has been used.

Of the three elements, Ca, Sr, and Ba, the large cation Ca is contained mainly in clinopyroxene, while the other cations Sr and Ba do not enter into the three major phases (olivene, orthopyroxene and clinopyroxene) and in the two minor phases (garnet and spinel) by crystal structure control in the mantle conditions. When the mantle materials are gradually heated, small degrees of partial melting produces strong
enrichment of Sr and Ba in the melt and therefore, Sr/Ca and Ba/Ca ratios of the melt are the largest one. With increasing degrees of partial melting, Sr and Ba contents of the early melt is diluted with further melting of the Sr and Ba-poor mineral phases. At a stage, when garnet and clinopyroxene begin to melt, Ca content of the melt increases with addition of Ca from them and the Sr/Ca and Ba/Ca ratios of the melt accordingly decreases with a constant Sr/Ba ratio. Orthopyroxene having small amounts of Ca and lack of Sr and Ba hardly changes Sr/Ca and Ba/Ca ratios of the melts with a still constant Sr/Ba ratio. The melt evolved by complete melting of the mantle materials has the same Sr/Ca and Ba/Ca ratios as in the mantle materials. Therefore, a series of melts derived directly from the mantle materials with different degree of partial melting will follow a Sr/Ca-Ba/Ca evolutionary line with a slope of 45° through the mantle material as shown in Fig (5.1).

At any stage of partial melting, if the melt starts crystal fractionation it will follow the following trend. The fractinating clinopyroxene will preferentially take Ca and exclude Sr and Ba thus increasing Sr/Ca and Ba/Ca ratio. (Onuma et al., 1968; Matsui et al., 1977). But the increase in the Ba/Ca is certainly much greater than the Sr/Ca in the melt. In the case of plagioclase fractionation Sr/Ca ratio in the melt does not change, while Ba/Ca ratio increases greatly. This is because it takes both Ca and Sr with similar degree and excludes Ba by the crystal structure control (Higuchi and Nagasawa, 1969; Mastui et al., 1977). Thus, a series of melts via clinopyroxene and plagioclase fractionation make another SB systematics with a gentler slope through the primary magma as shown in Fig (5.1). It should be noted, however, that
Fig 5.1 Ba/Ca vs Sr/Ca systematics plot showing partial melting percentages for RJY basalts. The slope corresponds to nearly constant Sr/Ba ratio with variable Ca in the plot. After (Onuma and Montoya, 1982) + Pangidi lower flow; o Pangidi upper flow and o Kateru upper flow.
olivene, orthopyroxene and magnetite fractionation process do not change both Sr/Ca and Ba/Ca ratios, since these minerals do not accept the triad (Ca, Sr and Ba). But the SB systematics does not rule out the possibility of olivene fractionation in the primary magama during its ascent.

A rough estimate of 30 to 35 percent of partial melting can be attributed for the derivation of parental melts of Rajhamundry basalts. The SB systematics also indicates that plagioclase and pyroxene are the possible fractionating phases in the evolution of RJY basalts.

However, the effect of secondary alteration on these elements Ca, Sr and Ba are considered before drawing conclusions. It is observed that the alteration in RJY basalt is limited and do not influence the results above. The results were also cross checked using the equations proposed by Chen-Hsia-Chen,(1988).

5.2.2 Partial melting estimations (Chan-Hsia-Chen, 1988)

Equation 1

\[ F_0 = \frac{1}{0.957} \left[ \frac{(Na_2O + K_2O)_S}{(Na_2O + K_2O)_m} - 0.0149 \right] \]

Equation 2

\[ F_C = \frac{0.9348(Al_2O_3/SiO_2)_S/(Al_2O_3/SiO_2)_m - 0.1532}{0.108(Al_2O_3/SiO_2)_S/(Al_2O_3/SiO_2)_m + 0.597} \]

The subscripts 'S' and 'm' represent source and supposedly primary magma or melt respectively. A correct estimate or choice of
source composition and composition of primary magma are important for the calculation.

