MINERALOGICAL EVOLUTION IN THE BARDA ACID ROCKS

FELDSPAR

PLAGIOCLASE

Plagioclase in the Barda acid complex, occurs mainly in the form of euhedral to subhedral phenocrysts which are mostly rimmed by alkali feldspar host with micrographic intergrowth. Plagioclase phenocrysts in the different varieties of acidic rocks do not differ significantly in their chemical composition. The composition ranges from $An_{27.5}$ to $An_{33.5}$. Magmatic resorption of the phenocrysts is well seen in the granophyres, but it is scarcely developed or absent in the felsites and rhyolite. The rim of alkali-feldspar overgrowth around plagioclase phenocrysts is lacking in the felsitic and rhyolitic rocks. Zoning in plagioclase phenocrysts have frequently been traced in the granophyres. In this context, it should be mentioned that, in the granitic magma containing appreciable lime, two feldspars will crystallize in the early stage; and the plagioclase with greater anorthite content may cause the liquid to become more depleted in lime which will make the liquid move into the field of alkali feldspar, particularly if the plagioclase becomes zoned and it fails to react with the liquid (Tuttle, 1952).

Another form of plagioclase, with low anorthite content (albitic) occurring in the miarolitic and submiarolitic patches in the granophyre, forms rim around alkali feldspar. During the final stage of crystallization in the miarolitic and submiarolitic areas of granophyre, the greater concentration of volatile components may lower the liquidus curve, and as a result the alkali feldspar and plagioclase would crystallize simultaneously in even lime-poor rocks. In such a case, alkali feldspar would show rims of plagioclase on some
grains while rims of potash-rich feldspar on the other, if the equilibrium between the crystals and liquids are not maintained (Tuttle, 1952).

A third form of plagioclase, has been rarely noted in the rhyolitic glass and has been considered as a product of devitrification under low temperature conditions.

The optic axial angle measurements of plagioclase phenocrysts, indicate a high to transitional state (Tuttle and Bowen, 1958), as represented by their $2V_x$ ranging between $66^\circ$ to $68^\circ$. The measurements of optic axial angles on low temperature sodic plagioclase indicates that a $2V_x$ of less than $80^\circ$ does not occur in them (Tuttle and Bowen, 1958).

Plagioclase phenocrysts are amongst the earliest formed minerals, but in some cases plagioclase is slightly preceded or succeeded by clinopyroxene phenocrysts.

**ALKALI FELDSPAR**

Alkali feldspars in the acidic rocks, occur mainly in the form of micropegmatitic intergrowth with quartz as large subhedral to euhedral plates and they mostly have a core of plagioclase grain as nucleus. The intergrowths are in various forms from coarse micrographic to crypticographic. Spherulitic groundmass in the felsite is also considered as very fine and radiating intergrowth of quartz and alkali feldspar. Another form of feldspar (orthoclase, as free euhedral to subhedral grains) occurs in the interstitial miarolitic and submiarolitic spaces of granophyre and they crystallised in the latest stage under volatile-rich conditions. The free grains in the miarolitic-submiarolitic areas, as mentioned earlier, are rimmed with albite and show indistinct perthitic growth.
The alkali feldspar grains show transitional to high temperature character by their optic axial angles \( (2V_x) \) which range between \( 46^\circ \) to \( 63^\circ \) and indicate that to the low sanidine-high albite series of alkali feldspar (Tuttle and Bowen, 1958). The alkali feldspars of the low sanidine-high albite series are high temperature modifications, and they are found in volcanic and subvolcanic rocks.

In the rhyolites and felsites, which are considered to be the finer varieties of granophyre, it has been found that the alkali feldspar is not pure, but contains a large amount of albite in solid solution. Hence the modal analysis only gives an apparent location of the rocks, whereas actually the bulk composition of the rocks lie more near the centre of the ternary quartz-orthoclase-albite diagram.

Alkali feldspar may be considered as one of the last formed minerals to crystallise in the groundmass.

**CRYSTALLIZATION PHENOMENA**

Tuttle and Bowen (1958) classified the salic igneous rocks, whose compositions are close to "Petrogeny's Residua System" (Bowen, 1937 cited in Tuttle and Bowen, 1958), into two broad groups, based on the nature of their feldspars as follows:

(A) Hypersolvus granites, syenites and nepheline syenites, characterised by the absence of plagioclase, except as a component of perthite.

