

Chemical mass transfer in magmatic processes

I. Thermodynamic relations and numerical algorithms

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Abstract. Thermodynamic and mathematical relations are presented to facilitate the description of an algorithm for the calculation of chemical mass transfer in magmatic systems. This algorithm extends the silicate liquid solution model of Ghiorso et al. (1983) to allow for the quantitative modelling of natural magmatic processes such as crystal fractionation, equilibrium crystallization, magma mixing and solid-phase assimilation. The algorithm incorporates a new method for determining the saturation surface of a non-ideal multicomponent solid-solution crystallizing from a melt. It utilizes a mathematical programming (optimization) approach to determine the stable heterogeneous (solids + liquid) equilibrium phase assemblage at a particular temperature and pressure in magmatic systems both closed and open to oxygen. Closed system equilibria are computed by direct minimization of the Gibbs free energy of the system. Open system equilibria are determined by minimization of the Korzhinskii potential (Thompson 1970), where oxygen is treated as a perfectly mobile component. Magmatic systems undergoing chemical mass transfer processes are modelled in a series of discrete steps in temperature, pressure or bulk composition, with each step characterized by heterogeneous solid-liquid equilibrium. A numerical implementation of the algorithm has been developed (in the form of a FORTRAN 77 computer program) and calculations demonstrating its utility are provided in an accompanying paper (Ghiorso and Carmichael 1985).

Introduction

This paper is the first in a series that will attempt to describe various aspects of chemical mass transfer in magmatic systems. The term chemical mass transfer here refers to any process which alters the composition of a solid or liquid phase in a magma in response to a change in the values of the intensive variables which describe the system (i.e., T , P , chemical potentials). Thus, chemical mass transfer broadly includes magmatic processes such as equilibrium crystallization, crystal fractionation and assimilation. It should be obvious that an understanding of these phenomena is required in order to appreciate fully the spatial aspects of mass transport in magmas: e.g., crystal settling, crystal floatation or convection.

The overall aim of this series of papers is to elucidate chemical mass transfer by providing a quantitative means

of calculating phase relations in evolving magmatic systems. Although all magmatic processes are by definition irreversible and represent *progress* of the system toward thermodynamic equilibrium, a prerequisite to understanding them in a quantitative fashion necessitates a fairly detailed description of the equilibrium (or reversible) state of the system. This argument is used below to develop an algorithm to model the precipitation of solid-phases in magmatic systems by utilizing equilibrium phase relations. In an accompanying paper (Ghiorso and Carmichael 1985, hereafter Part II), numerical applications of the algorithm described here are presented and compared to experimental and natural data on the equilibrium and fractional crystallization of basalts. Heat and density effects during crystallization are considered and calculations modelling solid phase assimilation are discussed. Additional aspects of chemical mass transport in magmas, including crystallization kinetics, will be taken up in subsequent contributions to this series.¹

There have been numerous attempts in recent years to quantify certain aspects of mineral-melt equilibria involving natural silicate liquids in order to model equilibrium crystallization or fractionation processes (Hostetler and Drake 1980; Langmuir and Hanson 1981; Nathan and van Kirk 1978; Nielsen and Dungan 1983; Nielsen 1985 unpublished paper). All of these models are based upon statistical evaluations of experimental phase equilibrium data and have been calibrated to empirical or semi-empirical mathematical expressions. As such, none of them provides sufficient information to establish the *thermodynamic stability* of the calculated phase assemblages. The empirical approaches generate phase relations which are *consistent* with available experimental data but they do not utilize a thermodynamically valid description of the solid and liquid phases to determine

1 In part III the calculation of crystal growth and nucleation of solid solutions due to successive degrees of under-cooling will be treated and the influence of steady-state phenomena on compositional gradients in multicomponent silicate liquids (i.e., Soret effect) will be examined. In Part IV a recalibration of the silicate liquid solution model of Ghiorso et al. (1983) will be undertaken to account better for leucite-liquid and sanidine-liquid equilibria in more alkalic melts. This will probably entail expanding the number of liquid components that describe potassium interactions in the liquid to account for this element's unusual behavior. Also in Part IV the calculation of crystallization trends in alkalic liquids will be attempted and a method of obtaining the compositions of liquids coexisting with an igneous mineral assemblage of specified composition will be developed

intermediate or final *equilibrium* states. This is essential if the processes involved in achieving equilibrium in these systems (e.g., nucleation and crystal growth) are to be studied or modelled (Bottinga et al. 1981; Dowty 1980).

The purpose of this paper is two-fold. First, to outline a computational algorithm which utilizes thermodynamically valid descriptions of solid and liquid phases to describe heterogeneous equilibrium in magmatic systems. This algorithm incorporates the silicate liquid solution model of Ghiorso et al. (1983) and appropriate activity/composition relations for minerals which precipitate in crystallizing igneous systems. Computational methods will be described for both open and closed systems. The second purpose is to outline an algorithm for modelling the crystallization of magmatic liquids by a succession of discrete steps in temperature, pressure or bulk composition, with each step characterized by solid-liquid equilibrium. This procedure will be generalized to describe the computation of equilibrium crystallization, crystal fractionation, solid phase assimilation and magma mixing as a function of temperature and pressure. The basic assumption that underlies this computational algorithm is that an overall irreversible process can be described by a series of equilibrium steps. This assumption is a familiar one to the geochemist who has performed mass transfer calculations in aqueous systems (c.f. Helgeson 1968; Helgeson et al. 1970; Reed 1982) and has proved useful in a wide variety of applications in chemical engineering (e.g. Smith and Missen 1982).

The procedures and methods outlined below require an internally consistent set of solid-liquid thermochemical data and a thermodynamically valid mixing model for the liquid, both of which have been previously discussed by Ghiorso et al. (1983, with slight modifications provided in the appendix to this paper). In what follows we will concern ourselves with the more theoretical aspects of chemical mass transfer in magmatic systems, namely, a description of the thermodynamic criteria for heterogeneous equilibrium, a review of mathematical methods for implementing these criteria, and the construction of an algorithm suited to modelling all aspects of chemical mass transfer. Many of the computational methods to be presented below are new only in the context of their application. However, most of these computational methods have been modified or extended to better suit the present purpose. We will, therefore, concentrate on the more significant of these modifications while presenting an overview of the general theory to place them in the correct context.

Notation

Scalars

a_{φ_i}	the activity of the i^{th} solid component in the solid phase φ
c	number of components in φ^{th} solid phase (i.e., equivalent to m_{φ})
f_{O_2}	the fugacity of oxygen in the system
G	the Gibbs free energy of the system
f	intermediate variable used in step 2 of algorithm 2
G_L	the Gibbs free energy of the liquid
$G_{M_1}, G_{M_2}, \dots, G_{M_p}$	the Gibbs free energy of the 1 st , 2 nd , ..., p^{th} solid
G_{O_2}	the Gibbs free energy of oxygen in the system
g_{φ_i}	the partial derivative of a_{φ_i} with respect to X_{φ_i} , evaluated at \mathbf{X}_{φ}
h	intermediate variable used in step 2 of algorithm 2