Direct estimation of partial melt percentages are not possible because parental magma compositions are unknown in the present study area. However, with the help of mass balance equation, the supposedly parental magma (m) composition are calculated, by adding dunite compositions to the average RJY basalts compositions in various proportions. The estimated compositions are similar to that of picritic basalt compositions, which are supposed to be parental to RJY basalts. The estimated partial melting percentages thus calculated for Equation No.1 and 2 of Chao-Hsia-Chen (1988) range from 28.7 to 32.9 and 31.7 to 34.6 respectively (Table. 5.1). These estimates are in agreement with the estimates using SB systematics. It can also be suggested from this, that major element Ca in RJY basalts has not been removed out of the system during the alteration of pyroxene to chlorite and that the alterations has effected only on minor scale.

5.3 FRACTIONAL CRYSTALLIZATION

Extensive fractional crystallization of gabbroic material is well documented for Deccan basalts (Sen, 1988). The model would also hold good in the case of RJY basalts also. The inset of Fig. (5.2a) shows how the overall trend of RJY basalts is best explained by gabbro fractination. The encloser 01-Cpx-Pl represents plausible compositional ranges of the fractionating gabbroic assemblages.

5.3.1 Oxide-oxide plots (Fig 5.2 a,b,c and d) of RJY tholeiites are
TABLE 5.1 Estimation of degree of partial melting by equations proposed by CHAO-HSIA CHEN (1988).

Compositions used in the calculation of parental melt. (in mole percent)

<table>
<thead>
<tr>
<th></th>
<th>Basalt (Average of 20 samples)</th>
<th>Dunite</th>
<th>Plagioclase (RJY Microprobe data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>0.4937</td>
<td>0.3829</td>
<td>0.505</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.0235</td>
<td>0.0009</td>
<td>0.0004</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.1272</td>
<td>0.0182</td>
<td>0.31</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.0385</td>
<td>0.0319</td>
<td>0.0</td>
</tr>
<tr>
<td>FeO</td>
<td>0.1006</td>
<td>0.0938</td>
<td>0.0051</td>
</tr>
<tr>
<td>MnO</td>
<td>0.0014</td>
<td>0.0071</td>
<td>0.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.0536</td>
<td>0.3794</td>
<td>0.0027</td>
</tr>
<tr>
<td>CaO</td>
<td>0.0996</td>
<td>0.0101</td>
<td>0.152</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.0283</td>
<td>0.0020</td>
<td>0.0311</td>
</tr>
<tr>
<td>K2O</td>
<td>0.0063</td>
<td>0.0008</td>
<td>0.0001</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.0025</td>
<td>0.0020</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Proportions of Basalt + Dunite + Plagioclase

Partial melting percentages with Percentages Equation I Equation III

<table>
<thead>
<tr>
<th>Basalt + Dunite + Plagioclase</th>
<th>Partial melting percentages with</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentages</td>
<td>Equation I</td>
</tr>
<tr>
<td>62.0 + 38.0 + 0</td>
<td>30.0 %</td>
</tr>
<tr>
<td>64.0 + 36.0 + 0</td>
<td>30.4 %</td>
</tr>
<tr>
<td>64.5 + 35.5 + 0</td>
<td>28.7 %</td>
</tr>
<tr>
<td>64.9 + 35.5 + 0</td>
<td>29.13 %</td>
</tr>
<tr>
<td>55.0 + 45.0 + 0</td>
<td>32.85 %</td>
</tr>
<tr>
<td>63.0 + 37.0 + 0</td>
<td>34.3 %</td>
</tr>
<tr>
<td>62.0 + 37.0 + .009</td>
<td>29.3 %</td>
</tr>
<tr>
<td>62.4 + 37.5 + .1</td>
<td>29.34 %</td>
</tr>
<tr>
<td>65.9 + 35.0 + .1</td>
<td>29.7 %</td>
</tr>
<tr>
<td>62.5 + 37.4 + .1</td>
<td>29.3 %</td>
</tr>
<tr>
<td>54.0 + 45.0 + 1.0</td>
<td>32.92 %</td>
</tr>
</tbody>
</table>
Fig. 5.2 Oxide - oxide plot (Wt%) of RJY basalts compared with the near solidus trends of the multicomponent system HK-66-KRB studied by Takashashi and Kushiro (1983)
compared with the near solidus trend of the multicomponent system MK-66-KRB studied by Takashahi and Kushiro (1983). Fields of western and central Deccan basalts are given for comparison in the plot (Sen, 1988). In these plots, the RJY samples plot away from the low pressure kink region in these plots suggesting more evolved character at low pressures than the Deccan basalts.

