[AMERICAN JOURNAL OF SCIENCE, VOL. 284, MARCH, 1984, P. 272-287]

FRACTIONAL CRYSTALLIZATION AND MELTING WITHIN BINARY SYSTEMS WITH SOLID SOLUTION

SVEN MAALØE
Department of Geology, Allegaten 41, 5014 Bergen, Norway

ABSTRACT. The composition of liquids and solids obtained by perfect fractional crystallization is calculated using the equilibrium compositions given by the phase relations and Rayleighs equation for fractionation. The equation derived for fractional crystallization has been applied for the albite–anorthite and fayalite–forsterite systems. It is shown that there is a certain amount of albitic liquid left during the final stage of the crystallization. The composition of the residua generated by fractional melting is almost constant by small degrees of partial melting when the initial solid contains less than 50 percent An or 50 percent Fo.

INTRODUCTION

It is now generally considered that fractional crystallization and partial melting in various forms predominantly control the compositions of magmas. The PT conditions and the processes that change the compositions of magmas may be estimated by comparing the trends of magmatic rocks with the results obtained from phase diagrams. The application of the phase relations for theoretical trend estimates occurs in two consecutive steps. First the phase relations have to be estimated, whereby a functional relationship may be obtained between the compositions of solid and liquid phases. Next the equation representing the relationship between solid and liquid phases may be incorporated in the equations considered to represent the natural processes.

The majority of igneous minerals display solid solution, and the theoretical fractionation trends based on phase relations can be estimated only if the effect of solid solution is taken into account. The compositional relationships of binary systems produced by fractional crystallization and partial melting will be considered here, and the albite–anorthite and fayalite–forsterite systems will be used as examples. The equations determined can be extended to ternary and multicomponent systems when the phase relations of these have been estimated with sufficient accuracy.

The total amount of the solid phase formed by the fractional crystallization will be called the fractionate whereas the solid formed at any given temperature is called the instant fractionate. The amount of fractionate or residual liquid is calculated using the Rayleigh (1902) equation:

$$x_s dW = d(x_l W) \tag{1}$$

where x_s and x_l are the mole fractions of a reference component in the solid and liquid phase, respectively. W is the amount of liquid given here in mole fraction or mole percent. The molar weights of albite and anorthite are similar, so the mole fractions are similar to the weight fractions. By the fayalite–forsterite system the mole and weight fractions will be rather different. By integration of (1) we obtain:

$$\ln\left(\frac{W}{W^0}\right) = \int_{x_l^0}^{x_l} \frac{dx_l}{x_s - x_l} \tag{2}$$

The integration of the right side of (2) can be performed only when a functional relationship has been found between x_s and x_l. The equations relating x_s and x_l can be of different forms, as discussed by Maalφe (1976, 1982). The variation in the liquid composition produced by fractional crystallization has been dealt with in various manners, and several treatments do not follow the constraints of the Rayleigh equation, with the consequence that incorrect or approximate results are obtained.

The phase relations of the albite–anorthite system were estimated by Bowen (1913) who also considered fractional crystallization. Bowen (1913, 1928) did not do any calculations but considered a stepwise crystallization where each step is controlled by equilibrium crystallization. This approach is useful for an approximate estimate but not entirely correct, as the continuous change in the fractionate is not taken into account, and Bowen (1913) concluded that there may only be a minute amount of albitic liquid formed. It will be shown here, using the Rayleigh equation, that the amount of residual albitic liquid can be quite large, and that the amount varies with the initial composition of the liquid.

It was suggested by Morse (1976) that the amount of fractionate could be estimated using the lever rule, assuming the residual amount of albitic liquid nil. This method yields approximate estimates of the composition of the fractionate, albeit the anorthite content of the fractionate is generally too low.

Powell (1978, p. 199) assumed a variable temperature dependent distribution coefficient but applied the Rayleigh equation for a constant distribution coefficient. This procedure is mathematically incorrect, and the results obtained are in error.

SOLUTIONS OF THE RAYLEIGH EQUATION

The Rayleigh (1902) equation for the albite–anorthite system was solved by Maalφe (1976) by using a functional relationship between the solid and liquid compositions estimated from the phase relations. A fairly accurate estimate of the fractionate within the albite–anorthite system is obtained using this equation:

$$\frac{x_l}{x_s} = px_l + q\sqrt{x_l} \tag{3}$$

The fractionate for the fayalite–forsterite system was estimated using the following equation (Maalφe, 1982):

$$\frac{x_l}{x_s} = px_l + q^3\sqrt{x_l} \tag{4}$$

where $p + q = 1$ in both cases. Both these equations assume that the ratio x_l/x_s is zero for $x_l = 0$. Strictly speaking this is impossible, as it would

imply a horizontal tangent to the liquidus curve at $x_l = 0$, which is inconsistent with the thermodynamics of the systems. However, these equations provide satisfactory results for x_l larger than 5 mole percent anorthite or forsterite and were adopted for reasons mentioned later. For some applications a different approach is warranted (Anderson and others, 1982), and the present paper will, therefore, represent a general solution, which is nearly as accurate as the estimated phase relations.

Assuming ideal solution we have for the albite–anorthite system (Maalφe, 1976):

$$\ln\left(\frac{x_l}{x_s}\right) = \frac{\Delta H_{an}}{R}\left(\frac{1}{T_{an}} - \frac{1}{T}\right) \tag{5}$$

where $\Delta H_{an} = 32.409$ cal/mole is the latent heat of fusion (Weill and others, 1980), R = the gas constant, T_{an} = the melting temperature of anorthite, and T = the temperature (°K). At $x_l = 0$, T is the melting point of pure albite (1391°K), and x_l/x_s is estimated as 0.0615. The albite–anorthite system is not completely ideal (Navrotsky and others, 1980), and a more accurate value for the ratio at $x_l = 0$ can be obtained from the phase relations by drawing tangents to the liquidus and solidus curves at $x_l = 0$. The intersections between the two tangents and a horizontal line will define the x_l/x_s ratio, which was estimated as about 0.08. The phase relations within the albite-rich part of the system have not been estimated with the same accuracy as the rest of the system, and the present estimate of the ratio is approximate. Having estimated x_l/x_s at $x_l = 0$, the ratio can be estimated as a function of x_l, and the following equation was obtained by a trial and error method as polynomial regression did not provide good results:

$$\frac{x_l}{x_s} = ax_l + b\sqrt{x_l} + c \tag{6}$$

Since x_l/x_s must equal 1.0 for $x_s = x_l = 1.0$, we have that:

$$a + b + c = 1.0 \tag{7}$$

For the albite–anorthite system the constants were estimated as:

$$a = 0.55,\ b = 0.40,\ c = 0.05 \tag{8}$$

Considering the value of x_l as given, the average deviation in x_s estimated from (6) and (8) is 0.63 mole percent An from the experimental values, and the maximum deviation is 1.9 mole percent An. For the fayalite–forsterite system the following constants were obtained:

$$a = 0.61,\ b = 0.25,\ c = 0.14 \tag{9}$$

The curves calculated from (6), (8), and (9) are shown in figures 1 and 2, where they may be compared with the experimental results.