L	the Korzhinskii potential of a system open to oxygen
l	the number of liquid components
m_1, m_2, \dots, m_p	the number of components in the 1 st , 2 nd , ..., p^{th} solid
n	the number of liquid and solid components in the system (i.e., $l + m_1 + m_2 + \dots + m_p$)
n_{O_2}	the excess oxygen content of the system (see Eq. 36)
P	pressure
p	the number of solid phases in the system
R	the universal gas constant
r	the ratio of ferric iron/total iron in the liquid
T	the absolute temperature
X_{φ_i}	the mole fraction of the i^{th} solid component in the solid phase φ
SSQ	intermediate variable used in step 7 of algorithm 2
y	intermediate variable used in step 2 of algorithm 2
α	steplength parameter of order unity defined by Eqs. (28) and (29)
γ_{φ_i}	the activity coefficient of the i^{th} solid component in the phase φ
ΔG_i	the free energy change for the i^{th} solid component melting to form a liquid at a particular T and P .
κ	the condition number of the projected Hessian of $G(\bar{\mathbf{H}})$
$\mu_{\text{O}_2}^0$	the chemical potential of oxygen in the magma
μ_{O_2}	the standard state chemical potential of oxygen in the system
$\mu_{\varphi_i}^0$	the standard state chemical potential of the i^{th} solid component in the solid phase φ
Σ_{φ}	the saturation index for the φ^{th} solid phase
τ	a number defined to be 10^{-t} where t is the number of significant digits desired in the computation
φ_i	the i^{th} end-member component in the solid phase φ

Vectors

\mathbf{b}	vector which describes the bulk composition of the system in terms of liquid components
\mathbf{g}	vector of chemical potentials of each component in the system
$\tilde{\mathbf{g}}$	the projected gradient of the system
\mathbf{g}_L	vector of chemical potentials of each component in the liquid
$\mathbf{g}_{M_1}, \mathbf{g}_{M_2}, \dots, \mathbf{g}_{M_p}$	vector of chemical potentials of each component in the 1 st , 2 nd , ..., p^{th} solid
\mathbf{g}_{O_2}	the gradient of the Gibbs free energy of oxygen with respect to \mathbf{n}
\mathbf{n}	vector of moles of all liquid and solid components in the system ($\hat{\mathbf{n}}$ and \mathbf{n}' are particular guesses for \mathbf{n})
\mathbf{n}_L	vector of moles of each component in the liquid
$\mathbf{n}_{M_1}, \mathbf{n}_{M_2}, \dots, \mathbf{n}_{M_p}$	vector of moles of each component in the 1 st , 2 nd , ..., p^{th} solid
$\mathbf{n}_1, \mathbf{n}_2$	compositional vectors defined by Eq. (21) and which denote the constrained and unconstrained parts of the vector \mathbf{n}
\mathbf{X}_{φ}	vector of mole fractions of the c solid components in the φ^{th} phase, i.e., $[X_{\varphi_1}, X_{\varphi_2}, \dots, X_{\varphi_c}]^T$ ($\hat{\mathbf{X}}_{\varphi}$ is a particular guess for \mathbf{X}_{φ})
λ	vector of Lagrange multipliers for the active equality constraints in the system (Eq. 34)
ν_i	stoichiometric reaction coefficients for each liquid component in the reaction which describes the dissolution of the i^{th} solid component

Matrices

\mathbf{C}	block matrix which embodies the bulk composition constraint on the system (Eq. 9)
\mathbf{H}	second derivative matrix (Hessian) of the Gibbs free energy of the system

$\hat{\mathbf{H}}$	the projected Hessian of the system
\mathbf{H}_L	second derivative matrix (Hessian) of the free energy of the liquid
$\mathbf{H}_{M_1}, \mathbf{H}_{M_2}, \dots, \mathbf{H}_{M_p}$	second derivative matrix (Hessian) of the Gibbs free energy of the 1 st , 2 nd , ..., p^{th} solid solution
\mathbf{H}_{O_2}	second derivative matrix of the Gibbs free energy of oxygen
\mathbf{I}_l	identity matrix of order l
\mathbf{K}	an orthogonal matrix which right diagonalizes \mathbf{C} Eq. (18). It may be partitioned $\mathbf{K}^T = [\mathbf{K}_1 : \mathbf{K}_2]^T$
\mathbf{R}	upper triangular matrix formed by right diagonalizing \mathbf{C} . It may be partitioned $\mathbf{R} = [\mathbf{R}_{11} : \mathbf{O}]$ (see Eqs. 18, 19)
$\mathbf{T}_{M_1}, \mathbf{T}_{M_2}, \dots, \mathbf{T}_{M_p}$	matrix which transforms a mole vector for the 1 st , 2 nd , ..., p^{th} solid from solid into liquid compositional variables
\mathbf{O}_i^j	matrix of zeros with i rows and j columns

Symbols

$ _{\hat{n}}$	evaluated at \hat{n}
\mathbf{n}^T	the transpose of \mathbf{n}
$\ \mathbf{n}\ $	the euclidian (or L_2) norm of \mathbf{n} , i.e. $\ \mathbf{n}\ = (\mathbf{n}^T \mathbf{n})^{1/2}$
\ln	natural (base e) logarithm

Computing heterogeneous equilibria in closed magmatic systems

Basic thermodynamic relations

Consider a closed system, say a crystallizing body of magma, which consists of both liquid and solid phases. For the sake of simplicity let us assume that this system has *one* liquid and p solid phases. Furthermore, let the composition of the liquid be described in terms of l thermodynamic components, which for convenience may be taken as equivalent to those used by Ghiorso et al. (1983).² Then we may define \mathbf{n}_L to be a vector of length l whose 1st element is the number of moles of the 1st component (Si_4O_8) in the liquid, whose 2nd element is the number of moles of the 2nd component (Ti_4O_8) in the liquid, etc; \mathbf{n}_L thus describes the composition of the liquid phase. If we write the total Gibbs free energy of the liquid as G_L , then:

$$\mathbf{g}_L \equiv (\partial G_L / \partial \mathbf{n}_L)_{T,P} \quad (1)$$

where \mathbf{g}_L is an l -vector whose elements are simply the chemical potentials of the l -components in the liquid. The equivalence of the gradient of G_L to a vector of chemical potentials results from the fact that the l -components are linearly independent compositional variables. Note that in Eq. (1) we have taken the derivative of a scalar with respect to a vector to be a vector following the suggestion of Graham (1981). The utility of expressing these common thermodynamic relations in a somewhat unfamiliar vector notation will become evident below where the equilibrium criteria are expressed, using this notation, in compact, closed form. Now for each of the p solid phases in the system we can define the total Gibbs free energy, $G_{M_1}, G_{M_2}, \dots, G_{M_p}$, associated with each phase. Additionally, for each solid phase there is a vector, \mathbf{n}_{M_i} , of length m_i (for the i^{th} mineral), whose elements are the number of moles of each end-member component that describes the solid solution. For example, in the plagioclase feldspars the compositional vector for

² $\text{Si}_4\text{O}_8, \text{Ti}_4\text{O}_8, \text{Al}_{16/3}\text{O}_8, \text{Fe}_{16/3}\text{O}_8, \text{Cr}_{16/3}\text{O}_8, \text{Fe}_4\text{Si}_2\text{O}_8, \text{Mn}_4\text{Si}_2\text{O}_8, \text{Mg}_4\text{Si}_2\text{O}_8, \text{Co}_4\text{Si}_2\text{O}_8, \text{Ni}_4\text{Si}_2\text{O}_8, \text{Ca}_4\text{Si}_2\text{O}_8, \text{Na}_{16/3}\text{Si}_8/3\text{O}_8, \text{K}_{16/3}\text{Si}_8/3\text{O}_8, \text{P}_{16/5}\text{O}_8, \text{Sr}_8\text{O}_8, \text{H}_2\text{O}$

the solid phase would contain three elements consisting of the number of moles of the end-member components $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 in the feldspar. With these definitions a gradient analogous to Eq. (1) may be defined for each mineral:

$$\mathbf{g}_{M_i} \equiv (\partial G_{M_i} / \partial \mathbf{n}_{M_i})_{T,P} \quad (2)$$

where as before the m_i elements of \mathbf{g}_{M_i} are the chemical potentials of the end-member components that describe the mineral solid-solution (again utilizing the fact that end-member components are taken to be linearly independent compositional variables).