5.3.2 Various incompatible elements such as TiO₂, K₂O, show enrichments with increasing differentiation (decreasing Mg-Number) suggesting fractional crystallization to be the dominant process in the evolution of RJY basalts (Fig. 5.3).

These basalts show a strong enriched LREE distribution patterns, suggesting garnet to be the principle residual phase in the source. Positive correlation between total REE and SiO₂ (Fig. 5.4) suggests the role played by fractional crystallization mechanism for these basalts. REE contents also increases with the increase of TiO₂ and P₂O₅ contents (Fig. 5.5) in these rocks. Titanium is present in pyroxenes. Therefore the contents of pyroxenes have great influence on the concentration of REE in RJY basalts. SiO₂ shows positive correlation with Na₂O and K₂O and negative correlation with CaO and MgO. This is characteristic of clinopyroxene fractionation from the melt and this further supported by positive correlation of Ni and Cr and positive correlation of Cr and Sc against Mg number also indicate fractionation of clinopyroxene.

Consistency in the normalized (Ce/Yb) and HREE abundances are clear indicators of pyroxene fractionation (Kay et al., 1979; Saunders, 1984). RJY basalts do not show any Europium anomalies.

5.3.3 Increase of Al₂O₃ wt percent with increasing fractionation
(decreasing Mg number) suggest plagioclase fractionation (Fig. 5.6). The plagioclase fractionation is further substantiated in the plot of Mg-number versus Sr ppm (Fig. 5.7). Sr is notably partitioned into plagioclase rather than other phases. Buffering of Sr to almost a constant value is absolutely typical of gabbro fractionation because the partition coefficients (plagioclase/liquid) is about 2 and since half the extract is typically plagioclase the bulk partition coefficient is about one (Cox, 1980; Cox and Howkesworth 1985). Though Sr is considered to be partially affected by secondary mobilization, its conspicuous negative anomaly in the spidergrams (Fig. 5.8) would strongly reflect the plagioclase fractionation. Absence of Europium negative anomaly in RJY basalts alone doesn't rule out the possibility of plagioclase fractionation. Generally continental basalts does not show Eu anomalies (Culler and Graph., 1984; Cox et al., 1980).

5.3.4 In Al2O3/TiO2 versus Ti ppm plot (Fig. 5.9) after Pearce and Flower (1977), vectors for 50 percent fractionation are drawn. RJY samples show fractionation of pyroxenes dominating over plagioclase phase. Since olivene, orthopyroxene and plagioclase have very low Kd values for Ti, it should be effected mainly by the fractionation of clinopyroxene (Pearce and Norry, 1979).

5.3.5 Al-Si Cation Plot: An approximate melt field in the Al-Si space that could coexist with pyrolite-3 is shown with contours for different pressures, temperatures and percentages of melting (Francis et al., 1983). The majority of the samples fall in 1250°- 1300° C temperature grid. However, two samples show 1250°C temperature. The plot also suggests negative relationship between Al and Si indicating plagioclase
Fig. 5.3 Mg number vs various elemental plots for RJY basalts
Ni and Cr shows positive correlation and TiO2, 
K2O, Sc and Ba show negative relationship.
Fig. 5. Total REE as a function of SiO$_2$ indicating the role of differentiation-fractionation for RJY basalts
Fig. 5.5a  Plot indicating the trend between total REE and TiO$_2$ for RJY basalts