From eq (6) we have:

$$x_s = \frac{x_l}{a + b\sqrt{x_l} + c} \tag{10}$$

Letting $x_1 = x$, the integral of (2) now becomes using (10):

$$\ln\left(\frac{W}{W^0}\right) = \int_{x^0}^{x} \frac{dx}{\frac{x}{ax + b\sqrt{x} + c} - x} \tag{11}$$

By substituting $y = \sqrt{x}$ and by rearrangement we get:

$$\ln\left(\frac{W}{W^0}\right) = \int_{y^0}^{y} \frac{2(ay^3 + by^2 + cy)dy}{(1-c)y^2 - ay^4 - by^3} \tag{12}$$

The determination of the solution to this integral is elaborate and will not be shown here, but the derivation can be obtained on request. The solution is given by:

$$\begin{aligned}\ln\left(\frac{W}{W^0}\right) = \Bigg[& -\ln(a + b - by - ay^2) \\ & + \frac{b}{2a+b} \ln\left(\frac{ay + a + b}{-ay + a}\right) \\ & - \frac{2ca}{(2a+b)(a+b)} \ln\left(y - \frac{c-1}{a}\right) \\ & - \frac{2c}{2a+b} \ln(y-1) \\ & + \frac{2c}{a+b} \ln(y) \Bigg]_{y^0}^{y}\end{aligned} \tag{13}$$

Using the constants for the albite–anorthite system we obtain the following:

$$\begin{aligned}\ln\left(\frac{W}{W^0}\right) = \Bigg[& -\ln(0.95 - 0.4y - 0.55y^2) \\ & + 0.2667 \ln\frac{0.55y + 0.95}{-0.55y + 0.55} \\ & - 0.0386 \ln(y + 1.7273) \\ & - 0.0667 \ln(y-1) \\ & + 0.10526 \ln(y) \Bigg]_{y^0}^{y}\end{aligned} \tag{14}$$

For the olivine system the solution is given by:

$$\ln\left(\frac{W}{W^0}\right) = \Big[-\ln(0.86 - 0.25y - 0.61y^2)$$

$$+ 0.1701 \ln \frac{0.61y + 0.86}{-0.61y + 0.61}$$
$$- 0.1351 \ln (y + 1.4098)$$
$$- 0.1783 \ln (y - 1)$$
$$+ 0.3256 \ln (y) \Big]_{y^0}^{y} \qquad (15)$$

By solving (14) and (15) it should be noted that ln (−a) − ln (−b) is equal to ln (a/b).

ALBITE–ANORTHITE SYSTEM, FRACTIONAL CRYSTALLIZATION

The variation in the composition of plagioclase liquids by fractional crystallization is shown in figure 3, the curves have been calculated using

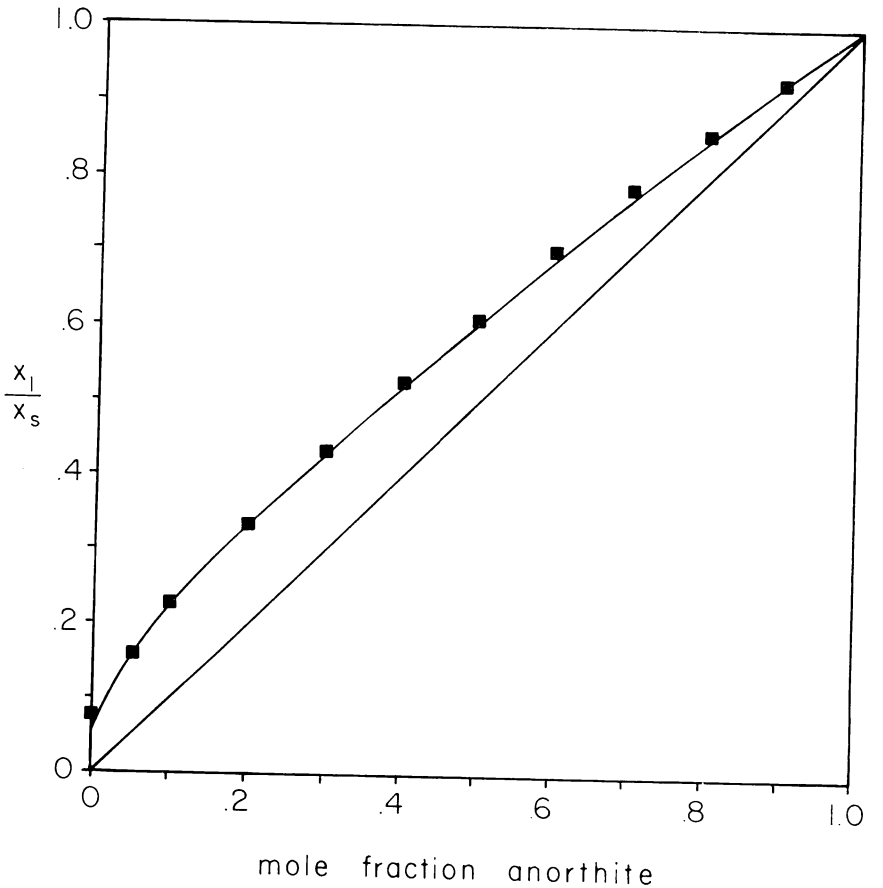

Fig. 1. The mole ratio x_l/x_s plotted as a function of x_l for the albite–anorthite system at 1 bar using the phase relations of Bowen (1913) and Greig and Barth (1938). The squares show the experimental data, while the curve has been plotted using eq (6) with the constants (8).