(B) Subsolvus granites, syenites and nepheline syenites characterised by both potassium feldspar and plagioclase feldspar.
In the present study of Barda acid igneous complex, nearly all the salic igneous rocks are found to contain two separate feldspar phases, plagioclase and potassium feldspar disregarding the perthite component. So, apparently it seems that they fall under the subsolvus granite class of Tuttle and Bowen. Such subsolvus granites may originally crystallise as two feldspar granite or as one feldspar granite which later exsolved or recrystallised into two feldspars. However, the granophyres and felsites of the present area are subvolcanic in nature and they are definitely not expected to belong to the subsolvus class of granitic rocks, whose temperature of crystallisation (or, recrystallisation) should be lower than those of the subvolcanic rocks.

Many rhyolites, which are definitely hypersolvus, contain two separate feldspar phases, which have been explained by Tuttle and Bowen (1958, p. 130-131) as follows: "The appearance of two feldspars during crystallization in rhyolitic, trachytic and phonolitic magmas depends to a large extent upon the amount of solid solution between the feldspars and on the temperature of crystallization. If the potassium, sodium and lime feldspars are completely miscible with each other at magmatic temperature, then obviously only one feldspar, a ternary solid solution, will precipitate during crystallization. On the other hand, if the solid solution is limited to the binary systems, NaAlSi_2O_8 - CaAl_2Si_2O_8 and NaAlSi_2O_8 - KAlSi_2O_8, two feldspars will precipitate during crystallization if the magma carries all three in solution. The compositional variations in the feldspars of these rocks indicate that the actual relations are intermediate between these two extremes - that is, limited ternary solid solutions at high temperatures decreasing at lower temperatures."

In the ternary system of NaAlSi_2O_8 - KAlSi_3O_8 - CaAl_2Si_2O_8 of Tuttle and Bowen (1958), which is shown in the Figure 53, the curve IKSP represents the solidus curve and DFK_L represents the two feldspar boundary or cotectic
curve. The curve $DFK_L$ corresponds to liquid compositions which are in equilibrium with two feldspars - alkali feldspars from $P$ to $K_s$ and plagioclase feldspars from $K_s$ to $L$. The trend of crystallization has been indicated by the arrows in the diagram. It has been shown that for a composition to the right of the solidus curve $LK_sP$, the equilibrium of crystallization is such that the initial plagioclase feldspar crystallises until the field boundary is reached, after which the second feldspar, obviously the alkali feldspar crystallises along with the first, reacting with the liquid until all the liquid is used up. The plagioclase changes composition along $L\beta$ and alkali feldspar from $P$ to $B$. This is because initial lime content is excess over the limited ternary solid solution between the feldspars. But for the liquids in the area between $KsK_LF$ (such as granitic liquids, which are lime-poor), the early phase separating is a plagioclase, until the liquid reaches the field boundary when it is joined by an alkali feldspar. As crystallization proceeds, the plagioclase reacts with the liquid and finally disappears, leaving an alkali feldspar and a liquid. Further crystallization will affect the liquid composition leaving the field boundary, moving towards the Ab-Or side line, while the alkali feldspar crystals move to attain the composition of initial mixture ($X$). Crystallization will finally be completed when the crystals reach the composition $X$, and the last drop of the liquid is used up. Now, if the liquids in the region $KsK_LF$, are affected in such a way that the reaction between the early formed plagioclase and the liquid is hindered, such as by quenching due to near surface intrusions, then finally the melt would produce two feldspars - plagioclase and alkali feldspars, in salic rocks, as in the present area.

In the rocks of the present area, the plagioclase phenocrysts, in most cases show signs of magmatic resorption (Fig. 14) and have a thin rim of alkali feldspar (Fig. 34) which gradually passes into granophyric intergrowth, and is suggestive of the presence of reaction between the plagioclase and residual melt, as discussed by Tuttle and Bowen (1958, p. 130-131).
TERNARY DIAGRAM OF THE SYSTEM NaAlSiO$_3$ - KAlSiO$_4$ - CaAl$_2$Si$_2$O$_8$

(DIAGRAM TAKEN FROM TUTTLE AND BOWEN, 1958, PAGE-133)

