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differentiation processes in mafic magmas**

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CRFRAC: A MBASIC PROGRAM FOR SIMULATING DIFFERENTIATION PROCESSES IN MAFIC MAGMAS

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ABSTRACT.

Mineral-melt phase equilibria can be calculated by combining single component distribution coefficients with stoichiometric, site occupancy and charge balance constraints imposed upon the solid phases. CRFRAC uses equations of the type $\ln D_i^{s/l}$ (adapted from Nielsen and Dungan, 1983) as a data base for the definition of phase equilibria conditions in mafic magmas; on the base of these relations the program identifies the solid assemblage, and for each increment of the crystallization process it establishes a system of equations, such as:

$$\sum_{i=1}^n X_i^m \cdot k_i^{M_j} = 1$$

(X_i^m = concentration of componente i in the melt $k_i^{M_j} = X_i^{M_j} / X_i^m$; M_j = mineral j (1 to r)

the solution of which allows to model several magmatic differentiation processes operating at low-pressure; these include, perfect fractional crystallization and/or concurrent fractionation, magma chamber recharge, contamination and depletion of the magma chamber by eruption. Given the parental magma composition CRFRAC will calculate (for each increment of crystallization) the liquidus temperature and f_{O_2} , the identity proportion and chemical composition of the mineral phases comprising the liquidus assemblage, as well as, the mass fraction and composition of the residual magma.

RESUMO

Relações de equilíbrio sólido-líquido em sistemas magmáticos operando a baixa pressão podem ser calculadas utilizando coeficientes de distribuição elementares em conjugação com constrangimentos impostos às fases sólidas por estequiometria e balanço de cargas. O programa CRFRAC utiliza relações do tipo $\ln D_i^{s/l}$ (ligeiramente modificadas de Nielsen and Dungan, 1983) como argumento básico para a definição das condições de equilíbrio de fases em magmas máficos; com base nestas relações o programa caracteriza a paragénesis sólida e em cada incremento do processo de cristalização estabelece um sistema de equações:

$$\sum_{i=1}^n X_i^m \cdot k_i^{M_j} = 1$$

(X_i^m = concentração componente i no líquido; $k_i^{M_j} = X_i^{M_j} / X_i^m$; M_j = mineral j (1 to r)

cujas soluções permitem modelar de forma quantitativa vários processos de diferenciação magmática a baixa pressão. Estes incluem cristalização fracionada e ACF, operando (ou não) simultaneamente com recarga e/ou esvaziamento da câmara magmática durante a erupção vulcânica. Dada a composição inicial do magma parental, o programa CRFRAC calcula (para cada incremento de cristalização) a temperatura e f_{O_2} do sistema, a natureza, proporção e composição química dos minerais constituintes da associação sólida, bem como, a quantidade relativa e composição química do magma residual.

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1 – INTRODUCTION

When examining chemical variations within igneous rocks suites the effects of possible fractionation processes are tested most easily with simulation models. As a consequence, there have been numerous attempts in recent years to quantify certain aspects of mineral-melt equilibria in order to model either equilibrium or fractional crystallization in natural silicate liquids (Nathan and Van Kirk, 1978; Hostetler and Drake, 1980; Langmuir and Hanson, 1981; Nielson and Dungan, 1983; Ghiorso and Carmichael, 1985). In most of the studies cited, magmatic evolution within magma chambers is simulated by combination of Rayleigh fractionation with magma mixing and/or wall-rock assimilation. Langmuir and Hanson (1981) and Nielsen and Dungan (1983) provided relatively simple methods and the necessary data for calculating phase equilibria in mafic magmas; O'Hara and Mathews (1981) developed general equations to simulate compositional effects of fractional crystallization in open-system magma chambers. However, the calculations required to apply these procedures to natural systems are lengthy and involved, and cannot be performed without computer assistance. This report describes a MBASIC program – CRFRAC – that has been written to perform these calculations.

CRFRAC models low-pressure fractional crystallization processes in natural mafic magma bodies. It combines these use of a two-lattice model for the activity of silicate melt components (Nielsen and Drake, 1979; Nielsen and Dungan, 1983) with the single element mineral/melt distribution coefficients (Langmuir and Hanson, 1981) technique, in order to calculate mineral-melt equilibria and fractional crystallization paths. In addition the program will calculate the liquid lines of descent for concurrent fractionation, magma chamber recharge, contamination and depletion of the magma chamber by eruption.

The initial code of CRFRAC uses (with minor modifications) data and the numerical algorithm developed by Nielsen and Dungan (1983) and Nielsen (1985) to calculate liquidus temperatures and equilibrium mineral compositions; in this respect it is essentially a BASIC version of the EQUIL program written by Nielsen (1985). However, CRFRAC, then goes a step beyond by incorporating explicit calculation of the relative phase proportions in the liquidus assemblages, as well as bulk solid/liquid element partitioning, thus, providing a closer approach to reality.