Fig. 5.5b  Plot indicating the trend between the total REE and P$_2$O$_5$
Fig. 5.6 Al2O3 wt% variation as a function of Mg number suggesting plagioclase fractionation of RJY basalts (Cox, 1980)

Fig. 5.7 Sr ppm variation as a function of Mg # indicating plagioclase fractionation (Cox, 1980)
fractionation (Fig. 5.10)

5.3.6 MgO-FeO Plot: Fig. 5.11 shows that all the samples plot well below the compositions of the melts that could be in equilibrium with pyrolite at 101 Kpa. They show large variation of cation percent FeO for a limited range of cation percent MgO. There is not much difference in samples from both lower and upper flows and they plot around 1200°C temperature contour. The position of majority of samples indicate that they could not have been derived through differentiation from a melt in equilibrium with a pyrolite source.

As indicated by the olivene fractionation curves, below 1300°C both FeO and MgO start decreasing in the melt if only olivene fractionates. This is because below 1300°C, distribution coefficients of FeO between olivene and basaltic melt is 1 (Langmuir & Hanson, 1980). As suggested from the plot, the increase of FeO is due to joining of plagioclase and pyroxenes as liquidus phases with olivene.

5.4. CRUSTAL CONTAMINATION

There is abundant evidence that continental tholeiitic magmas may have undergone extensive crustal contamination (Carter et al., 1978; Thompson et al., 1984; Beane, 1986). It would be essential to investigate the effect of this important process on RJY basalts which would alter its primary chemistry.

Various elemental ratios such as K/Sr and Rb/Sr are used to investigate the crustal contamination during the ascent of magma.

It can be seen that K/Sr and Rb/Sr ratios for RJY basalts fall in
Fig. 5.9 TiO2 - Al2O3 plot for RJY basalts showing vectors of 50% fractionation is indicated (after Pearce and Flower, 1977)
Fig. 5. Plot of cation percent Al-Si space which could coexist with pyrolite-3 is shown with contours of different pressures, temperatures and extent of melting (Francis, 1983). The plot suggests negative relationship between Al-Si. This relationship could indicate plagioclase saturation and fractionation.
Fig. 5.11 Plot of MgO vs FeO (cation mole percent) for RJY basalts. Description of the plot given in (Hanson and Langmuir, 1978). Note the FeO enrichment character of the basalts and the samples lie outside the melt field.
the range of mantle values. The absence of any correlation between Ni (compatiable) and K2O (incompatible) elements also suggest no role of crustal component in changing RJY basalt chemistry.

Higher MgO content is characteristic of magmas generated at higher temperatures and can assimilate more crustal material during their ascent (Campbell, 1985). The lower MgO contents of RJY basalts would suggest that assimilation by the magma, if any, has taken place only before the magma entered the chamber and not in the feeder dykes which connects magma chambers to surface.

Longhi (1981) has made a key observation which allows us to further investigate whether crustal components have played any role in changing the chemistry of the RJY basalts or not. He points out that Ca-poor pyroxene (pigeonite) is an important phase in continental basalts and its crystallization precedes that of Ca-rich pyroxene (augite). The reverse is true in case of oceanic basalts. He argues that primary melts derived from the mantle that fractionates at pressures less than 5 kbars, should crystallize Ca-rich pyroxene before Ca-poor pyroxene. Thus, the oceanic crystallization sequence is normal and the continental crystallization sequence is anomalous. Longhi (1981) showed that the difference between the continental and oceanic tholeiites can be explained if continental tholeiites are contaminated by a silicic crustal melt.

The relative dominance of Ca-rich pyroxene phase to Ca-poor pyroxene in RJY basalts and higher temperature of crystallization for Ca-rich pyroxenes compared to Ca-poor pyroxenes, indicate that the silicic crustal component is absent in the melt. However, the presence of pigeonite (although in minor quantity) in RJY basalts does not rule out
the complete possibility of crustal contamination. This may be further substantiated by the higher K/Sr value of these rocks in comparison to the mantle values.