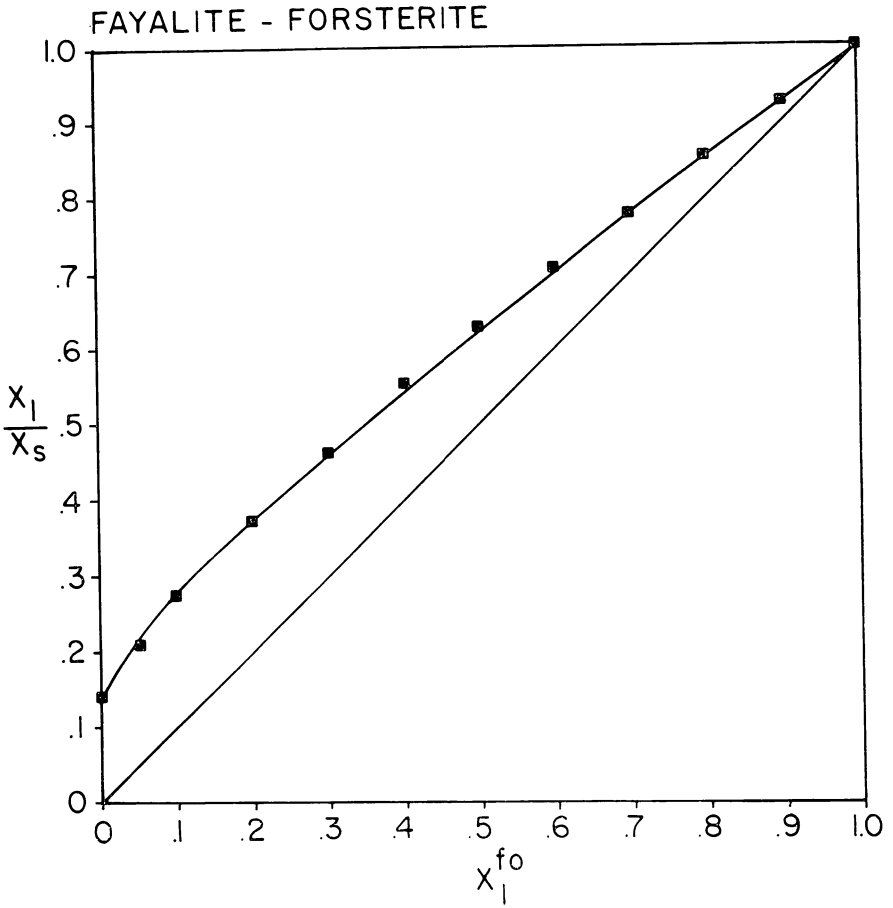

Fig. 2. The mole ratio x_l/x_s for the fayalite–forsterite system. The squares show the experimental data as estimated by Bowen and Schairer (1935). The curve has been plotted using eq (6) with the constants (9).

(14). The variation in the anorthite content will be dependent on the initial anorthite content of the liquids. Liquids with a high anorthite content display a small variation in the anorthite content during the initial stage of fractionation, whereas the decrease is rapid during the terminal stage. Liquids with a small anorthite content have a more constant decrease in the anorthite content with increasing degree of fractionation. The amount of residual liquid consisting of albite will increase with decreasing anorthite content of the initial liquid. The variation in the amount of liquid and their anorthite content are shown in detail in table 1. Let us consider a liquid that initially contains 50 mole percent An. When the percentage of anorthite in the liquid becomes 1 mole percent An, there is 22.74 mole percent liquid left, and when the anorthite content becomes 1 ppm, there is still 12.72 mole percent liquid left.

These percentages do not vary significantly for appropriate values of the constants a, b, and c, as long as c is larger than zero. Considering the errors of analysis by XRF and microprobe analysis, it is evident that for practical applications there is a substantial amount of residual albitic liquid left.

Using eq (3) by Maaløe (1976) the residual amount of liquid with 1 mole percent An is estimated as 22.38 mole percent, while the result here is 22.74 mole percent liquid. The difference is small, and the original equation, which has $c = 0$, was therefore considered appropriate as it gives a definitive value for the amount of residual albitic liquid for $x_1 = 0$. For $c = 0$ this amount is estimated as 19.95 mole percent liquid.

The variation in the composition of the instant fractionate, that is, the plagioclase that forms at any given temperature, is shown in figure 4. The variation is similar to that shown by the liquids. The variation in the compositions of solid and liquid for a liquid with an initial anorthite