2 - METHOD

2.1 - Distribution coefficients

For any component, i , distributed between a mineral and a melt, a requirement for equilibrium is that

$$\mu_i^s = \mu_i^m \quad (1)$$

where μ_i^s and μ_i^m are chemical potentials of an independently variable component, i , in the mineral and melt. Choosing the standard state as the pure phase (solid or melt) at the temperature and pressure of interest, the chemical potentials in the two phases are related to the activities (a) by

$$\mu_i^s = \mu_{i,0}^s + RT \ln a_i^s \quad (2)$$

$$\mu_i^m = \mu_{i,0}^m + RT \ln a_i^m \quad (3)$$

so, at 1 bar pressure

$$\ln k(l) = \ln \frac{a_i^s}{a_i^m} = \frac{\mu_{i,0}^m - \mu_{i,0}^s}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (4)$$

where $k(l)$ is the equilibrium constant, ΔH^0 and ΔS^0 are molar enthalpy and entropy changes during the reaction, R is the gas constant, and T the equilibrium temperature in degrees Kelvin. Since $a_i = X_i \gamma_i$, substitution yields,

$$\ln D_i^{s/l} = \ln(X_i^s/X_i^m) = \ln k(l) - \ln(\gamma_i^s/\gamma_i^m) \quad (5)$$

where $D_i^{s/l}$ is the distribution coefficient for component i between mineral and melt, γ is the activity coefficient, and X is the concentration. Thus, if the chemical compositions of the phases are expressed in terms of cation mol %, then $D_i^{s/l}$ will describe the equilibrium relationships between the mole fractions of component i in the coexisting mineral (s) and melt (Langmuir and Hanson, 1981.).

As easily seen from (4) and (5), mineral-melt distribution coefficients are dependent on both temperature and composition. The linear correlation often observed between mineral-melt distribution coefficients and inverse temperature may be expressed, by analogy with (4), in terms of the equation

$$\ln D_i^{s/l} = -A/T + B \quad (6)$$

where A and B are constants calculated by linear least-squares regression through a data set (e.g. Roeder and Emslie, 1970; Langmuir and Hanson, 1981; Nielsen and Dungan, 1983). The degree to which distribution coefficients are dependent compositionally is a function of the chosen reactions and how the mixing properties of the phases involved are formulated (see O'Nions and Powell, 1977). For the purposes of this study, the equations describing the thermal dependence of the distribution coefficients were adopted from those proposed by Nielsen and Dungan (1983; Tab.3) and the two lattice melt component activity model of Nielsen and Drake (1979) was used to eliminate the effects of the compositional dependence of distribution coefficients the formulation of the mixing properties of minerals and melts adopted by CRFRAC was discussed in detail by Nielsen and Dungan (1983) and only a few practical aspects will be reviewed here.

2.2 - Mixing in mineral and melts

In the melt component activity model adopted here (see Bottinga and Weill, 1972; Nielsen and Darke, 1979) the silicate melt is inferred to consist of a polymerized irregular network of tetrahedrally coordinated cations (primarily Si and Al) which is modified by larger cations occupying higher coordination sites. The network forming (NF) components are SiO_2 , NaAlO_2 , and KAlO_2 and the network modifiers (NM) are MgO , FeO , CaO , $\text{AlO}_{1.5}$ (excess over Na^+ and K^+), $\text{FeO}_{1.5}$, $\text{CrO}_{1.5}$, and TiO_2 . According to Nielsen and Drake (1979) the activities of melt components are calculated by assuming that components mix ideally only with their like components with no mixing between network-forming and network-modifying quasi-lattices.

After recalculating the analytical results into cation mole fractions, melt component activities are defined as:

$$a_{\text{SiO}_2}^{\text{m}} = X_{\text{SiO}_2}^{\text{NF}} = X_{\text{SiO}_2}^{\text{m}} / (X_{\text{SiO}_2}^{\text{m}} + X_{\text{NaO}_{0.5}}^{\text{m}} + X_{\text{KO}_{0.5}}^{\text{m}}) \quad (7)$$

$$a_{\text{TiO}_2}^{\text{m}} = X_{\text{TiO}_2}^{\text{NF}} = X_{\text{TiO}_2}^{\text{m}} / \sum \text{NM} \quad (8)$$

$$a_{\text{AlO}_{1.5}}^{\text{m}} = X_{\text{AlO}_{1.5}}^{\text{m}} = (X_{\text{AlO}_{1.5}}^{\text{m}} - X_{\text{NaO}_{0.5}}^{\text{m}} - X_{\text{KO}_{0.5}}^{\text{m}}) / \sum \text{NM} \quad (9)$$

$$a_{\text{CrO}_{1.5}}^{\text{m}} = X_{\text{CrO}_{1.5}}^{\text{m}} / \sum \text{NM} \quad (10)$$

$$a_{\text{FeO}_{1.5}}^{\text{m}} = X_{\text{FeO}_{1.5}}^{\text{m}} / \sum \text{NM} \quad (11)$$

$$a_{\text{FeO}}^{\text{m}} = X_{\text{FeO}}^{\text{m}} / \sum \text{NM} \quad (12)$$

$$a_{\text{MgO}}^{\text{m}} = X_{\text{MgO}}^{\text{m}} / \sum \text{NM} \quad (13)$$

$$a_{\text{CaO}}^{\text{m}} = X_{\text{CaO}}^{\text{m}} / \sum \text{NM} \quad (14)$$

$$a_{\text{NaAlO}_2}^{\text{m}} = X_{\text{NaAlO}_2}^{\text{m}} = X_{\text{NaO}_{0.5}}^{\text{m}} / (X_{\text{SiO}_2}^{\text{m}} + X_{\text{NaO}_{0.5}}^{\text{m}} + X_{\text{KO}_{0.5}}^{\text{m}}) \quad (15)$$

$$a_{\text{KAlO}_2}^{\text{m}} = X_{\text{KAlO}_2}^{\text{m}} = X_{\text{KO}_{0.5}}^{\text{m}} / (X_{\text{SiO}_2}^{\text{m}} + X_{\text{NaO}_{0.5}}^{\text{m}} + X_{\text{KO}_{0.5}}^{\text{m}}) \quad (16)$$