With these definitions the Gibbs free energy of the system, G , may be written:

$$G = G_L + \sum_{i=1}^p G_{M_i} \quad (3)$$

and a compositional vector for the entire system may be constructed by stacking up the vectors already defined:

$$\mathbf{n} \equiv \begin{bmatrix} \mathbf{n}_L \\ \mathbf{n}_{M_1} \\ \mathbf{n}_{M_2} \\ \vdots \\ \mathbf{n}_{M_p} \end{bmatrix} \quad (4)$$

The dimension of \mathbf{n} is taken to be n , where:

$$n = l + \sum_{i=1}^p m_i \quad (5)$$

The chemical potential of each component in all phases can be represented by the n -vector \mathbf{g} such that:

$$\mathbf{g} \equiv \begin{bmatrix} \mathbf{g}_L \\ \mathbf{g}_{M_1} \\ \mathbf{g}_{M_2} \\ \vdots \\ \mathbf{g}_{M_p} \end{bmatrix} \quad (6)$$

Clearly,

$$\mathbf{g} = (\partial G / \partial \mathbf{n})_{T,P} \quad (7)$$

if all n system components are treated as independent variables.

The criterion for equilibrium in this closed heterogeneous liquid/solid system is that G should be minimized at constant temperature and pressure, with respect to the elements of the vector \mathbf{n} , subject to the bulk composition of the system. Or, stated alternatively, the chemical elements which compose the system must distribute themselves proportionally between the solid and liquid phases such that G , defined by Eq. (3), assumes a minimum value at a particular temperature and pressure. To state the equilibrium criteria in more compact mathematical form we must relate the compositional vector \mathbf{n} to the bulk composition of the system.

Let \mathbf{b} be a vector of length l whose elements are the number of moles of each of the l -components that describe the composition of the system (liquids+solids). With no loss of generality we may take these "system components" to be equivalent to those used to describe the composition of the liquid (see footnote 2). Doing so, however, necessitates that we devise some means of expressing the compositions of the solid phases in terms of the adopted "system components." To perform this transformation we define

the matrices \mathbf{T}_{M_i} , with l -rows and m_i -columns, such that:

$$\mathbf{b} = \mathbf{n}_L + \sum_{i=1}^p \mathbf{T}_{M_i} \mathbf{n}_{M_i} \quad (8)$$

To provide an example of a particular \mathbf{T}_{M_i} , we may again consider the plagioclase feldspars. Let $\mathbf{n}_{M_i} = [n_{\text{CaAl}_2\text{Si}_2\text{O}_8} \ n_{\text{NaAlSi}_3\text{O}_8} \ n_{\text{KAlSi}_3\text{O}_8}]^T$ (where $n_{\text{CaAl}_2\text{Si}_2\text{O}_8}$ denotes the number of moles of $\text{CaAl}_2\text{Si}_2\text{O}_8$, etc.) and $\mathbf{b} = [b_{\text{Si}_4\text{O}_8} \ b_{\text{Ti}_4\text{O}_8} \ b_{\text{Al}_{16/3}\text{O}_8} \ b_{\text{Fe}_{16/3}\text{O}_8} \ b_{\text{Cr}_{16/3}\text{O}_8} \ b_{\text{Fe}_4\text{Si}_2\text{O}_8} \ b_{\text{Mn}_4\text{Si}_2\text{O}_8} \ b_{\text{Mg}_4\text{Si}_2\text{O}_8} \ b_{\text{Co}_4\text{Si}_2\text{O}_8} \ b_{\text{Ni}_4\text{Si}_2\text{O}_8} \ b_{\text{Ca}_4\text{Si}_2\text{O}_8} \ b_{\text{Na}_{16/3}\text{Si}_8/3\text{O}_8} \ b_{\text{K}_{16/3}\text{Si}_8/3\text{O}_8} \ b_{\text{P}_{16/5}\text{O}_8} \ b_{\text{Sr}_8\text{O}_8} \ b_{\text{H}_2\text{O}}]^T$, then

$$\mathbf{T}_{M_i} = \begin{bmatrix} 3/8 & 5/8 & 5/8 \\ 0 & 0 & 0 \\ 3/8 & 3/16 & 3/16 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1/4 & 0 & 0 \\ 0 & 3/16 & 0 \\ 0 & 0 & 3/16 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

which compactly describes the linear component transformation desired to translate plagioclase components into liquid components:

$$n_{\text{Si}_4\text{O}_8}^{\text{feldspar}} = 3/8 n_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{feldspar}} + 5/8 n_{\text{NaAlSi}_3\text{O}_8}^{\text{feldspar}} + 5/8 n_{\text{KAlSi}_3\text{O}_8}^{\text{feldspar}}$$

$$n_{\text{Ti}_4\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Al}_{16/3}\text{O}_8}^{\text{feldspar}} = 3/8 n_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{feldspar}} + 3/16 n_{\text{NaAlSi}_3\text{O}_8}^{\text{feldspar}} + 3/16 n_{\text{KAlSi}_3\text{O}_8}^{\text{feldspar}}$$

$$n_{\text{Fe}_{16/3}\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Cr}_{16/3}\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Fe}_4\text{Si}_2\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Mn}_4\text{Si}_2\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Mg}_4\text{Si}_2\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Co}_4\text{Si}_2\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Ni}_4\text{Si}_2\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Ca}_4\text{Si}_2\text{O}_8}^{\text{feldspar}} = 1/4 n_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{feldspar}}$$

$$n_{\text{Na}_{16/3}\text{Si}_8/3\text{O}_8}^{\text{feldspar}} = 3/16 n_{\text{NaAlSi}_3\text{O}_8}^{\text{feldspar}}$$

$$n_{\text{K}_{16/3}\text{Si}_8/3\text{O}_8}^{\text{feldspar}} = 3/16 n_{\text{KAlSi}_3\text{O}_8}^{\text{feldspar}}$$

$$n_{\text{P}_{16/5}\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{Sr}_8\text{O}_8}^{\text{feldspar}} = 0$$

$$n_{\text{H}_2\text{O}}^{\text{feldspar}} = 0.$$

Equation (8) may be written in a much more convenient form if an l by n block composite matrix³ \mathbf{C} is defined such that:

$$\mathbf{C} = [\mathbf{I}_l : \mathbf{T}_{M_1} : \mathbf{T}_{M_2} : \dots : \mathbf{T}_{M_p}] \quad (9)$$

where \mathbf{I}_l is the identity matrix of order l . With Eqs. (4) and (9) Eq. (8) becomes:

$$\mathbf{b} = \mathbf{Cn} \quad (10)$$

³ A block composite matrix is one which can be divided up, or *partitioned*, into sub-matrices. The partitions are denoted in this paper by colons

and embodies the bulk composition constraint on our multiphase system.

The problem of posing the equilibrium criterion in a heterogeneous closed magmatic system can now be succinctly written:

$$\begin{aligned} &\text{minimize } G \\ &\text{with respect to } \mathbf{n} \end{aligned} \quad (11)$$

such that $\mathbf{b} = \mathbf{Cn}$

where it is understood that G is a non-linear function of \mathbf{n} .