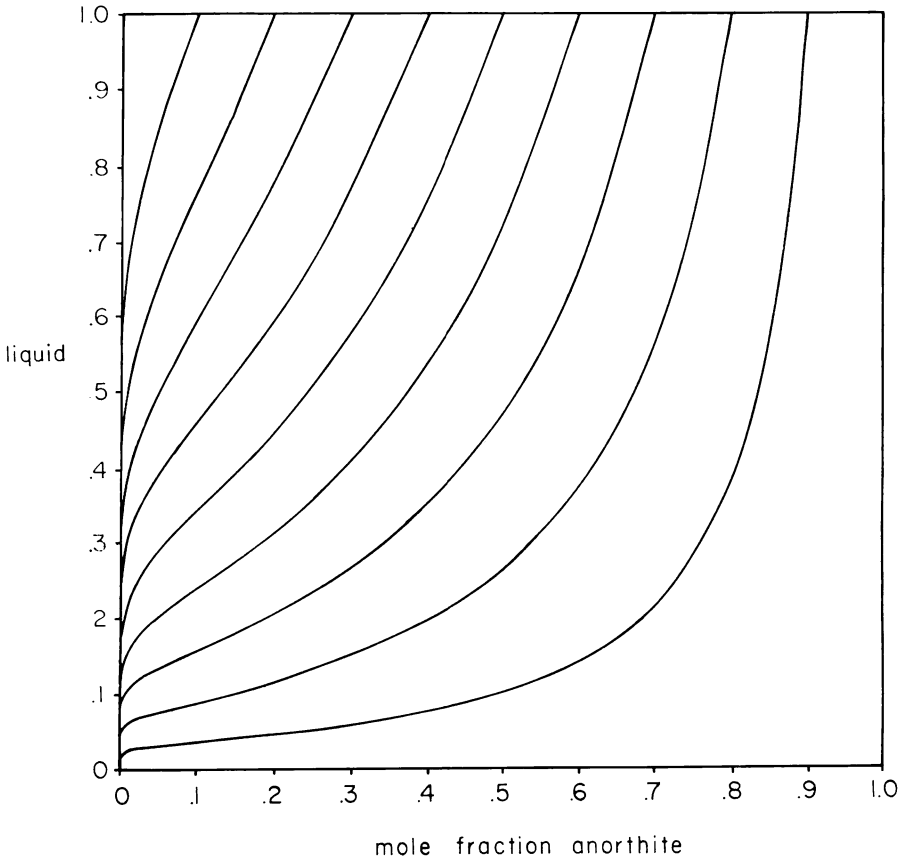

Fig. 3. The variation in the anorthite content and the amount of liquid by perfect fractional crystallization of plagioclase liquids. The curves have been calculated using (14).

TABLE 1

The anorthite contents of plagioclase liquids in mole percentages

mole percent An	liquid left								
90									100.00
80								100.00	38.59
70							100.00	56.45	21.78
60						100.00	65.80	37.14	14.33
50					100.00	71.34	46.94	26.50	10.22
40				100.00	74.80	53.36	35.11	19.82	7.65
30			100.00	76.83	57.47	40.99	26.96	15.23	5.88
20		100.00	77.57	59.59	44.58	31.80	20.92	11.81	4.56
10	100.00	76.18	59.09	45.40	33.96	24.23	15.94	8.99	3.47
1	66.95	51.00	39.56	30.40	22.74	16.22	10.67	6.02	2.32
1 ppm	37.45	28.53	22.13	17.00	12.72	9.07	5.97	3.37	1.30
10^{-4} ppm	23.04	17.55	13.62	10.46	7.83	5.58	3.67	2.07	0.80

content of 50 mole percent An is compared in figure 5. This diagram shows the variation that one would expect for a gabbroic intrusion, x_s^e is the composition of the instant fractionate, and the curve for x_s^e shows the variation in the cumulate that would form, and x_l^e shows the variation in the anorthite content of the liquid. Three different features might change the variation in anorthite content with structural height in an intrusion. The diagram shown in figure 5 has been calculated assuming the cross section of the liquid enclosure as constant. If an intrusion is funnel shaped or its cross section varies in some other manner, then the shape of the curves in figure 5 will be different. Secondly if plagioclase remains suspended in the magma due to an increasing viscosity by decreasing temperature, then the variation will also be different from that calculated. Thirdly, the relative proportions between the minerals vary during the crystallization and that will also modify the variation in anorthite content with structural height.

The phase relations encountered by fractional crystallization are summarized in figure 6 (Bowen, 1913; Greig and Barth, 1938). The variation in anorthite content is shown for 4 different liquids. The curves labeled x_f show the anorthite content of the integral fractionate. It is evident that for the anorthite-rich liquids there will only be a small decrease in the anorthite content of the fractionate with decreasing temperature, whereas the decrease is larger for the albite-rich liquids. The fractionating liquids will end up crystallizing almost pure albite for a period of time, and that will cause a thermal arrest on the cooling curves of fractionating systems. This temperature effect has been observed by experimental work on the Ge–Si system, which is similar to the albite–anorthite system (Thurmond, 1953), presenting experimental evidence that the fractionation eqs (14) and (15) do yield a correct result.

The more viscous magmas like andesitic and granitic magmas may undergo cooling and crystallization without gravitative fractionation. When that is the case then the crystals will remain suspended in the magma at the same position as they nucleate, and the crystallization will

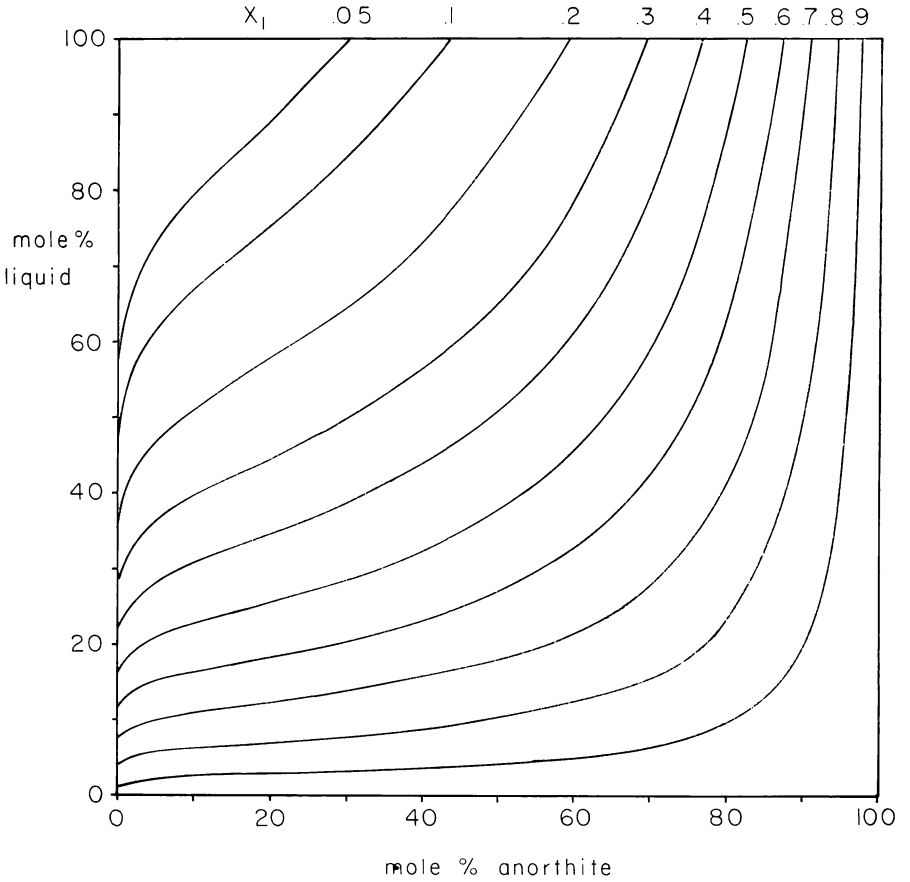

Fig. 4. The variation in the anorthite content of the solid formed at any given temperature, that is, the instant fractionate, within the albite–anorthite system. The anorthite content of the initial liquids is shown above the diagram.

therefore be fractional on a local scale. The theoretical zoning developed by this type of crystallization is shown in figure 7 for 3 different liquids, assuming a spherical shape of the crystals. The presence of a residual albitic solid is much less evident here than from the curves of figure 4, due to the volume increase with the third power of the radius. This diagram only shows theoretical zoning, the zoning pattern of natural phenocrysts will no doubt be more complex due to kinetic factors that cause reverse and oscillatory zoning.