The principle behind the Irvine-Longhi argument can be illustrated using the system Forsterite-Diopside-Silica (Fig. 5.12). The path ABCD represents true fractional crystallization path for RJY basalts, where Ca-rich pyroxene crystallizes before Ca-poor pyroxene. If the melt assimilates silicious rock before crystallization, the liquid follows the AEFD path and Ca-poor pyroxene starts crystallizing first.

When compared to MORB, the continental basalts are enriched in LREE along with some incompatible trace elements, as evident in RJY basalts (present study) Columbian river basalts (Carlson, 1981); Still water complex, (Selpes et al., 1983); and Deccan basalts (Subba Rao et al., 1988). Such enrichment may be attributed to the assimilation of LREE enriched crustal component (Taylor, 1980; Depolo, 1981; Grove and Baker, 1984), and to the melting of LREE enriched mantle itself (Frey and Green, 1974; Stosch and Seek, 1980). Since crustal contamination played an insignificant role in case of RJY basalts, the enrichment of LREE and incompatible elements can be attributed to the partial melting of LREE enriched upper mantle. Plots such as P205 vs TiO2, and Zr vs Y (Fig. 5.13 a & b) for RJY basalts shows source enrichment in incompatible elements. Sen (1986) points out that even if trace amounts of an earlier enriched crust is melted together with a largely peridotitic (depleted) upper mantle, the basaltic magmas so produced may have a higher concentration of incompatible trace elements.

In case of Deccan basalts, components such as N-MORB type
Fig. 5.12 Eqilibrium phase diagram for the system diopside - foresterite - silica showing only the fields in which various crystals appear as primary phases (after Bowen, 1914; Kushiro, 1972)
Fig. 5.13 Plots showing P2O5 versus TiO2 and Zr versus Y indicating enrichment of these elements relative to chondrites in RJY basalts
depleted mantle and old enriched subcontinental mantle are being suggested to have controlled the compositions of primary magma before it reached crustal magmatic chamber (Mahoney et al., 1982; Cox and Howkesworth, 1985; Beane et al., 1986; Sen, 1986).

Such an assumption of an enriched mantle source for RJY basalts simplifies the problem of trace element enrichment. Better insight into this problem may be possible by isotopic study that needs to be carried out.

5.5. GEOTHERMOMETRY

Various methods for calculating the temperature of crystallization of mineral phases are employed and the estimations by different methods gave similar results (Table 5.2). The methods employed are summarised as follows.

5.5.1 French and Cameron (1981) method:

The RJY basalt data belongs to class I of MgO/Al2O3 wt percent plot of Cameron and French (1977). Thus coefficient of class I are used for calculating the temperature of crystallization of plagioclases and pyroxenes.

The equation used for estimations is as follows:

\[ T^\circ C = a_1 x_1 + a_2 x_2 + a_3 x_3 + \ldots \ldots a_n x_n + K \]

Where \( a_1 \ldots a_n \) are coefficients of \( x_1 \ldots x_n \) (which are wt percentages of the
Table 5.2 Temperature of crystallization of plagioclase and pyroxene phases of RJY basalts