Methods of computing chemical equilibria

We must now decide how to implement the equilibrium criterion given by Eq. (11). Van Zeggeren and Storey (1970) and more recently Smith and Missen (1982) have reviewed available methods for solving the problem posed by Eq. (11). These methods fall largely into two types. The first involves transformation of the problem into one of the equality of chemical potentials in every phase at equilibrium. Mathematically, this becomes an exercise in solving sets of highly non-linear equations (which incorporate the bulk composition constraint) in \mathbf{n} for a given \mathbf{b} , T and P . In the notation we have developed this set of equations can be written:

$$\mathbf{T}_{M_1}^T \mathbf{g}_L = \mathbf{g}_{M_1}$$

$$\mathbf{T}_{M_2}^T \mathbf{g}_L = \mathbf{g}_{M_2}$$

$$\vdots \quad \vdots \quad \vdots$$

$$\mathbf{T}_{M_p}^T \mathbf{g}_L = \mathbf{g}_{M_p}$$

$$\mathbf{C} \mathbf{n} = \mathbf{b}$$

where the first $n-l$ equalities correspond to zeroing the free energy change at a particular T and P for the reaction denoting the melting of each end-member solid component in each solid phase. The chemical potentials are incorporated into these equations as the elements of \mathbf{g}_L , \mathbf{g}_{M_i} , etc.

In the earth sciences these "chemical potential" methods have become quite popular and form the basis of the heterogeneous equilibrium phase of the mass transfer calculations describing water-rock interaction discussed by Helgeson (1968), Helgeson et al. (1970), Wolery (1979), Reed (1982) and Helgeson and Murphy (1983). Graphically derived methods based upon the equality of chemical potentials have been utilized by Brown and Skinner (1974) to compute stable solid-solid and solid-liquid assemblages and by Barron (1976a, 1976b, 1978a, 1978b, 1981, 1983), Kimberley (1980), and Ghiorso (1984) to determine the compositions of coexisting immiscible phases.

The other type of method for the solution of the problem posed by Eq. (11) is the direct minimization of the free energy of the system using techniques of non-linear optimization theory (c.f. Gill et al. 1981). These methods have been widely used in chemical engineering but have been restricted to systems involving essentially pure solid phases (e.g. White et al. 1958). Reviews of free energy minimization methods can be found in Van Zeggeren and Storey (1970), Seider et al. (1980), Castillo and Grossmann (1981) and Smith and Missen (1982). Russian geochemists have embraced the free energy minimization approach in favor of "chemical potential" methods (Karpov and Kaz'min 1982; Karpov et al. 1973; Shvarov 1976; Dorofeyeva and Khodakovskiy 1981; Ryzhenko et al. 1981) and have even applied it to open systems (Shvarov 1978). Recently, Saxena

(1982) and Saxena and Eriksson (1983) have applied free energy minimization methods to the computation of mineral phase relations at a wide variety of temperatures and pressures.

Direct free energy minimization is the most general and the most straight forward of the mathematical techniques used to solve Eq. (11). Largely because of the numerical stability of minimization methods, and their ease of programming, they will be adopted for the calculation of chemical equilibrium in the mass transfer algorithm proposed here. In order to describe the computational procedure in some detail, we need to consider an additional compositional derivative of Eq. (7). We begin by writing:

$$\mathbf{H}_L = (\partial \mathbf{g}_L / \partial \mathbf{n}_L)_{T,P} \quad (12)$$

where \mathbf{H}_L is an l by l symmetric matrix whose elements are the second cross partial derivatives of G_L with respect to the moles of each component in the liquid. \mathbf{H}_L is commonly referred to as the Hessian or second derivative matrix. Bear in mind in the subsequent discussion that the Hessian is a matrix and that in Eq. (12) we have taken the derivative of a vector with respect to a vector to be a matrix, after Graham (1981).⁴ As before, in defining \mathbf{H}_L the elements of \mathbf{n}_L are considered to be independent variables. In a similar manner for each of the p minerals in the system we may define:

$$\mathbf{H}_{M_i} = (\partial \mathbf{g}_{M_i} / \partial \mathbf{n}_{M_i})_{T,P} \quad (13)$$

where \mathbf{H}_{M_i} is the m_i by m_i symmetric Hessian matrix for the i^{th} solid phase. The Hessian matrix, \mathbf{H} , for the entire heterogeneous solid-liquid system can be expressed in a form analogous to Eq. (7):

$$\mathbf{H} \equiv (\partial \mathbf{g} / \partial \mathbf{n})_{T,P} \quad (14)$$

where it is easy to show that:

$$\mathbf{H} = \begin{bmatrix} \mathbf{H}_L : \mathbf{O}_{M_1}^L : \mathbf{O}_{M_2}^L : \dots : \mathbf{O}_{M_p}^L \\ \mathbf{O}_L^{M_1} : \mathbf{H}_{M_1} : \mathbf{O}_{M_2}^{M_1} : \dots : \mathbf{O}_{M_p}^{M_1} \\ \vdots : \vdots : \vdots : \vdots : \vdots \\ \mathbf{O}_L^{M_p} : \mathbf{O}_{M_1}^{M_p} : \mathbf{O}_{M_2}^{M_p} : \dots : \mathbf{H}_{M_p} \end{bmatrix} \quad (15)$$

Note that \mathbf{H} is block diagonal with dimension n by n and can be seen to be symmetric (the symbols \mathbf{O}_j^i denote a block of zeroes comprising i rows and j columns). Having defined the Hessian of the Gibbs free energy for the system we can proceed with the mechanism of computing the equilibrium state.

The great difficulty in minimizing the free energy function in Eq. (11) stems from its non-linearity. Therefore, the trick to solving the problem is the simplification of G . To perform this simplification we will generalize to non-ideal systems the procedure outlined by White et al. (1958).

4 For example, if $\mathbf{g} = (\partial G / \partial \mathbf{n})$ and both \mathbf{g} and \mathbf{n} are 3-vectors, then:

$$\mathbf{H} = (\partial \mathbf{g} / \partial \mathbf{n}) = \begin{bmatrix} (\partial^2 G / \partial n_1^2)_{n_2, n_3} & (\partial^2 G / \partial n_1 \partial n_2)_{n_3} & (\partial^2 G / \partial n_1 \partial n_3)_{n_2} \\ (\partial^2 G / \partial n_2 \partial n_1)_{n_3} & (\partial^2 G / \partial n_2^2)_{n_1, n_3} & (\partial^2 G / \partial n_2 \partial n_3)_{n_1} \\ (\partial^2 G / \partial n_3 \partial n_1)_{n_2} & (\partial^2 G / \partial n_3 \partial n_2)_{n_1} & (\partial^2 G / \partial n_3^2)_{n_1, n_2} \end{bmatrix}$$

where since G is an exact function of \mathbf{n} ,

$$(\partial^2 G / \partial n_i \partial n_j) = (\partial^2 G / \partial n_j \partial n_i)$$

and \mathbf{H} is a 3 by 3 symmetric matrix

Let $\hat{\mathbf{n}}$ be a particular vector (a specific choice of \mathbf{n}) which approximates the minimum value of G , i.e., $\hat{\mathbf{n}}$ is a good guess for the equilibrium configuration (see step 3 of the following algorithm). Then the Taylor series expansion of G about the multi-dimensional point $\hat{\mathbf{n}}$ is:

$$G = G|_{\hat{\mathbf{n}}} + \mathbf{g}^T|_{\hat{\mathbf{n}}}(\mathbf{n} - \hat{\mathbf{n}}) + \frac{1}{2}(\mathbf{n} - \hat{\mathbf{n}})^T \mathbf{H}|_{\hat{\mathbf{n}}}(\mathbf{n} - \hat{\mathbf{n}}) + \text{higher order terms} \quad (16)$$

where the symbol $|_{\hat{\mathbf{n}}}$ refers to evaluating the associated quantity (on the left) at the "point" $\hat{\mathbf{n}}$. For example, $G|_{\hat{\mathbf{n}}}$ means the Gibbs free energy of the system when $\hat{\mathbf{n}}$ describes the distribution of components amongst the phases at this particular bulk composition. Suppose we take values to \mathbf{n} to be "close" to $\hat{\mathbf{n}}$, that is suppose

$$(\mathbf{n} - \hat{\mathbf{n}})^T(\mathbf{n} - \hat{\mathbf{n}}) \simeq 0,$$

then the higher order terms in Eq. (16) can be ignored and G can be approximated as a quadratic function of \mathbf{n} . This reduces the free energy minimization problem to:

$$\begin{aligned} &\text{minimize } [G|_{\hat{\mathbf{n}}} + \mathbf{g}^T|_{\hat{\mathbf{n}}}(\mathbf{n} - \hat{\mathbf{n}}) + \frac{1}{2}(\mathbf{n} - \hat{\mathbf{n}})^T \mathbf{H}|_{\hat{\mathbf{n}}}(\mathbf{n} - \hat{\mathbf{n}})] \\ &\text{with respect to } \mathbf{n} \\ &\text{subject to } \mathbf{C}\mathbf{n} = \mathbf{b}. \end{aligned} \quad (17)$$

The solution requires only the straight forward procedure of determining the minimum of a constrained quadratic function. A particular solution has been provided by Betts (1980a, 1980b) and is based upon generalized inverse methods used in the solution of linear least squares problems (Lawson and Hanson 1974). This method of solution of Eq. (17) has been adopted and a brief outline is provided here.

The constraint described by Eq. (10) imposes certain relationships amongst the elements of the compositional vector \mathbf{n} . For instance, one can't independently change the moles of MgO in the liquid and Mg_2SiO_4 in the olivine in a system containing only olivine and liquid at constant bulk composition. In fact it is easy to appreciate that as there are l bulk composition constraints and n compositional variables, only $n-l$ can be independently varied. This implies that to define uniquely the n -dimensional component vector, \mathbf{n} , in light of the bulk composition constraint, requires only $n-l$ variables. Mathematically, this is equivalent to breaking our n dimensional solid-liquid component space up into two subspaces, one which contains the constraints and has dimension l , and another which is "perpendicular" or orthogonal to the constraints of dimension $n-l$. An orthogonal⁵ or projection matrix, \mathbf{K} , of dimension n by n can be constructed to perform this breakdown (Lawson and Hanson 1974). It is convenient to define \mathbf{K} such that

$$\mathbf{C}\mathbf{K} = \mathbf{R} \quad (18)$$

where \mathbf{R} has l rows and n columns and possesses the interesting structure

$$\mathbf{R} = [\mathbf{R}_{11} \ \mathbf{O}_{n-l}^l], \quad (19)$$

which is all the more unusual in that \mathbf{R}_{11} is an l by l non-singular triangular (!) matrix. We can write, since \mathbf{K} is orthogonal

$$\mathbf{C} = \mathbf{R}\mathbf{K}^T$$

which when substituted into Eq. (10) yields

$$\mathbf{R}\mathbf{K}^T \mathbf{n} = \mathbf{b}. \quad (20)$$

5 An orthogonal matrix is one whose columns are mutually perpendicular, that is if the column elements are treated as vectors, then the dot product of any two distinct column vectors is zero. It follows that if the columns of an orthogonal matrix have unit euclidian length, then the inverse of this matrix is equal to its transpose

Now if we partition \mathbf{K}^T such that

$$\mathbf{K}^T = [\mathbf{K}_1 : \mathbf{K}_2]^T$$

where \mathbf{K}_1 has n rows and l columns and \mathbf{K}_2 has n rows and $n-l$ columns then Eq. (10) becomes

$$\mathbf{R}_{11} \mathbf{K}_1^T \mathbf{n} = \mathbf{b}.$$

But this expression leaves the last $n-l$ elements of \mathbf{n} undefined! Exploiting this we partition the vector \mathbf{n} into two parts, \mathbf{n}_1 and \mathbf{n}_2 , such that

$$\mathbf{n} = \mathbf{K}_1 \mathbf{n}_1 + \mathbf{K}_2 \mathbf{n}_2 \quad (21)$$

where \mathbf{n}_1 has length l and \mathbf{n}_2 has length $n-l$ and uniquely compute the elements of \mathbf{n}_1 :

$$\mathbf{n}_1 = \mathbf{R}_{11}^{-1} \mathbf{b}. \quad (22)$$

The undefined vector \mathbf{n}_2 corresponds to the set of independent compositional variables in the system, any one of which can be varied without violating the bulk composition constraint (Eq. 10) which is presently contained in the vector \mathbf{n}_1 . The Gibbs free energy minimization problem (Eq. 17) can be restated using Eq. (21) as

$$\begin{aligned} \text{minimize } [G|_{\hat{\mathbf{n}}} + \mathbf{g}^T|_{\hat{\mathbf{n}}}(\mathbf{K}_1 \mathbf{n}_1 + \mathbf{K}_2 \mathbf{n}_2 - \hat{\mathbf{n}}) \\ + \frac{1}{2}(\mathbf{K}_1 \mathbf{n}_1 + \mathbf{K}_2 \mathbf{n}_2 - \hat{\mathbf{n}})^T \mathbf{H}|_{\hat{\mathbf{n}}}(\mathbf{K}_1 \mathbf{n}_1 + \mathbf{K}_2 \mathbf{n}_2 - \hat{\mathbf{n}})] \end{aligned} \quad (23)$$

with respect to \mathbf{n}_2 where the bulk composition constraint is absent because minimization is performed with respect to \mathbf{n}_2 instead of \mathbf{n} . The minimum of this quadratic function is easily found by taking the derivative with respect to \mathbf{n}_2 and setting the result equal to zero. Thus Eq. (23) implies (using differentiation formulas from Graham, 1981):

$$\mathbf{K}_2^T \mathbf{g}|_{\hat{\mathbf{n}}} + \mathbf{K}_2^T \mathbf{H}|_{\hat{\mathbf{n}}} \mathbf{K}_1 \mathbf{n}_1 + \mathbf{K}_2^T \mathbf{H}|_{\hat{\mathbf{n}}} \mathbf{K}_2 \mathbf{n}_2 = 0 \quad (24)$$

$$\text{or} \quad \mathbf{K}_2^T \mathbf{H}|_{\hat{\mathbf{n}}} \mathbf{K}_2 \mathbf{n}_2 = -\mathbf{K}_2^T \mathbf{g}|_{\hat{\mathbf{n}}} - \mathbf{K}_2^T \mathbf{H}|_{\hat{\mathbf{n}}} \mathbf{K}_1 \mathbf{n}_1$$

which the reader will recognize as a linear system of equations in $n-l$ unknowns. For clarity in notation, the following definitions are adopted:

$$\tilde{\mathbf{g}} \equiv \mathbf{K}_2^T \mathbf{g} \quad (25)$$

and

$$\tilde{\mathbf{H}} \equiv \mathbf{K}_2^T \mathbf{H} \mathbf{K}_2 \quad (26)$$

where $\tilde{\mathbf{g}}$ is known as the projected gradient and is a vector of length $n-l$ and $\tilde{\mathbf{H}}$ is referred to as the projected Hessian and is a symmetric matrix of dimension $n-l$. Equation (24) becomes

$$\tilde{\mathbf{H}}|_{\hat{\mathbf{n}}} \mathbf{n}_2 = -\tilde{\mathbf{g}}|_{\hat{\mathbf{n}}} - \mathbf{K}_2^T \mathbf{H}|_{\hat{\mathbf{n}}} \mathbf{K}_1 \mathbf{n}_1 \quad (27)$$

which yields a solution vector, \mathbf{n}_2 , for the minimization problem posed by Eq. (23).