ALBITE–ANORTHITE, PARTIAL MELTING

The treatment of fractional melting is essentially the same as for fractional crystallization. The basic differential equation for fractional melting is similar to the Rayleigh eq (1) and was first derived by Shaw (1970). Let Q be the amount of solid, and Q^0 the initial amount of solid — we then have:

$$x_l dQ = d(x_s Q) \tag{16}$$

so that:

$$\ln\left(\frac{Q}{Q^0}\right) = \int_{x_s^0}^{x_s} \frac{dx_s}{x_l - x_s} \tag{17}$$

The solution of this integral requires that x_l is expressed as a function of x_s. A suitable equation for the fayalite–forsterite system was proposed by Maaløe (1982), and the equation may also be used for the albite–anorthite system:

$$x_l = ax_s^4 + bx_s \tag{18}$$

The constants a and b were estimated as follows:

$$x_l = 0.84x_s^4 + 0.16x_s \tag{19}$$

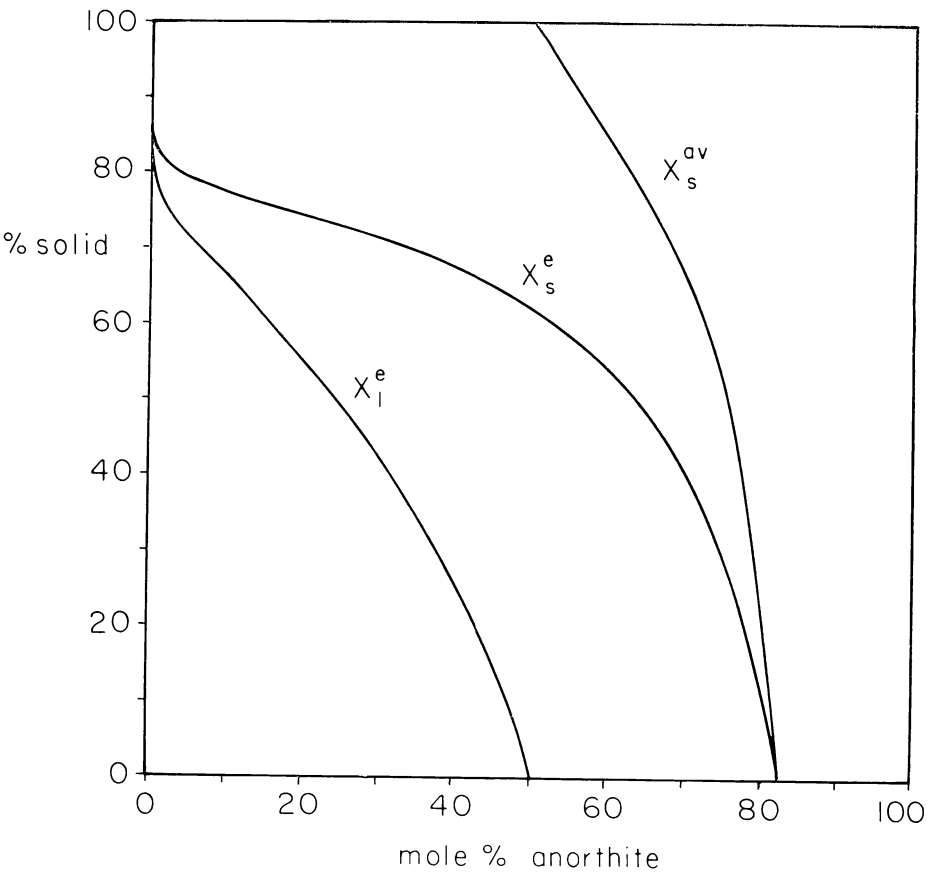

Fig. 5. The variations in anorthite content for a liquid that initially contained 50 mole percent An. Here x_l^e is the composition of the liquid, x_s^e is the composition of the instant fractionate, or the "cumulate," and x_s^{av} is the average composition of the integral fractionate.

The equation provides approximate values for x_l, but the results obtained here are accurate within 5 percent relative. By integration of (17) using (18) we obtain:

$$\ln\left(\frac{Q}{Q^0}\right) = \left[-\frac{1}{3a} \ln\left(\frac{x_s^3}{x_s^3 - 1}\right)\right]_{x_s^0}^{x_s} \tag{20}$$

The variation in amount of liquid estimated by (20) is shown in figure 8. For plagioclase with a low anorthite content quite large amounts of liq-