It is well known (e.g. Osborn, 1962) that different crystallization sequences can arise from identical bulk liquid compositions by varying the ferric/ferrous ratios. CRFRAC includes a routine (adapted from Nielsen, 1985) where the oxidation state of Fe in the melt is calculated as a function of temperature, composition and $f\text{O}_2$, according to the relations of Sack et al. (1980); $f\text{O}_2$, is an input parameter, defined (initially) by the user as a deviation (in log units) from the quartz-fayalite-magnetite (QFM) buffer (Wones and Gilbert, 1969).

Olivine - and plagioclase - melt equilibria are modeled using single element distribution coefficients (see Roeder and Emslie, 1970; Langmuir and Hanson, 1981), meaning that in equations

$$\text{MgO}^{\text{NM}}(\text{m}) + 1/2 \text{SiO}_2^{\text{NF}}(\text{m}) = \text{MgSi}_{1/2}\text{O}_2(\text{ol}) \quad (17)$$

$$\text{FeO}^{\text{NM}}(\text{m}) + 1/2 \text{SiO}_2^{\text{NF}}(\text{m}) = \text{FeSi}_{1/2}\text{O}_2(\text{ol}) \quad (18)$$

$$\text{CaO}^{\text{NM}}(\text{m}) + 2\text{AlO}_{1.5}^{\text{NM}} + 2\text{SiO}_2^{\text{NF}}(\text{m}) = \text{CaAl}_2\text{Si}_2\text{O}_8(\text{pl}) \quad (19)$$

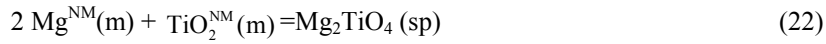
$$\text{NaAlO}_2^{\text{NF}}(\text{m}) + 3\text{SiO}_2^{\text{NF}}(\text{m}) = \text{NaAlSi}_3\text{O}_8(\text{pl}) \quad (20)$$

$a_{\text{MgSi}_{1/2}\text{O}_2}^{\text{ol}}$, $a_{\text{FeSi}_{1/2}\text{O}_2}^{\text{ol}}$, $a_{\text{An}}^{\text{pl}}$, $a_{\text{Ab}}^{\text{pl}}$ are evaluated as the cation mole fractions of Mg and Fe in olivine and Ca and Na in plagioclase.

In spinel (TM_2O_4) the distribution of Mg, Fe^{3+} , Al and Cr is estimated as single oxide solid-melt distribution coefficients; it is further assumed that Mg and Fe^{2+} mixed ideally on the M and T sites, with Ti occupying only the octahedral M sites. The activity of Mg_2TiO_4 is evaluated as

$$a_{\text{Mg}_2\text{TiO}_4}^{\text{sp}} = (X_{\text{Ti}}^{\text{sp}})(X_{\text{Mg}}^{\text{sp}})^2 \quad (21)$$

and $X_{\text{Ti}}^{\text{sp}}$ calculated from $X_{\text{Mg}}^{\text{sp}}$ values on the basis of the available experimental data for the equilibrium relation



$X_{\text{Fe}^{2+}}^{\text{sp}}$ is calculated based upon spinel stoichiometric relations, by realizing that the coupled substitution



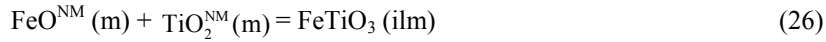
implies that

$$X_{\text{Fe}^{2+}}^{\text{sp}} = 1/3 + X_{\text{Ti}}^{\text{sp}} - X_{\text{Mg}}^{\text{sp}} \quad (24)$$

For ilmenite (M1 M2 O_3) it is assumed that all Fe is Fe^{2+} , that Fe, Mg and Cr mix ideally on the M1 site with Ti filling the M2 site. The activity of ilmenite is evaluated as

$$a_{\text{FeTiO}_3}^{\text{ilm}} = X_{\text{Fe}^{2+}}^{\text{M1}} \quad (25)$$

through the equilibrium relation



and the distribution of Mg and Cr evaluated by using single oxide distribution coefficients.