(SHOWS THE APPROXIMATE COMPOSITION OF LIQUIDS COEXISTING IN EQUILIBRIUM WITH TWO FELDSPARS. THE TEMPERATURES REPRESENTED BY THIS DIAGRAM ARE RELATIVELY HIGH AND ARE BELIEVED TO BE COMPARABLE TO THOSE EXISTING IN TRACHYTIC LAVAS. ARROWS INDICATE THE DIRECTION OF FALLING TEMPERATURES, THE FIELD BOUNDARY HAS BEEN LOCATED BY EXAMINING ANALYSIS OF EXTRUSIVE ROCKS IN WHICH THE FELDSPAR PHENOCRYSTS HAVE ALSO BEEN ANALYSED AND BY NOTING THE COMPOSITION OF TWO ANALYSED FELDSPARS COEXISTING IN EXTRUSIVE ROCKS, IN WHICH THE ROCK OR THE GROUNDMASS HAS ALSO BEEN ANALYSED.)
It is noteworthy that coarse grained granophyres of the present area show lower plagioclase content (3.37 percent) than the fine grained type having 5.02 percent plagioclase whereas the former has higher alkali-feldspar content (58.50 percent) than the latter (53.1 percent). This supports the view that plagioclase in coarse granophyre has reacted because of slow cooling and converted into solid solution with alkali feldspar, whereas in fine granophyre this reaction was hindered because of quick chilling.

QUARTZ

Quartz grains in the Barda acidic locks occur maintain the forms of coarse micrographic to fine cryptographic intergrowths with alkali feldspar. They are considered to have formed at higher temperatures, but ultimately changed to the lower forms. The rare euhedral phenocrysts of β-quartz (Fig. 24) have been preserved in the variety of contact granophyre. Another form of quartz occurs interstitially in the miarolitic and submiarolitic spaces in association with the late formed low temperature minerals; some of these quartz grains contain fluid inclusions. A few euhedral lath-shaped tridymite grains have been observed in felsite (Sp. No. 3/13.2, referred to in Chapter VII) with indications of quartz-tridymite co-existence.

The temperature pressure span of a granophyric magma to form quartz, tridymite, hedenbergite (derived from ferrowoolastonite) has been obtained as 950° to 980°C and 600-100 bar from the Skaergaard granophyre crystallization path (Lindsley, et al. 1969).

CLINOPYROXENE

Clinopyroxene in the acidic rocks of the present area occurs with a wide range of compositions from augite to aegirine-augite and acmite through
the intermediate stages of ferrosalite, ferroaugite and hedenbergite. Pure acmite appears to be restricted to the miarolitic cavities, whereas the other varieties are present as phenocrysts and in groundmass, commonly in the interstitial areas. The distribution of the different varieties of pyroxene in the acidic rocks of the present area, are briefly stated as follows:

(1) Augite, ferrosalite and ferroaugite are found in the microgranite and coarser granophyre; the pyroxene grains in coarse granophyre are rimmed by alkali-rich types and appears to be acmite restricted to the miarolitic cavities.

(2) In the finer granophyre, the pyroxenes are ferroaugite and hedenbergite with occasional rim of alkali-rich type, and mostly occur in association with fayalitic olivine.

(3) In the felsitic and rhyolitic rocks, the varieties are ferroaugite, hedenbergite and prizary aegirine-augite. No zoning by alkali type has been traced.

The ranges in composition have been observed as Augite (Ca_{42}Mg_{32}Fe_{26}) - Ferrosalite (Ca_{46}Mg_{18,5}Fe_{35}) - Ferroaugite (Ca_{38,5}Mg_{21}Fe_{40,5}) - Hedenbergite (Ca_{48,5}Mg_{8,5}Fe_{43}) - Aegirine-augite (CaMgFe^{+++})_{78} (NaFe^{+++})_{22} - Acmite. The presence of this range of composition is indicative of some differentiation in the magma. The initial pyroxene, augite is with Mg/Fe ratio higher than unity; in the ferrosalite the ratio becomes lower than 0.8; whereas in ferroaugite and hedenbergite the ratios are in between 0.26 to 0.17. In the next stage, it is characterised by its conversion to aegirine-augite containing 22 percent acmite molecule and in the further advanced stage pure acmite has been formed. It is therefore, evident that the course of crystallization led
to a substantial decrease of magnesia and concomitant enrichment in iron, alkalies, together with a slight increase in calcium content. There is also noticed a regular variation (Fig. 54) in $N_{y}$ when plotted with $N_{y}$ of pyroxene trend in acidic rocks.