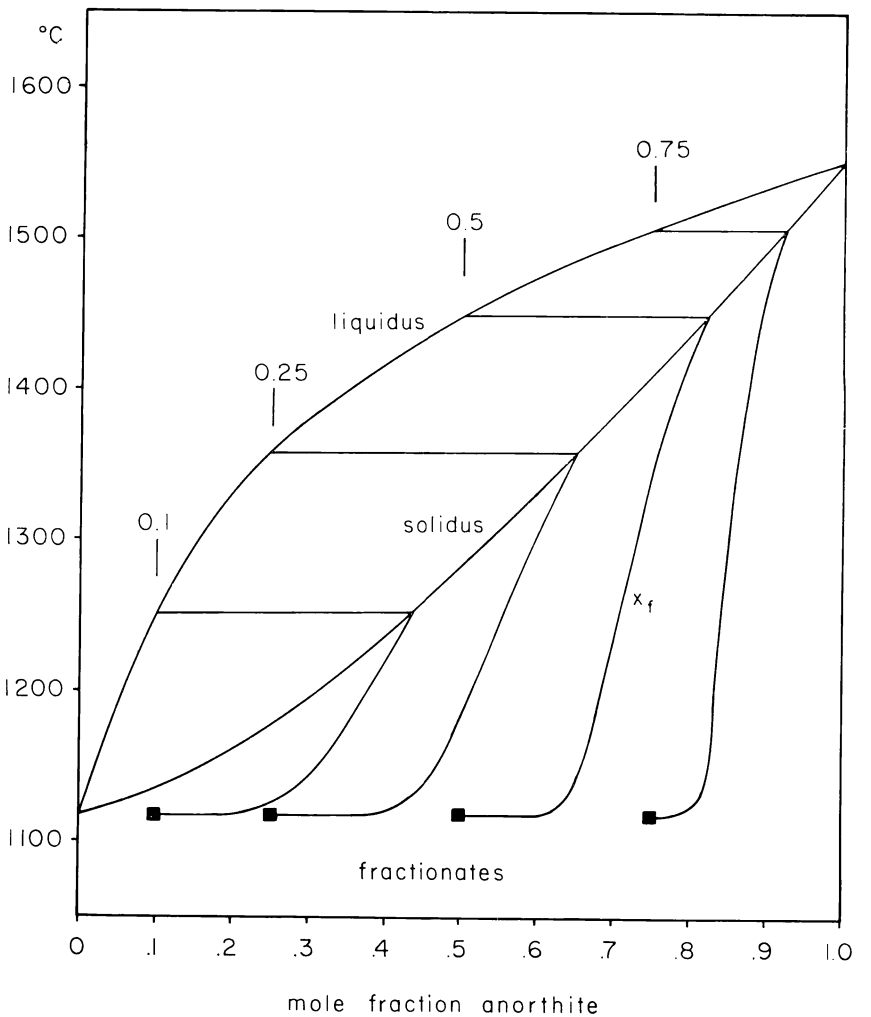

Fig. 6. This diagram shows the difference in the solid compositions produced by equilibrium crystallization and fractional crystallization. By fractional crystallization the instant fractionate follows the solidus curve, and the average composition of the integral fractionate is shown for 4 different initial liquid compositions as x_f.

uid can be produced while the anorthite content of the solid remains nearly constant. For solids with more than 50 mole percent An there is initially a more or less linear relationship between the amount of liquid and the anorthite content of the residual plagioclase. The variations displayed suggest that anatexis of granitoid rocks will change only the anorthite content of the residuum or palaeosome very slightly. The anorthite content of plagioclase in gabbroic rocks will vary significantly with the degree of melting.

The composition of the plagioclase liquids formed at different degrees of melting is shown in figure 9. The liquid compositions shown are those of the accumulated liquid, that is, the average composition of the total amount of liquid generated. The variation in the composition of

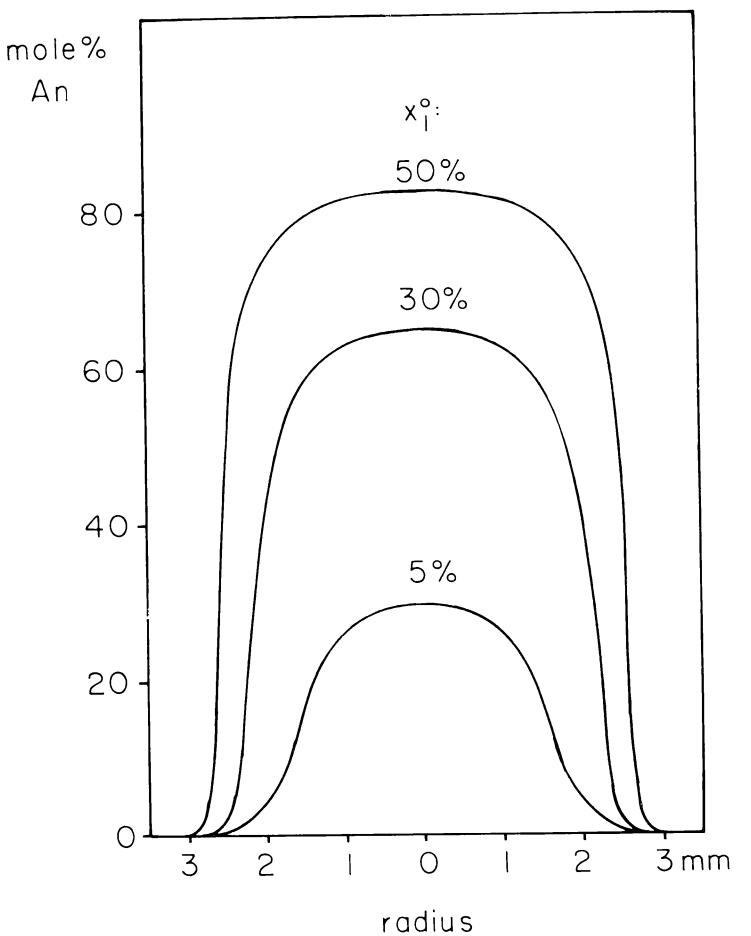

Fig. 7. The zoning patterns developed by perfect fractional crystallization of 3 different plagioclase liquids. It is assumed that the crystal has a spherical shape and a volume of 100 mm^3.

this liquid is small at small degrees of partial melting, especially for liquids formed from plagioclase with less than 50 mole percent An. This result might imply that the normative anorthite content of migmatitic schlieren is virtually independent of the degree of partial melting, when the source has a granitic or granodioritic composition.

FAYALITE–FORSTERITE SYSTEM

It is evident from figures 1 and 2 that the x_l/x_s versus x_l curve for the fayalite–forsterite system is similar to the curve for the albite–anorthite system, and as a consequence the fractionation diagram for the liquids are similar (fig. 10). The equilibrium relationships of basaltic magmas are different from those of the binary system, as was shown by Roeder and Emslie (1970), and the fractionation of olivine from basaltic magmas is calculated using the phase relations determined by Roeder and Emslie (1970), Irvine (1977), Maaløe (1982).