<table>
<thead>
<tr>
<th>Method</th>
<th>Mineral</th>
<th>Katera Upper flow</th>
<th>Pangidi Upper flow</th>
<th>Pangidi Lower flow</th>
<th>Average of Upper flow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cpx</td>
<td>1249 C</td>
<td>1258 C</td>
<td>1254 C</td>
<td>1253 C</td>
</tr>
<tr>
<td>Nielsen and Dungan (1983)</td>
<td>Augite</td>
<td>1254 C</td>
<td>1265 C</td>
<td>1247 C</td>
<td>1259 C</td>
</tr>
<tr>
<td></td>
<td>Cpx</td>
<td>1245 C</td>
<td>1251 C</td>
<td>1240 C</td>
<td>1248 C</td>
</tr>
<tr>
<td>Nathon and Vankirk (1984)</td>
<td>Plagioclase</td>
<td>1172 C</td>
<td>1166 C</td>
<td>1157 C</td>
<td>1169 C</td>
</tr>
<tr>
<td></td>
<td>Cpx</td>
<td>1229 C</td>
<td>1218 C</td>
<td>1202 C</td>
<td>1223 C</td>
</tr>
<tr>
<td>Glazner (1984)</td>
<td>An60,85</td>
<td>1140 C</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plagioclase</td>
<td>1190 C</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
twelve oxides and $K$ is a constant. The coefficients and constants of basalts class I used in the method are from (French and Cameron, 1981). The average error in the temperature calculations for plagioclase is $\pm 3.3^\circ C$ and for clinopyroxenes is $\pm 10.5^\circ C$.

5.5.2 Nielsen and Dungen (1983) method:

It has been demonstrated that the modelling of mafic phase equilibria using a two-lattice melt component activity model, based on the Boltinga and Weill (1972) approach to the mixing properties of silicate melts can be successfully implemented to modelling the crystallization of mafic magmas.

This model assumes that the melt is composed of two independent quasi-lattices, i.e., the net work formers and the net work modifiers. The significant reduction of the effects of composition on major and minor element distribution relations makes this model superior for the calculation of mineral-melt equilibria to models in which melt components are assumed to be simple cation mole fractions.

Empirical, single component distribution coefficients have been determined by the calculation of linear least-squares regressions of experimental mineral-melt pair compositions. These functions have been combined with an alternative algorithm in a computer model of crystallization processes in mafic systems.

This model reproduces the input data set within $20^\circ C$ and $3.1\%$ (1.) for oxides in olivine, plagioclase, pyroxene, spinel and ilmenite. Calculated crystallization sequences for 52 natural mafic compositions were compared to with published experimentally-data mineral
crystallization sequences. The 1..precisions for temperature were within 15° C for the initial crystallization temperatures of olivene, high Ca pyroxene and plagioclase.

The network forming components are SiO2, NaAlO2 and KA102, and the network modifying components are MgO, FeO, CaO, AlO1.5, TiO2, MnO and CrO1.5. The activities of the melt components are calculated assuming that the components mix ideally within their quasi-lattices with no mixing between quasi-lattices. As examples, the activities of NaAlO2, MgO and AlO1.5 are defined as:

\[ a_{NaAlO2}^1 = X_{NaAlO2}^{NF} = X_{Na}^1 \left( X_{Na}^1 + X_{K}^1 + X_{Si}^1 \right) \]
\[ a_{MgO}^1 = X_{MgO}^{NM} = X_{MgO}^1 \left( X_{MgO}^1 \right) \]
\[ a_{AlO1.5}^1 = X_{AlO1.5}^{NM} = X_{Al}^1 - X_{Na}^1 - X_{K}^1 \left( X_{Al}^1 \right) \]

Where \( a_{SiO2}^{fi} \) is the activity of SiO2 in the liquid, \( X_{Mi}^{fi} \), \( X_{Mi}^{NF} \), and \( X_{Mi}^{NM} \) are cation normalized mole fractions of melt component \( i \) in the Liquid, network formers, and network modifiers respectively.

The generalized formula for pyroxene is \( (M1)(M2)^{206} \). \( M1 \) is the smaller of the two octahedral \( M \) sites and is preferentially occupied by Mg, Fe, Al, Ti and Cr. \( M2 \) is preferentially occupied by Ca, Mu, and Na along with Mg and Fe. \( T \) is a tetrahedral coordinated site occupied by Si and Al. The mixing properties of both high-Ca and low-Ca-pyroxene may be
approximated by evaluating the contribution to the entropy and enthalpy of mixing on and between all three sites, M1, M2 and T, with a two M site distribution model. The pyroxene component activity model used for the purpose of this investigation assumes that at magmatic temperatures cations mix ideally on each M site, with complete disorder of Al between the M1 and T sites. In this case, the activity of the enstatite component in either pyroxene may be expressed as:

\[ a_{\text{px}}^{\text{Mg}_2\text{Si}_2\text{O}_6} = x_{\text{Mg}}^{\text{M1}} x_{\text{Mg}}^{\text{M2}} (x_{\text{Si}}^{\text{T}})^2 \]