We are at a stage now to describe a free energy minimization algorithm to determine the equilibrium compositions of phases in a heterogeneous system. We will assume that at equilibrium in a closed system of specified bulk composition (\mathbf{b}) a liquid is stable along with p mineral phases. In addition, we will assume we know the identity of those solids which are present in the equilibrium phase assemblage. Determining this equilibrium phase assemblage is discussed in some detail below.

Algorithm 1: Heterogeneous equilibrium in a closed system

Step 1:

Generate an orthogonal matrix \mathbf{K} , from the known constraint matrix \mathbf{C} according to Eq. (18). This is most easily accomplished, numerically, by the application of successive Householder transformations (Lawson and Hanson 1974) in the process of right diagonalizing \mathbf{C} to form \mathbf{R} .

Step 2:

Solve for \mathbf{n}_1 of Eq. (22). Note that as \mathbf{R}_{11} is triangular and non-singular (the bulk composition constraints are not contradictory), the system of l -equations, $\mathbf{R}_{11} \mathbf{n}_1 = \mathbf{b}$, can be solved by straight-forward back-substitution.

Step 3:

Choose an initial guess, $\hat{\mathbf{n}}$, for the solution vector \mathbf{n} . In magmatic systems experience suggests (with no previous knowledge of the particular case) allocating components by taking trivial masses for the solids, preserving the expected mole fraction ratios of end-members in each phase, and assigning the remainder to the liquid phase. The convergence rate of the algorithm is not seriously affected by the choice for the initial masses of the solid phases.

Step 4:

Form the quantities G (Eq. 3), \mathbf{g} (Eq. 6) and \mathbf{H} (Eq. 14) evaluated at $\hat{\mathbf{n}}$. To do this for magmatic systems we need free energy models for the liquid and solid phases involved. These have been described by Ghiorso et al. (1983, with some modifications provided in the Appendix of this paper) and will not be reiterated here.

Step 5:

Compute the projected gradient, $\tilde{\mathbf{g}}$ (Eq. 25), the projected Hessian, $\tilde{\mathbf{H}}$ (Eq. 26) and the quantity on the right-hand side of Eq. (27).

Step 6:

Solve the system of equations defined by Eq. (27). Betts (1980a, 1980b) has suggested a scheme for doing this which uses methods that have wide application in least squares analysis (Lawson and Hanson 1974; Ghiorso 1983). The scheme takes into account the potential numerical instability of a projected Hessian, particularly if this matrix tends towards being indefinite. In this context, to be indefinite is symptomatic of a phase rule violation (see below).

Step 7:

Form \mathbf{n} according to Eq. (21).

Step 8:

Check for convergence. Form the norm of the vector $\mathbf{n} - \hat{\mathbf{n}}$, i.e., $\|\mathbf{n} - \hat{\mathbf{n}}\|$, where the norm is taken to be the L2 norm (Dahlquist and Björck 1974):

$$\|\mathbf{n} - \hat{\mathbf{n}}\| \equiv [(\mathbf{n} - \hat{\mathbf{n}})^T (\mathbf{n} - \hat{\mathbf{n}})]^{\frac{1}{2}}$$

If $\tau = 10^{-t}$, where t is the number of significant digits desired in the elements of \mathbf{n} , and if $\|\mathbf{n} - \hat{\mathbf{n}}\| \leq \tau^{\frac{1}{2}}(1 + \|\mathbf{n}\|)$ we have an indication of convergence. Proceed to step 10. If $\|\mathbf{n} - \hat{\mathbf{n}}\| > \tau^{\frac{1}{2}}(1 + \|\mathbf{n}\|)$ then the predicted value of \mathbf{n} is "far" from the guess, $\hat{\mathbf{n}}$. Presumably \mathbf{n} is a better description of the equilibrium state of the system. We correct the situation by performing another quadratic minimization with a new guess for $\hat{\mathbf{n}}$ (Step 9).

Step 9:

Determine a new vector $\hat{\mathbf{n}}$. The vector \mathbf{n} , determined in Step 7, may not be the best approximation to the minimum value of G since it was obtained assuming G could be expressed as a quadratic function of \mathbf{n} . In general \mathbf{n} will approach the equilibrium distribution of components as the guess

$\hat{\mathbf{n}}$ nears that equilibrium distribution and the quadratic approximation improves. Although we could take our new guess for $\hat{\mathbf{n}}$ (the concentration vector for the “equilibrium” distribution of components in the system) to be the newly computed \mathbf{n} , this is occasionally infeasible and it is more often convenient to define:

$$\mathbf{n}' \equiv \hat{\mathbf{n}} + \alpha(\mathbf{n} - \hat{\mathbf{n}}) \quad (28)$$

where α is a constant (of order unity) usually referred to as the steplength parameter, and is determined such that $G_{|\mathbf{n}'}$ is minimized, i.e.,

$$dG(\mathbf{n}')/d\alpha = 0. \quad (29)$$

Equation (29) is most easily solved by performing a low-accuracy uni-dimensional minimization such as a success-failure linear search with parabolic inverse interpolation (Algorithm No: 17 of Nash 1979). Having obtained a suitable α we take the new guess for $\hat{\mathbf{n}}$ to be \mathbf{n}' and proceed to step 4 to solve a new quadratic minimization program. This procedure insures that the new $\hat{\mathbf{n}}$ is at least a minimum of G in the search direction, $\mathbf{n} - \hat{\mathbf{n}}$, which is the quadratic approximation to the direction of steepest descent on the G surface at $\hat{\mathbf{n}}$. In addition, in determining \mathbf{n}' using Eqs. (28) and (29), α can be bounded so that the elements of \mathbf{n}' never become physically implausible (i.e., the concentration of a solid can be prevented from becoming negative, etc.). Therefore, this step in the algorithm implicitly maintains the feasibility of the vector $\hat{\mathbf{n}}$.