For both high – and low – Ca pyroxenes, major phase component activities are evaluated by assuming complete disorder and ideal mixing on the sites. Therefore,

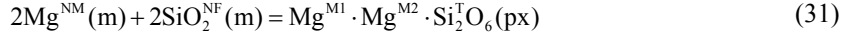
$$a_{\text{Enst}}^{\text{px}} = X_{\text{Mg}}^{\text{M2}} \cdot X_{\text{Mg}}^{\text{M1}} \cdot (X_{\text{Si}}^{\text{T}})^2 \quad (27)$$

$$a_{\text{Fs}}^{\text{px}} = X_{\text{Fe}}^{\text{M2}} \cdot X_{\text{Fe}}^{\text{M1}} \cdot (X_{\text{Si}}^{\text{T}})^2 \quad (28)$$

$$a_{\text{Di}}^{\text{px}} = X_{\text{Ca}}^{\text{M2}} \cdot X_{\text{Mg}}^{\text{M1}} \cdot (X_{\text{Si}}^{\text{T}})^2 \quad (29)$$

$$a_{\text{Hed}}^{\text{px}} = X_{\text{Ca}}^{\text{M2}} \cdot X_{\text{Fe}}^{\text{M1}} \cdot (X_{\text{Si}}^{\text{T}})^2 \quad (30)$$

where a_i^{px} are related to melt composition by appropriate pyroxene-melt reactions (see Nielsen and Drake, 1979; data set 3), such as



The distribution of Al, Cr and Ti are evaluated as oxide coefficients. The distribution of Ca, Fe and Mg between M1 and M2 sites (and consequently, pyroxene compositions) are estimated from a_i^{px} values (ignoring for simplicity the contribution from the tetrahedral site) on the basis of following relations (see also Nielsen, 1985),

$$a_{\text{Di}}^{\text{px}} / a_{\text{Hed}}^{\text{px}} = X_{\text{Mg}}^{\text{M1}} / X_{\text{Fe}}^{\text{M1}} \quad (32)$$

where $X_{\text{Mg}}^{\text{M1}} \approx 1 - X_{\text{Fe}}^{\text{M1}}$; therefore, rearranging (32),

$$X_{\text{Fe}}^{\text{M1}} \approx 1 / (1 + (a_{\text{Di}}^{\text{px}} / a_{\text{Hed}}^{\text{px}})) \quad (33)$$

$$X_{\text{Fe}}^{\text{M2}} = a_{\text{Fs}}^{\text{px}} / a_{\text{Fe}}^{\text{M1}} \quad (34)$$

$$X_{\text{Ca}}^{\text{M2}} = a_{\text{Hed}}^{\text{px}} / a_{\text{Fe}}^{\text{M1}} \quad (35)$$

$$X_{\text{Mg}}^{\text{M2}} = a_{\text{Enst}}^{\text{px}} / (1 - X_{\text{Fe}}^{\text{M1}} - \sum X_{\text{R}^{3+}}^{\text{M1}} - X_{\text{Ti}}^{\text{M1}}) \quad (36)$$

$$X_{\text{Mg}}^{\text{M1}} = 1 - X_{\text{Fe}}^{\text{M1}} - \sum X_{\text{R}^{3+}}^{\text{M1}} - X_{\text{Ti}}^{\text{M1}} \quad (37)$$

2.3 – Phase equilibria

In order to be stable, a crystalline phase must specific stoichiometric, site occupancy and charge balance constraints; in addition, for each phase the sum of the mole fractions of the components must be one. During solid-melt equilibria, for each mineral, comprising n phase components, there will be n equations of type (4), in addition to the equation

$$\sum_{i=1}^n X_i^{\text{A}} = 1 \quad (\text{mineral A}) \quad (38)$$

describing mass balance and stoichiometric relations. For example, in olivine (see Appendix 2),

$$\ln \frac{X_{\text{MgO}}^{\text{ol}}}{a_{\text{MgO}}^{\text{m}} \cdot (a_{\text{SiO}_2}^{\text{m}})^{1/2}} = 6700 / T - 3.73 \quad (39)$$

$$\ln \frac{X_{\text{FeO}}^{\text{ol}}}{a_{\text{FeO}}^{\text{m}} \cdot (a_{\text{SiO}_2}^{\text{m}})^{1/2}} = 6874 / T - 4.97 \quad (40)$$

$$X_{\text{MgO}}^{\text{ol}} + X_{\text{FeO}}^{\text{ol}} = 0.66667 \quad (41)$$

Given the melt composition (converted to melt component activities; see eqs. 7-16), the solution of the above systems of equations is easily achieved (e.g. by iterative method) allowing the calculation of liquidus temperatures and compositions of the crystallizing minerals. The identity of the liquidus phase (or phase assemblage) is determined (for each melt composition) by comparison of the calculated equilibrium temperatures; after some testing, we have decided that, for practical purposes, any mineral with a liquidus temperature lying within 0.3° Kelvin of the highest calculated equilibrium temperature would belong to the liquidus assemblage.