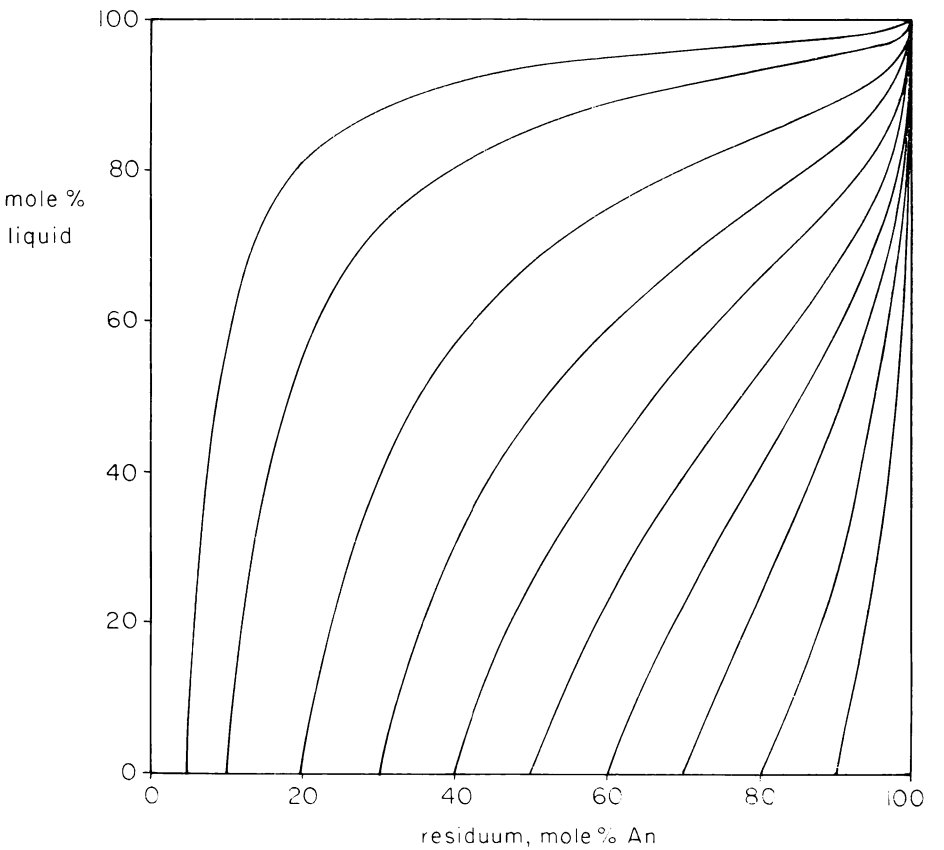

Fig. 8. The amounts of liquid formed by fractional partial melting of plagioclase and the composition of the residuum.

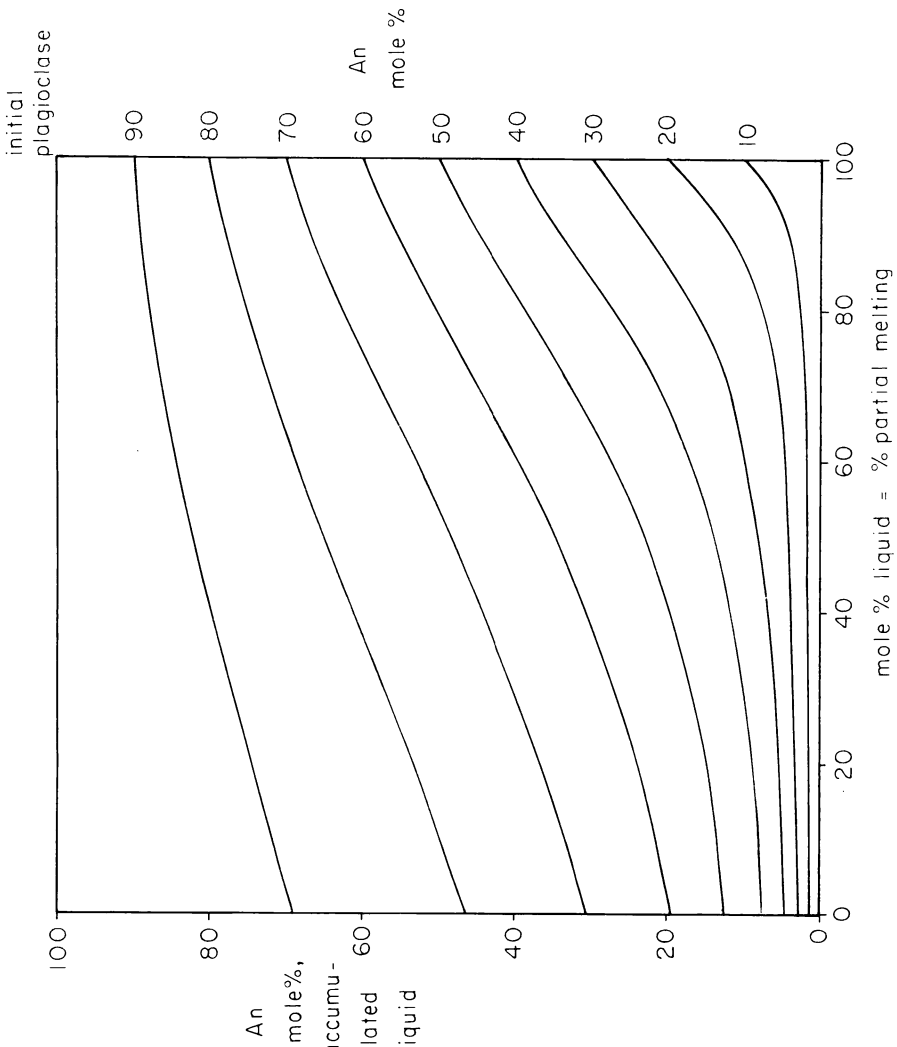

Fig. 9. The anorthite contents of the accumulated liquids, that is, the average anorthite content of all liquid generated.