Step 10:

Verify convergence. In reaching this step in the algorithm we have tentatively concluded that \mathbf{n} is sufficiently “close” to $\hat{\mathbf{n}}$ to indicate that the truncated Taylor series expansion (Eq. 17) is an adequate approximation to G and that \mathbf{n} represents a compositional vector that minimizes the Gibbs free energy of the system. Practical, and very general, methods of verifying that \mathbf{n} is a minimizer have been discussed by Murray (1972), Gill and Murray (1974) and Gill et al. (1982). In brief, the norm of the projected gradient must be less than some specified tolerance parameter; usually

$$\|\tilde{\mathbf{g}}\| < 10\tau \|\mathbf{g}\|$$

or less stringently

$$\|\tilde{\mathbf{g}}\| < \tau^{\frac{1}{2}} \|\mathbf{g}\|.$$

This is demanded to insure that \mathbf{n} corresponds to a stationary point (maximum, minimum or saddle point) of G . In addition to this criterion the projected Hessian must be computationally positive definite.⁶ This insures that \mathbf{n} defines a *minimum* of G . The tendency for a matrix to be indefinite is given by its condition number, κ (Lawson and Hanson 1974). Specifically, in verifying that $\tilde{\mathbf{H}}$ is positive definite we demand that the projected Hessian satisfy the requirements of a Cholesky decomposition (Nash 1979) and that

$$\kappa < \|\tilde{\mathbf{g}}\|^{-\frac{1}{2}}$$

⁶ A matrix, $\tilde{\mathbf{H}}$, is positive definite if for any non-zero vector \mathbf{x} of appropriate length the scalar quantity $\mathbf{x}^T \tilde{\mathbf{H}} \mathbf{x}$ is always positive. If this quantity is sometimes positive, sometimes negative, and sometimes zero, the matrix $\tilde{\mathbf{H}}$ is said to be indefinite. Positive definite matrices are characteristic of surfaces that are concave up. An indefinite matrix characterizes a surface which contains a saddle point

or less stringently

$$\kappa < 10 \|\tilde{\mathbf{g}}\|^{-1}.$$

With verification of convergence the equilibrium vector \mathbf{n} has been achieved.

In implementing the proposed algorithm in magmatic systems certain problems immediately arise: 1) How are the equilibrium phases and guesses for their initial compositions determined? 2) What happens when a phase drops out of the equilibrium assemblage as during a reaction relationship between olivine and liquid to produce orthopyroxene? 3) How are the calculations modified for a realistic open system approach? We proceed now to these topics.

Supporting algorithms, computational peripherals and modifications for open systems

a) Determining the saturation point for a solid solution

Consider a dissolution reaction corresponding to the melting of one mole of the i^{th} end-member component, ϕ_i , in the solid phase ϕ at a particular T and P . If v_i corresponds to a vector of length l whose elements are the stoichiometric reaction coefficients for each liquid component, then the Gibbs free energy change for the reaction of interest is just

$$\Delta G_i = v_i^T \mathbf{g}_L - \mu_{\phi_i}^0 - RT \ln a_{\phi_i} \quad (30)$$

where \mathbf{g}_L is a vector of liquid chemical potentials (defined by Eq. 1), $\mu_{\phi_i}^0$ is the standard state⁷ chemical potential of ϕ_i , R is the universal gas constant and a_{ϕ_i} is the activity of the i^{th} end-member component in the phase ϕ . Equation (30) can be rearranged to facilitate calculating the solid activity from the liquid chemical potentials:

$$a_{\phi_i} = \exp [(-\Delta G_i + v_i^T \mathbf{g}_L - \mu_{\phi_i}^0)/RT]. \quad (31)$$

It should be noted that ΔG_i is nothing more than the negative chemical affinity of the dissolution reaction of interest. Equation (31) may be used to determine the saturation surface for a solid solution. We will demonstrate this using two cases, both of which are a modification of the approach taken by Reed (1982).

Case 1) An ideal solid solution

Here, trivially, a_{ϕ_i} may be taken to be X_{ϕ_i} where X_{ϕ_i} denotes the mole fraction of the i^{th} component in the ϕ^{th} phase. Let us tentatively assume that at this particular T and P and liquid composition (\mathbf{n}_L) the solid solution, ϕ , is just saturated and that it should be present in the final liquid/solid equilibrium assemblage. Then accordingly, we take ΔG_i to be zero in Eq. (31) and we may calculate an X_{ϕ_i} for each end member in the solid solution. If we sum these mole fractions for each component the result is a number termed the saturation index and denoted Σ_{ϕ} by Reed (1982):

$$\Sigma_{\phi} \equiv \sum_{\text{all } i} X_{\phi_i}. \quad (32)$$

If Σ_{ϕ} is equal to one, our assumption that the phase is just saturated ($\Delta G_i = 0$) is justified and this mineral should appear in an initial guess of the equilibrium phase assem-

⁷ Here taken to be unit activity of the pure substance at any T and P . Therefore, the activity of the *pure* end-member component is always unity

blage in the system. If Σ_ϕ is greater than unity the phase ϕ is supersaturated and should precipitate from the liquid at this P and T . Only if Σ_ϕ is less than unity is its absence from the system at this P , T and bulk composition suggested. Thus if the solid solution is ideal, determining the saturation point is quite straight forward. It is obviously trivial if we consider a pure solid (a one-component solid solution).

Case 2) Non-ideal solid solution

In this case the situation is a bit more complex since the activity coefficient for ϕ_i ($\gamma_{\phi_i} = a_{\phi_i}/X_{\phi_i}$) is generally a function of all the components in the solid solution. If there are c components in this solid solution we are faced with solving independently, a system of c non-linear equations of the form of Eq. (31). There are numerous numerical algorithms available for performing this task, most of which are based upon Marquardt's method (c.f. Nash 1979). Experience has shown, however, that the majority of these are inadequate for the present application owing to the fact that unless an initial guess for the various X_{ϕ_i} 's is quite good, the highly non-linear nature of the problem makes attainment of a solution unlikely. This is especially the case if the solid is highly supersaturated, where it often happens that during the calculation the X_{ϕ_i} 's become physically unreal and the γ_{ϕ_i} 's become uncomputable. To alleviate these difficulties a new algorithm has been developed for solving c non-linear equations in c unknowns. It is based upon a Gauss-Seidel method of solution (Dahlquist and Björck, 1974) and incorporates a damped-Newton search (Späth 1967) to maintain the feasibility of the X_{ϕ_i} 's.

Algorithm 2: Calculation of Σ_ϕ for a c -component non-ideal solid solution

Step 1:

Choose an initial guess. If we define \mathbf{X}_ϕ to be a vector of length c whose elements are $X_{\phi_1}, X_{\phi_2}, \dots, X_{\phi_c}$, then $\hat{\mathbf{X}}_\phi$ will denote our initial guess. It has proved convenient to take $\hat{X}_{\phi_1} = a_{\phi_1}, \hat{X}_{\phi_2} = a_{\phi_2}$, etc. This particular choice is equivalent to assuming that the solid solution is ideal. *Furthermore, we initially let $\mathbf{X}_\phi = \hat{\mathbf{X}}_\phi$.*

Perform the next five steps for $i=1, 2, \dots, c$, i.e., for each end-member of the solid solution:

Step 2:

Compute the gradient of a_{ϕ_i} with respect to the mole fraction of ϕ_i evaluated at \mathbf{X}_ϕ . This number will be denoted g_{ϕ_i} . Note that in this algorithm the X_{ϕ_i} 's are treated as independent variables as we are trying to discover if they sum to unity. If the gradient is not computable the initial guess (Step 1) is infeasible. *Let*

$$\begin{aligned} y &= X_{\phi_i}, \\ f &= g_{\phi_i}, \\ X_{\phi_i} &= y + |y/10|, \\ h &= |y/10|. \end{aligned}$$

This initializes the Newton step length.

Step 3:

If $|h| \leq |\tau^3 X_{\phi_i}|$ go to step 6.