CRFRAC models magma chamber magmatic evolution as an incremental process. In each cycle the original mass of magma is reduced by certain amount which represents the mass fraction crystallized and the mass fraction which escapes as lava; simultaneously, variable amounts of digested roof rocks and of parental magma may be added to yield a new mixed magma. According to O'Hara and Mathews (1981), for a periodically replenished, periodically tapped, continuously fractionated magma chamber, in each cycle the mass balance equation for any component, *i*, may be written:

$$X_i^m(n) \cdot MF(n) = X_i^m(n-1) \cdot MF(n-1) \cdot (1 - \bar{C} - E \cdot \bar{C}) \cdot (1 - \bar{C})^{D_i^{s/l}(n-1)} + A \cdot \bar{C} \cdot X_i^{mA} + R \cdot C \cdot X_i^{mR} \quad (42)$$

where,

n : cycle number

\bar{C} : mass fraction crystallized during each cycle

E : eruption factor ($E \cdot \bar{C}$ = mass fraction that escapes as lava)

A : assimilation factor

R : replenishment factor

MF(*n*) : Mass fraction of residual mixed magma at the end of cycle *n*

$D_i^{s/l}(n)$: bulk solid-liquid distribution coefficient for component *i* during cycle *n*

X_i^{mA} : concentration of component *i* in contaminant

X_i^{mR} : concentration of component *i* in replenishing magma batch

$X_i^m(n)$: concentration of component *i* in mixed magma

Because $D_i^{s/l}(n)$ values will change with both temperature and melt composition, \bar{C} (magma differentiation increment monitor parameter - see equation (42)) should be kept as small as possible; however, very small values of \bar{C} will result in an unreasonably high computing time. On the basis of several experiments, \bar{C} was taken to be 0.001 (0.1%); smaller fractionation intervals had no significant effect upon the solid/liquid compositions produced at any advanced step.

MF(*n*) in equation (42) may be expressed as a function of *MF*(*n*-1) by the relation

$$MF(n) = MF(n-1) \cdot (1 - \bar{C} - E \cdot \bar{C}) + A \cdot \bar{C} + R \cdot \bar{C} \quad (43)$$

given that *MF*(0)=1, and that $X_i^m(0)$, *E*, *A*, *R*, X_i^{mA} and $X_i^{mR} = X_i^m(0)$ are all input parameters defined by the user (\bar{C} =constant as discussed before), the solution of equation (42) for each differentiation cycle depends only on the evaluation of $D_i^{s/l}(n-1)$.

The bulk solid-liquid distribution coefficient may be expressed as:

$$D_i^{s/l}(n-1) = \sum_j X_j \cdot k_i^j(n-1) \quad (44)$$

where the summation is over the mineral phases comprising the liquidus assemblage, X_j is the proportion of mineral j in the solid assemblage, and $k_i^j(n-1)$ is the distribution coefficient for component i between mineral j and melt ($k_i^j(n-1) = X_i^j(n-1) / X_i^m(n-1)$). Stoichiometric constraints may be used together with k_i^j 's combining the definition of k_i^j expressed as

$$X_i^j(n-1) = k_i^j(n-1) \cdot X_i^m(n-1) \quad (45)$$

with equation (38) to yield (Langmuir and Hanson, 1981)

$$\sum_j k_i^j(n-1) \cdot X_i^m(n-1) = 1 \quad (46)$$

Because we are using small enough differentiation increments it may be safely assumed that k_i^j 's will remain (close enough to) constant during the entire cycle; thus, at the end of increment $(n-1)$

$$\sum_j k_i^j(n-1) \cdot X_i^m(n) = 1 \quad (47)$$

must also hold true. For a system comprising p mineral phases and r chemical components, $p-1$ equations, of type (47)

$$\left. \begin{aligned} k_1^1(n-1) \cdot X_1^m(n) + k_2^1(n-1) \cdot X_2^m(n) + \dots + k_r^1(n-1) \cdot X_r^m(n) &= 1 \\ k_1^2(n-1) \cdot X_1^m(n) + k_2^2(n-1) \cdot X_2^m(n) + \dots + k_r^2(n-1) \cdot X_r^m(n) &= 1 \\ \vdots \\ k_1^{p-1}(n-1) \cdot X_1^m(n) + k_2^{p-1}(n-1) \cdot X_2^m(n) + \dots + k_r^{p-1}(n-1) \cdot X_r^m(n) &= 1 \end{aligned} \right\} \quad (48)$$

in addition to the equation

$$X_1 + X_2 + \dots + X_p = 1 \quad (49)$$

(the sum of mineral proportions in the liquidus assemblage must sum one) will suffice to describe phase equilibria among the p mineral phases and melt. In (48) each $X_i^m(n)$ ($i=1$ to r) may be expressed as a function of $X_i^m(n-1)$ according to equation (42); therefore, by combining (49) with (44)

$$D_i^{s/l}(n-1) = \sum_{j=1}^{p-1} X_j \cdot k_i^j(n-1) + (1 - \sum_{j=1}^{p-1} X_j) \cdot k_i^p(n-1) \quad (50)$$

substituting (50) into (42) (and dividing (42) by $MF(n)$), and finally by substitution of the right side of rearranged (42)'s for each $X_i^m(n)$ in (48), we are left with $(p-1)$ independent variables and $(p-1)$ equations. The

number of unknowns equals the number of equations, and a unique solution may be calculated. Indeed, the resulting system of nonlinear equations can be solved numerically, by Newton's method (e.g. Burden et al., 1978) allowing to calculate the compositions and proportions of solid phases and melt for each increment of the differentiation process. To model fractional crystallization (combined or not with wall-rock assimilation, eruption and replenishment) CRFRAC removes an increment of the liquidus phase assemblage from the liquid (adding it to the total solids); because the compositions of solids and liquid in general differ, the composition of the liquid changes as crystallization proceeds. New minerals appear on the liquidus of the residual melt and will be removed according to the procedures outlined above.