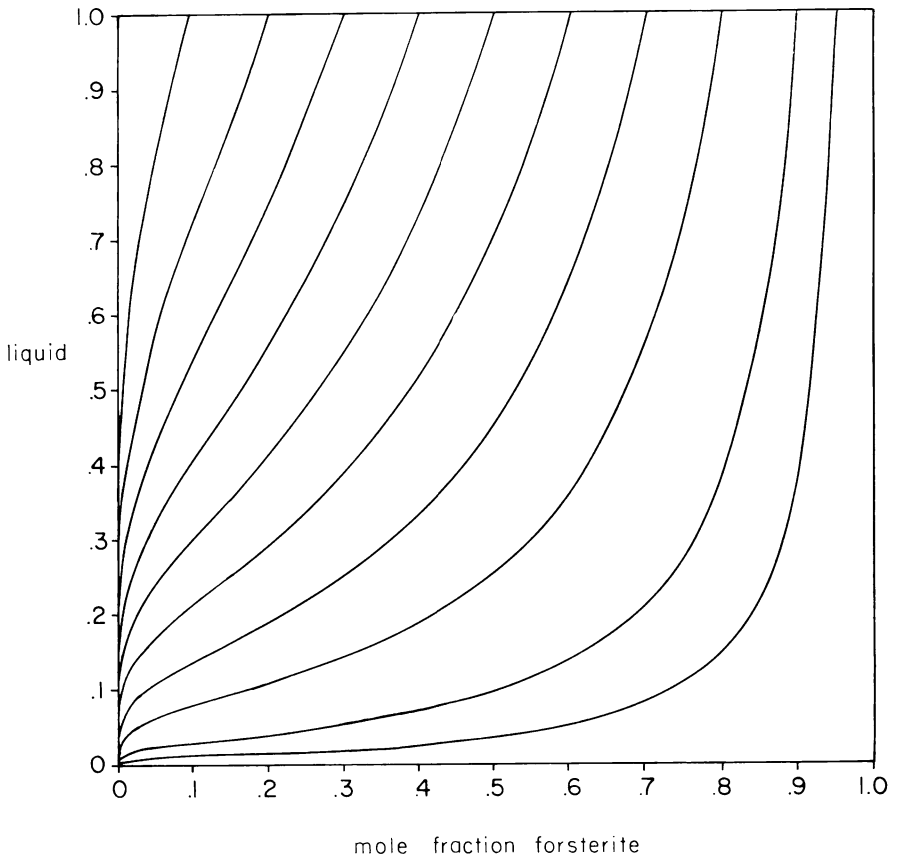

Fig. 10. The variation in the forsterite content of olivine liquids by fractional crystallization. The curves have been estimated using eq (15).

The calculation method shown above for fractional crystallization can also be extended to ternary liquids. However, the phase relations of ternary systems with plagioclase or olivine as binary components have not been estimated within the ternary fields. The thermodynamic properties of these ternary liquids are not yet known sufficiently well for a calculation of the tie lines (Bottinga, Weill, and Richet, 1981; Navrotsky and others, 1980). An approximate estimate of the fractionation within the albite–anorthite–diopside system has been given by Maaløe (1976), but a more accurate treatment is not possible at present.

CONCLUSIONS

Eq (13) represents a general equation for the calculation of the fractionation in systems with solid solution of the albite–anorthite type. The amount of residual liquid is not nil but varies with the initial composition of the liquids. The results obtained here are based on perfect fractional crystallization and represent a limiting case; however, they can easily be

applied for partial fractional crystallization (Maaløe, 1976). The theoretical fractionation curves have petrogenetic applications, because they may reveal various features of natural fractionation processes.

References

Anderson, A. T., Friedman, R., Otto, T., Wood, T. V., and Wyszynsky, J., 1982, The fractional crystallization of plagioclase in the Hat Creek basalt: Observations and theory: Jour. Geology, v. 90, p. 545-558.

Bottinga, Y., Weill, D. F., and Richet, P., 1981, Thermodynamic modelling of silicate melts, *in* Newton, R. C., Navrotsky, A., and Wood, B. J., eds., Thermodynamics of minerals and melts: New York, Springer Verlag, p. 207-245.

Bowen, N. L., 1913, The melting phenomena of the plagioclase feldspars: Am. Jour Sci. 4th ser., v. 35, p. 577-599.

———— 1928, The evolution of igneous rocks: Princeton, N.J., Princeton Univ. Press, 334 p.

Bowen, N. L., and Schairer, J. F., 1935, The system MgO–FeO–SiO_2: Am. Jour. Sci. ser. 5, v. 29, p. 151-217.

Greig, J. W., and Barth, T. F. W., 1938, The system Na_2O–Al_2O_3–$2SiO_2$ (nephelinite, carnegieite)–Na_2O–Al_2O_3–$6SiO_2$ (albite): Am. Jour. Sci. 5th ser., v. 35A, p. 93-112.

Irvine, T. N., 1977, Definition of primitive liquid compositions for basaltic magmas: Carnegie Inst. Washington Year Book v. 76, p. 454-465.

Maaløe, S., 1976, Quantitative aspects of fractional crystallization of major elements: Jour. Geology, v. 84, p. 81-94.

———— 1982, Geochemical aspects of permeability controlled partial melting and fractional crystallization: Geochim. et Cosmochim. Acta, v. 46, p. 43-57.

Morse, S. A., 1976, The lever rule with fractional crystallization and fusion: Am. Jour. Sci., v. 276, p. 330-346.

Navrotsky, A. R., Hon, R., Weill, D. F., and Henry, D., 1980, Thermochemistry of glasses and liquids in the systems: $CaMgSi_2O_6$–$CaAl_2Si_2O_8$–$NaAlSi_3O_8$, SiO_2–$CaAl_2Si_2O_8$–$NaSiAl_3O_8$ and SiO_2–Al_2O_3–CaO–Na_2O: Geochim. et Cosmochim. Acta, v. 44, p. 1409-1423.

Powell, R., 1978, Equilibrium thermodynamics in petrology: London, Harper & Row, 284 p.

Rayleigh, J. W. S., 1902, On the distillation of binary mixtures: Philos. Mag., ser. 6, v. 4, p. 521-537.

Roeder, P. L., and Emslie, R. F., 1970, Olivine-liquid equilibrium: Contr. Mineralogy Petrology, v. 29, p. 275-289.

Thurmond, C. D., 1953, Equilibrium thermochemistry of solid and liquid alloys of germanium and of silicon. I. The solubility of Ge and Si in elements of groups III, IV, and V: Jour. Phys. Chemistry, v. 57, p. 827-830.

Weill, D. F., Stebbins, J. F., Hon, R., and Carmichael, I. S. E., 1980, The enthalpy of fusion of anorthite: Contr. Mineralogy Petrology, v. 74, p. 95-102.