The pyroxene trend in the acidic rocks of the present area has been shown in Fig. 55 and compared with the pyroxene trends from the late stages of fractionation of the Skaergaard intrusion (Brown and Vincent, 1963) and that of British Tertiary acid glasses (Carmichael, 1960). In both these trends, however, the final pyroxene is a ferrohedenbergite, whereas in the present acid igneous complex, the pyroxene shows from their optical properties, that after a ferroaugite is produced, the pyroxene approached the hedenbergite-diopside line, forming hedenbergite and then acmite molecule (NaFe$^{3+}$ S$	ext{i}_2$O$_6$) begins to form upto 22 percent of the sodic pyroxene of aegirine-augite type.

The observations indicate that the iron-rich pyroxene formed earlier, and at a later stage, the sodic pyroxene aegirine-augite and acmite crystallised. It has been presumed that certain conditions were responsible by which iron-rich pyroxene was converted to sodic pyroxene; and at places the conditions were favourable for direct crystallization of alkali pyroxene. In this context, the role of oxidation of iron may be important, as the pyroxene of the diopside-hedenbergite series contain mainly Fe$^{2+}$, whereas the alkali pyroxene contains Fe$^{3+}$ as a major constituent. Regarding the origin of miarolitic acmite, De and Bhattacharyya (1971) postulated that there was a sudden rise of oxygen fugacity, as a result of dissociation of hydrogen in the H$_2$O-rich portion of the partially crystallising magma. Presumably, the dissociation of H$_2$O and escape of H$_2$ led to increased in oxygen fugacity which oxidised some of the FeO to Fe$_2$O$_3$. The separation of volatile-rich fraction from the rest of the magma, was caused by a sudden onset of the second boiling point at a late stage of crystallization.
Ny VERSUS 2Vz DIAGRAM SHOWING TYPES OF PYROXENES PRESENT IN THE ACIDIC ROCKS

TREND OF VARIATION IN PYROXENE COMPOSITION OF ACIDIC ROCKS.
TREND OF VARIATION IN COMPOSITION OF PYROXENES FROM THE BARDA ACIDIC ROCKS IN COMPARISON WITH THE PYROXENE TREND FROM THE LATE STAGES FRACTIONATION OF THE SKAERGAARD INTRUSION AND OF BRITISH TERTIARY ACID GLASSES

FIG. 55

PYROXENE TREND IN THE BARDA ROCKS (SMALL DOTS REPRESENT THE PLOT)
PYROXENE TREND IN SKAERGAARD INTRUSION (BROWN & VINCENT, 1963)
PYROXENE TREND IN BRITISH TERTIARY ACID GLASS (CARMICHAEL, 1960)
Titanomagnetite occurs as the main constituent of opaques, in the forms of coarse subhedral, skeletal to fine disseminated grains. Coarser grains occur as intergrowth with the silicates and hence they form either simultaneously or later than the silicates. Maghemitisation and martitisation in the titanomagnetite are more intense in the coarse granophyre in comparison to felsite and fine granophyre. Oxidation exsolution lamellae of ilmenite within magnetite have been found more frequently in the granophyre variety, rather than in the felsites. Discrete and euhedral laths of ilmenite occur more frequently in the interstitial spaces of coarse granophyre rather than in the finer granophyre and felsite. Primary intergrowths of ilmenite within titanomagnetite have been observed in the granophyric rock. Sulphides are rarely represented as dot-like to fine squarish grains of chalcopyrite, bornite, covellite and chalcocite which occur as inclusions within the silicates and titanomagnetite.

The mutual interlocking relations of these opaque minerals with the silicates, help to establish the evolution of opaque minerals in the acidic rocks.