3 - RESULTS

CRFRAC was designed primarily to simulate fractional crystallization processes during low-pressure differentiation of mafic magmas. The purpose of this section is to test the validity of the calculations, computational effectiveness and petrological applicability of the CRFRAC algorithm. To this end, crystallization calculations are performed on two varieties of basalt: 1) a N-MORB from near the Kane Fracture Zone (Tormey et al., 1987), and 2) an olivine tholeiite from Iceland (Wood, 1978).

Table I – Initial compositions of N-MORB and olivine tholeiite (wt %)

	N-MORB AII 96-18-1 Tormey et al., 1987	Olivine tholeiite V10 Wood (1978)
SiO ₂	50.67	47.44
TiO ₂	1.46	1.88
Al ₂ O ₃	15.39	15.18
Fe ₂ O ₃	-	1.29
FeO	9.29	9.80
MgO	8.59	8.92
CaO	11.21	11.21
Na ₂ O	3.14	2.27
K ₂ O	0.12	0.23

Table II – Low-pressure fractional crystallization of N-MORB
AII 96-18-1, Kane Fracture Zone: 22° - 25°N,
Mid Atlantic Ridge (Tormey et al., 1987).

	Liquidus Temp. °C		Crystal assemblage Phase proportions		Phase composition		F % Residual melt	
	CRFRAC	Experim.	CRFRAC	Experim.	CRFRAC	Experim.	CRFRAC	Experim.
Olivine in	1220	1218	100% ol	100% ol	Fo 85	Fo 85	Liq.	Liq.
Plagiocl. in	1194	1205	75% pl 25% ol	70% pl 30% ol	AN 65 Fo 84	AN 72 Fo 83	.97	0.99
Cpx. in	1184	1171	30% cpx 15% ol 55% pl	35% cpx 10% ol 55% pl	En 48 Fo 81 An 63	En 48 Fo 79 An 66	0.85	0.84

3.1 - Crystallization of Kane Fracture basalt

Our first example is designed to compare the results of CRFRAC numerical simulation with some recent experimental work on the 1 atm fractional crystallization of a N-MORB (Tormey et al., 1987) (see Table I). These simulations are important in order to test the utility of CRFRAC algorithm against factual data before attempting to apply the technique to calculate natural crystallization sequences.

One atmosphere FePt-loop experiments were performed by Tormey et al. (1987) on the lava composition show in Table I. Experimental oxygen fugacities were monitored using ZrO₂-CaO electrolyte cells and maintained at the quartz-fayalite-magnetite buffer.

Calculated liquidus temperatures, phase assemblages and phase compositions are compared to the experimental results in table II. The experimental liquidus occurs at 1218°C with the appearance of olivine; plagioclase precipitates at 1205°C, and olivine + plagioclase are joined by Ca-pyroxene at 1171°C when $F=0.84$, after a $\approx 50^\circ\text{C}$ interval of crystallization.

CRFRAC predicts correctly the crystallization sequence and the predictions are within $\approx 15^\circ\text{C}$ of the experimental determinations. Experimental and calculated crystallizing phase proportions and compositions tend to be 1-2 mole % more fosteritic than the experimentally determined values while the measured An-contents are 3-7 mole % higher than those calculated by CRFRAC.