5.5.3 Nathan and Vankirk (1984) method:

The study by the these authors demonstrates that a relatively simple model simulates many of the features of fractional crystallization of magmas through a broad range of liquid composition at one atmosphere pressure. As a liquid cools and crystallizes, the mineral assemblages evolves by progressive addition of new minerals occasionally with the replacement of an old minerals.

The fundamental premise for this study is that equilibrium phase relations of a liquid-crystal mixture are governed solely by the chemical composition of the liquid, given a fixed pressure. The liquid composition then determines the mineral assemblage, the mineral composition, and even the temperature of the liquid-crystal mix. The dependence of temperature and minerals on liquid composition is a consequence of restriction to equilibrium liquid-Crystal relations at constant pressure.
Mineral-temperature equation: The Crystallization temperature of each mineral is assumed to vary in a continuous manner with liquid composition. The principle of relative crystallization temperatures has been extended in this study to complex nine-component systems at one atmosphere pressure. Liquidus is conceived as a set of smooth surfaces each of which describes for one mineral the dependence of crystallization temperature on liquid composition. The surfaces are described by mineral temperature equations. For each crystallizing liquid, the equations are solved for the nine minerals of the model and only the mineral with the highest crystallization temperature may be in equilibrium with the liquid. Equilibrium of several minerals with a liquid requires that their crystallization temperature be higher than any others and equal to one another.

The crystallization temperature of each mineral has been approximated by equation of the form.

\[
T = a_0 + a_1 Al + a_2 Ti + a_3 Fe^{3+} + a_4 Fe^{2+} + a_5 Mg + a_6 Ca + a_7 Na + a_8 K + a_9 (\log_e \Pi) + a_{10} \sqrt{Al(Na + K)}
\]

Where the chemical symbols represent cation fractions in the liquid. The first term \(a_0\) is an empirical constant. The next eight terms account for the specific liquid compositions, in which the nine cations of constant sum have eight degrees of freedom. Arbitrarily, the ions of lesser abundance were selected to describe the composition of silicate liquids.

The very significant tenth term is \(a_9 (\log_e \Pi)\) where \(\Pi\) is the geometric mean of the fractions of the essential cations multiplies according to their ratios in the mineral.
for example plagioclase is shown as $\sqrt[5]{(\text{Na+Ca})(\text{Al})(\text{Si})^3}$ and augite as $\sqrt[4]{(\text{Ca})(\text{Mg+Fe}^{+2})(\text{Si})^2}$. Coefficient for the mineral temperature equation are given Nathon and Vankirk (1984).

5.5.4 Glazner’s (1984) method:

Activities of plagioclase were calculated by using Glazner’s (1984) method. It has been adopted to estimate temperature of crystallization of plagioclases. The activities of plagioclase component in basaltic melt can be calculated from the compositions of coexisting melt and crystals, provided that 1) the component is independently variable component of the crystal, and 2) approximate thermodynamic data for the component are known. This approach is used to calibrate the compositional dependence of the activities of anorthite. Glazner’s (1984) activity models for anorthite provide excellent geothermometers with standared deviation temperatures residuals of approximately $\pm 10^0$C.

The activity of anorthite can be calculated by first determining the mole fractions of the oxides in the melt and then computing the equation using the activity models as given for anorthite in Glazner’s, (1984) paper.

The temperature estimations of mineral phases suggest that Ca-rich pyroxene (augite) is first to crystallize followed by Ca-poor pyroxene (pigeonite) and plagioclase. The consistency of results by the various methods shows that the estimations are reliable.