Very small amount of sulphur in the acidic magma, favours crystallization of minor sulphides, which becomes immiscible from the silicate-oxide melt at higher temperature, but crystallised at lower temperature after the crystallization of silicates and oxides. It is evidenced by the fact that the sulphides occur as globular inclusions within the silicates and titanomagnetite. It may be noted that Vogt (1916-18, cited in Wager and Brown, 1967), has shown experimentally that sulphur in spite of its occurrence in very small quantities in the silicate melts forms an immiscible sulphide liquid of low crystallization temperature. Regarding the concept of immiscibility of these two referred melts, the system silicate-oxide and sulphide may be treated as binary, with the compositions plotted in terms of the proportions of the total silicates and oxides to total sulphides. It was estimated from the Skaergaard data (Wager and Brown, 1967, p. 179) that the silicate-oxide liquid in equilibrium with the sulphide liquid contained only about 0.05 percent.
of dissolved sulphides and the sulphide liquid include 3 to 10 percent of iron oxides and silicates. Discrete ilmenite and titanomagnetite grains formed simultaneously or after the crystallization of silicates. This is followed by the formation of oxidation-exsolution lamellae of ilmenite within titanomagnetite. Later the titanomagnetite was oxidized to martite and maghemite.

There have been controversies regarding the origin of magnetite-ilmenite \((\text{Fe}_3\text{O}_4 - \text{FeTiO}_3)\) exsolution intergrowths. There are opinions that the intergrowths may be the direct result of exsolution between magnetite and ilmenite or the ilmenite is derived indirectly from the subsolvus oxidation of ulvöspinel which was originally in solid solution with the magnetite \((\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{TiO}_4)\). Vincent (1960) supported the indirect derivation of ilmenite from the subsolvus ulvöspinel; but he found difficulty to explain some coarser or better developed magnetite-ilmenite intergrowths, with the help of his indirect origin theory. In this context, it is important to state that the exsolved ilmenite lamellae can become coarser or can even become vein-like during the long period of cooling at the necessary partial pressure of oxygen. Buddington and Lindsley (1964), reported the absence of solid solution between magnetite and ilmenite even at temperatures as high as \(1200^\circ\text{C}\). According to them, the ilmenite lamellae in the magnetite were the result of unmixing and oxidation during the cooling of the original magnetite-ulvöspinel solid solution.

The iron-titanium oxides help to establish the oxygen pressure and temperature conditions of crystallizing acidic magma. The mineral assemblages containing titanomagnetite, fayalite olivine and quartz in the ferrosalite-bearing or ferroaugite-bearing felsite, resemble the fayalite ferrogabbro of Skaergaard (Buddington and Lindsley, 1964). This assemblage indicates a low oxygen fugacity and a higher temperature as established, being \(f_{O_2} = 10^{-13}\) at a temperature of \(900^\circ\text{C}\).
The accessory and secondary minerals in the Barda acid igneous rocks include amphibole (alkalic), green biotite, chlorite, fluorite, zircon, calcite, sphene rimming iron ores, baryte, stilpnomelane, apatite, prehnite, diopsidic augite, iddingsite, rutile, brookite, and epidote, which occurs as alteration products after pyroxene and plagioclase and (or) as late formed low temperature minerals in the miarolitic and submiarolitic areas.

Alkali amphiboles occurring in association with alkali pyroxenes, are considered to form at lower temperature in the later stages of crystallization under the conditions of high partial pressures of water and oxygen. In this context, the rarity of alumina-rich amphiboles in the acidic rocks should be explained. Under the conditions of low water pressure in the volcanic and subvolcanic environments, pyroxene is the stable phase, at the temperatures just below their liquidus. Yoder and Tilley (1962) have shown experimentally that the lower water pressure favours the formation of pyroxene and the higher pressure for the amphiboles. Stilpnomelane occurs as hydrothermal alteration products of pyroxene. The alteration of plagioclase phenocrysts to epidote, and sericite and in the volcanic rocks, can be ascribed to a late stage deuteric activity by the volatile constituents. Iddingsite occurs as partial or complete pseudomorphs after olivine and it is also a deuteric or hydrothermal mineral.

The miarolitic and submiarolitic areas with low quartz, orthoclase, albite, baryte, fluorite, zircon, apatite, indicate them as crystallization products out of trapped hydrothermal fluids. The fluids contain, besides lime and alkalis, the rare elements like barium, fluorine, zirconium, titanium etc. The presence of those minerals indicate that the interstitial hydrous fluids were at temperatures, corresponding to early hydrothermal stages.
Sphene occurs in association with iron ores and probably forms at the expense of ilmenite at a temperature just above the solidus. Rutile and broocite have rarely been traced. Rutile may be a result of secondary oxidation of ilmenite-hematite solid solution. Broocite forms a solid solution series above 600°C, which may be the result of high temperature oxidation of magnetite-ilmenite intergrowth (Watkins, et al, 1970).