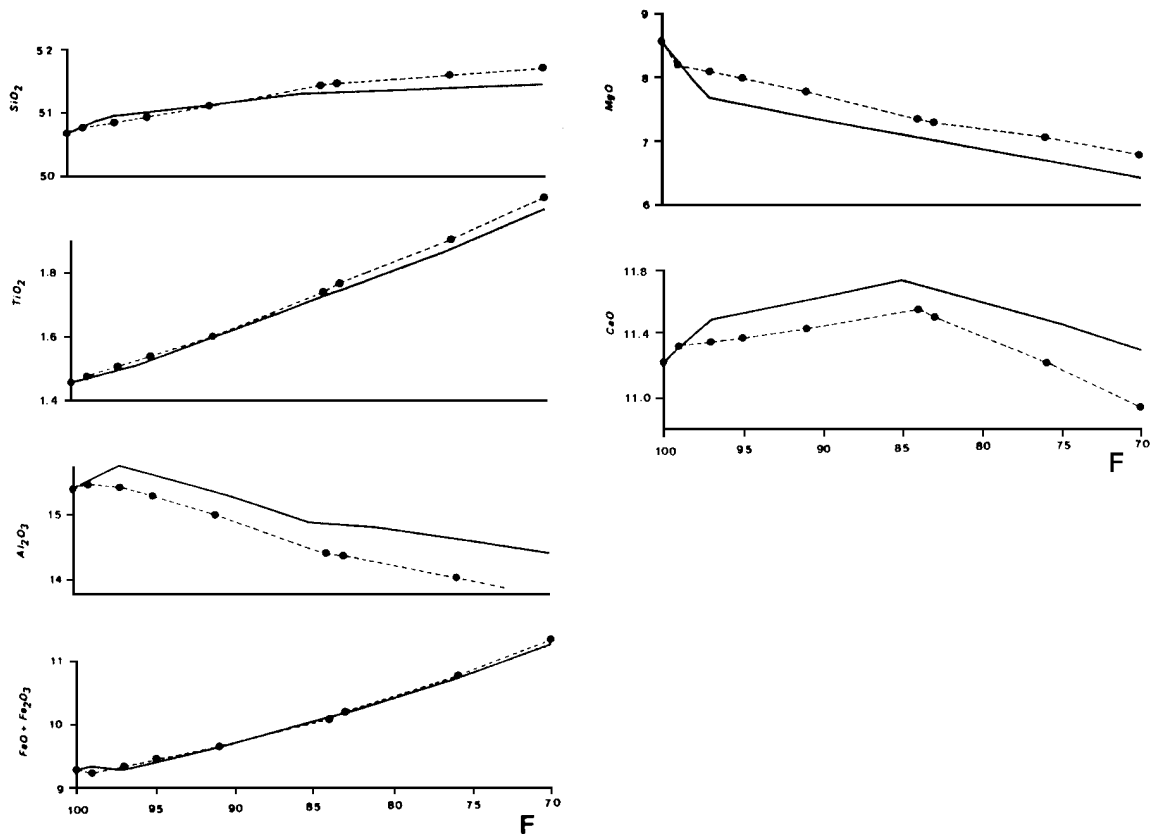


Fig. 1 – Calculated liquid variation diagram for the fractional crystallization of N-MORB All 96-18-1 (Tormey et al., 1987) along the QFM buffer at 1 bar, F = mass fraction of residual magma, Solid circles connected by dotted lines denote experimental data on the fractionation trend taken from Tormey et al., (1987).

As shown in figure 1, modelled and measured compositional trends of residual liquids are identical, with calculated Al_2O_3 , CaO and MgO trends slightly displaced relative to those determined experimentally. That the calculated residual liquids tend to become too rich in Al_2O_3 and CaO (and poorer in MgO) is a consequence of the fact that the experimentally determined F (% residual liquid) for the initiation of plagioclase precipitation is about 0.02 higher than the modelled value (0.97). It should be noted, however, that (even for Al_2O_3 , CaO and MgO) the calculated and experimental trends are almost parallel implying that CRFRAC predicted correctly the changes in bulk occurring during the crystallization sequence.

Overall, it seems fair conclude that the modelled liquidus temperatures, residual liquid and solid compositions, and mineral/melt proportions, reasonably reproduce the experimental data over a cooling interval where 30 % of melt crystallizes.

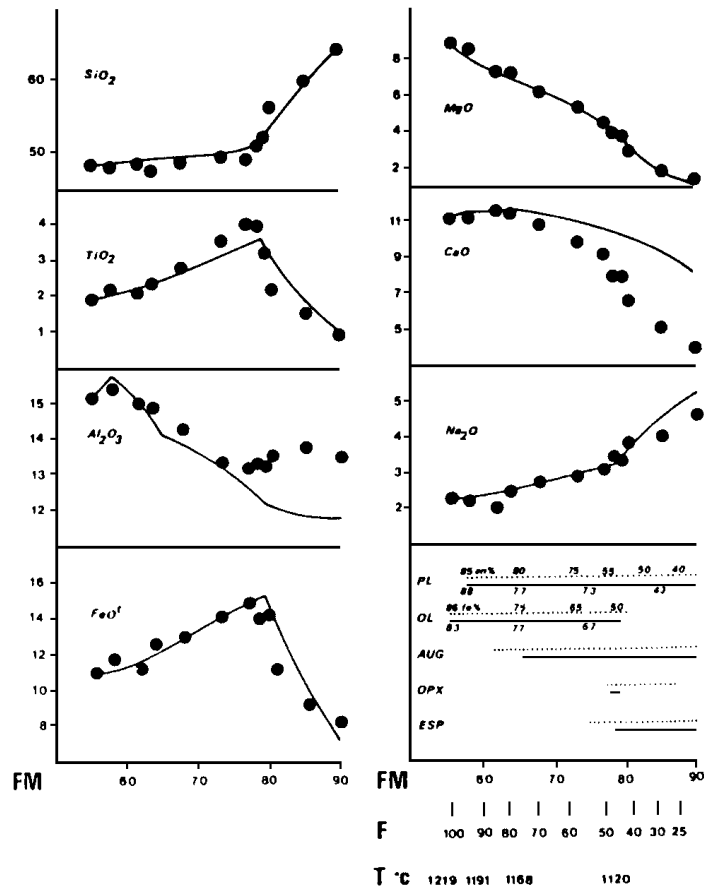


Fig. 2 – Calculated liquid variation diagram and phase relations for the fractional crystallization of olivine tholeiite V10 (Wood, 1978) along the QFM buffer at 1 bar. FM = $\text{FeO}^t/(\text{FeO}^t + \text{MgO})$, F = mass fraction of residual magma. Solid circles denote data on the Eastern Icelandic lava series taken from Wood (1978). At the base (right) of the figure, dotted lines correspond to the crystallization sequence inferred from petrographical studies (Carmichael, 1964; Good, 1978); numbers on those lines indicate measured phase compositions (An %, Fo %).

3.2 - Crystallization of an Icelandic olivine tholeiite

Sequences of lavas produced from evolving magma chambers associated with volcanic complexes often show compositional variations which comply with trends expected from fractional crystallization of basic parental magmas. Perhaps one of the best known of these volcanic complexes is represented by Tertiary lavas of Eastern Iceland (Carmichael, 1964; 1967). These lavas range continuously in composition from olivine tholeiites

to rhyolites and were interpreted (Carmichael, 1964, 1967; Wood, 1978) as having been derived by periodic eruption of shallow magma chambers undergoing crystal fractionation. We have selected the most primitive olivine tholeiite of comprehensive rock suite studied by Wood (1978) as the initial bulk composition for our fractional model (see Table I). If the composition of this olivine tholeiite is a reasonable approximation for the parental magmatic liquid of the Eastern Icelandic lava series, then the success of the modelled fractionation sequence can be judged against the analytical data obtained from the more evolved volcanic rocks.

The crystallization sequence may be inferred from the detailed studies of Carmichael (1964; 1967) on the Thingmuli volcanic center, and subsequent generalizations to entire Eastern Icelandic Tertiary lava series made by Wood (1978); as displayed in Fig. 2, the petrographic features observed in natural rocks are duplicated well by the results of CRFRAC calculations. The natural crystallization sequence is (Carmichael, 1964; Wood, 1978) olivine, plagioclase, augite and spinel; then, olivine is replaced by low-Ca pyroxene and (minor) ilmenite only returning to the liquidus in the icelandites and taking the place of orthopyroxene in the more acidic rocks. With the exception of ilmenite, which is suppressed from the liquidus assemblages due to severe limitations imposed by its modelled mixing properties (all Fe is Fe^{2+}), the most significant inconsistency in the calculated crystallization sequence concerns the very short low-Ca pyroxene crystallization interval without the reappearance of an iron-rich olivine. Similar problems were encountered by Ghiorso and Carmichael (1985) modelling which, most probably, reflect a failure in the liquid activity models (Nielsen and Drake, 1979; Ghiorso et al., 1983) to correctly predict olivine-liquid equilibria in SiO_2 -rich melts. Calculated phase equilibria indicates that olivine disappearance almost coincides with the first appearance of spinel and low-Ca pyroxene on the liquidus, which is in accordance with Carmichael's (1964) observations; the calculated appearance temperature of low-Ca pyroxene indicated in Fig. 2 is also consistent with the highest Fe-Ti oxide temperature (of about 1080°C) obtained by Carmichael (1967) on the Thingmuli lavas.

Variation diagrams of residual liquids produced from fractionation calculations are shown in figure 2. Compositions of the Tertiary Eastern Icelandic lavas reported by Wood (1967) are plotted for comparison. Calculated temperatures and mass fraction of residual liquids are also indicated at the base of the figure. The majority of natural compositions plotted in figure 2 show a good correlation with the calculated curves; major inconsistencies are reflected by Al_2O_3 and CaO which we ascribe to the (calculated) delayed spinel crystallization and to our simplifying assumptions on the pyroxene mixing properties. However, bearing in mind that a 0.25 wt. % error in the determination of any oxide in the parental magma composition could magnify itself into 1.00 wt. % error in the derived liquid at 75% crystallization, the general correspondence shown in figure 2 is remarkable.

4 - CONCLUSIONS

The examples and calculations reported in this paper further support previous claims (e.g. Carmichael et al., 1974) on the advantages of applying a thermodynamic approach to describe phase equilibria in magmatic systems. In this respect, it should be noted that the success of the CRFRAC program calculation scheme discussed here is due mostly to the generation of an internally consistent set of data by using a two-lattice melt component activity model approach to the mixing properties of silicate melts (Nielsen and Drake, 1979; Nielsen and Dungan, 1983).

It was shown that CRFRAC is able to reproduce accurately, the crystallization sequences, liquidus temperatures, phase proportions, phase compositions, and residual liquid chemical paths during fractional crystallization of mafic magmas. Through the definition of assimilation, replenishment and eruption factors (see Appendix 1) the program will also calculate the liquid lines of descent for concurrent fractionation, magma

chamber recharge, contamination, and tapping of the magma chamber. The fO_2 -T path followed by the differentiating system may also be altered by setting a non-zero value for the fugacity factor (see Appendix 1), which is related to the QFM buffer as given by Wones & Gilbert (1969). Because the relative roles of these processes are tied directly to the differentiation increment monitor parameter of CRFRAC, all the above processes can be modelled to take place simultaneously.

Notwithstanding all the versatility claimed for CRFRAC, one should not be over enthusiastic; there are still much need further experimental work and refinement of the model. For example, the lack of good solid-solution models for Na-, Ti-, Al-bearing pyroxenes, as well as, for amphiboles and micas, effectively prevents modelling phase relations in alkalic and calc-alkaline magmas.

However, and despite these limitations, we believe that the CRFRAC computational scheme will greatly facilitate the evaluation of hypotheses regarding the genesis of igneous rocks.

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