Step 4:

Compute the gradient of a_{ϕ_i} with respect to the mole fraction of ϕ_i evaluated at \mathbf{X}_ϕ (i.e. get a new g_{ϕ_i}). If the new vector \mathbf{X}_ϕ is infeasible (i.e., if the gradient cannot be evaluated at this \mathbf{X}_ϕ) proceed to step 5. Otherwise, perform a Newton iteration:

$$\begin{aligned} h &= -g_{\phi_i}(X_{\phi_i} - y)/(g_{\phi_i} - f) \\ y &= X_{\phi_i} \\ f &= g_{\phi_i} \\ X_{\phi_i} &= X_{\phi_i} + h \end{aligned}$$

Go to Step 3.

Step 5:

The gradient in step 4 could not be evaluated at \mathbf{X}_ϕ . Modify the new guess (this is the damped search of Späth 1967, which maintains the feasibility of \mathbf{X}_ϕ). Let

$$\begin{aligned} h &= h/2 \\ X_{\phi_i} &= X_{\phi_i} - h. \end{aligned}$$

Go to Step 3.

Step 6:

The i^{th} non-linear equation has been solved. Increment i . If $i < c$ go to step 2.

Step 7:

Determine if the current solution vector, \mathbf{X}_ϕ , satisfactorily satisfies all c simultaneous equations. Let

$$\begin{aligned} SSQ &= (\mathbf{X}_\phi - \hat{\mathbf{X}}_\phi)^T (\mathbf{X}_\phi - \hat{\mathbf{X}}_\phi) \\ \hat{\mathbf{X}}_\phi &= \mathbf{X}_\phi. \end{aligned}$$

If $SSQ \leq \tau$ then a successful solution has been obtained. If $SSQ > \tau$ go to step 2 to try another series of Newton searches.

Step 8:

Evaluate Σ_ϕ :

$$\Sigma_\phi = \sum_{i=1}^c X_{\phi_i}.$$

The algorithm is completed.

In the proposed algorithm for the calculation of Σ_ϕ for non-ideal solutions, a value of X_{ϕ_i} is changed continuously until the expression for the corresponding a_{ϕ_i} (Eq. 31) is satisfied. This is the essence of the Gauss-Seidel method and distinguishes it from Marquardt or Gauss-Newton procedure where all X_{ϕ_i} 's are modified continuously to attempt to satisfy all the equations simultaneously at every iteration. The numerical instability associated with the latter procedures, when applied to this particular problem, arises from this simultaneous adjustment. Such numerical instability is absent in the proposed algorithm. As might be suspected, the robustness of this algorithm over Marquardt and Gauss-Newton procedures is obtained with some sacrifice in rate of convergence.

A modification of the second algorithm must be introduced when the compositions of two phases can be expressed in terms of identical components. This situation arises when the two phases lie on opposite sides of a multi-component solvus as do plagioclase and alkali-feldspar in the system $\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8 - \text{KAlSi}_3\text{O}_8$. Here the

above algorithm for the calculation of Σ_ϕ in a non-ideal solution is used to determine the saturation point for each phase. Once one phase is saturated, however, the presence of the second is detected by determining when the composition of the first attempts to move into the multicomponent solvus. This requires the computation of a pseudo-binary solvus section at the temperature and pressure of interest. The activity matching algorithm of Barron (1976a, 1983) is used for this purpose.⁸

Once Σ_ϕ is known for a particular solid solution, a selection of probable solid phases in the equilibrium configuration of the system can be deduced and an initial approximation to their equilibrium composition (\mathbf{X}_ϕ) can be specified.

Dropping a phase from the system

In the course of the heterogeneous solid-liquid equilibrium algorithm described above elements of the compositional vector \mathbf{n} can become quite small. This usually occurs during the unidirectional minimization stage of the algorithm (Step 9). If this happens for all the components of a particular phase it means that this phase is to be dropped from the equilibrium system configuration. As will be documented in Part II, this phenomenon commonly occurs when the liquid encounters a peritectic such as olivine reacting out to form orthopyroxene during the crystallization of a tholeiite. In practice, a solid phase is dropped from the system if the sum of the molar amounts of all its end-member constituents is less than some small (trivial) mass. The system is then reconfigured and the minimization re-attempted in the absence of the offending phase.

If a liquid component approaches zero concentration, however, a more complicated problem arises. If solids and liquids coexist, the liquid *must* always contain some small amount of every component present in every solid. So we simply cannot set the concentration of a liquid component to zero if it gets “small”, but for computational reasons, we cannot let the concentration of the liquid component become as “small” as it would like. Furthermore, we must consider the possibility of subsequently resorbing a solid which contains this liquid component and we must recognize the likelihood that the impending disappearance of this liquid component might be an artifact produced by the quadratic approximation to the free energy function. The answer to these difficulties involves invoking an additional equality constraint which fixes the concentration of a liquid component at some small (trivial) value if the concentration of this component attempts to drop below this value. Algorithm (1) described above accommodates this solution perfectly.

Having solved the problem of preventing a liquid component from disappearing completely, we are now faced with determining when it should reappear (as for example when resorbing a solid). Associated with each of the active equality constraints in our system (Eq. 10) is a Lagrange multiplier. These may be denoted by the elements of the vector λ , where

$$\mathbf{C}^T \lambda \equiv \mathbf{g}|_{\text{equilibrium } \mathbf{n}}$$

or

$$\mathbf{C}^T \lambda \simeq \mathbf{g}|_{\text{other } \mathbf{n}} \quad (34)$$

(Gill et al. 1981). If the equality constraint associated with preventing the liquid component of interest from disappearing has a positive Lagrange multiplier, then the constraint is active (Gill et al. 1981) – The liquid is still trying to precipitate more of this component. If, however, for some particular value of \mathbf{n} determined at step 7 of the heterogeneous equilibrium algorithm, the value of the estimated Lagrange multiplier for this constraint is negative, the liquid is attempting to resorb a solid involving this component and the constraint should be removed. Therefore, checking the sign of the estimated Lagrange multipliers (Eq. 34) will determine when a liquid constraint should be removed. If removal is indicated the system of equality constraints is then reconfigured and the minimization re-attempted in the absence of the offending constraint.

Modifications for open system calculations

In Part II it will be demonstrated that in order to calculate, using the approach outlined here, the correct fractional crystallization and equilibrium crystallization trends of tholeiitic magmas, the magmatic system must be assumed to be open to oxygen. That is, the bulk composition constraint on both ferric and ferrous iron must be replaced with a single bulk composition constraint on total iron. This means that in the course of crystallization the system assimilates or expels oxygen as the need arises. Having made this observation it should be recalled that the composition of the “system” is defined in terms of an adopted set of liquid components (see footnote 2) which involve only one oxidation-reduction couple, that between ferric and ferrous iron. In a magma, other redox couples will certainly be present, as for example, those between dissolved carbon or sulfur species. Therefore, the need to incorporate oxygen transfer to model crystallization may, in part, be an artifact of our choice of compositional variables for the system. What is clearly necessary (see Part II) is for iron to be transferred between its oxidized and reduced melt species during crystallization. The net oxygen expelled or absorbed as a consequence of this transfer can be stored or provided by another melt redox couple functioning as a magmatic oxygen reservoir or, alternatively, via oxygen metasomatism into and out of the magma. In the latter case, the country rock functions as an external oxygen reservoir. Though the consequences of these alternatives are discussed in Part II, it should be recognized here that the idea of oxygen metasomatism is just hydrogen metasomatism in disguise. It is widely recognized that hydrogen can diffuse easily through crustal and mantle rocks (Sato 1978; Arculus and DeLano 1981). Therefore, it should be able to readily enter or leave a crystallizing magma chamber. As the fugacity of hydrogen in the magma is linked through the water content to the fugacity of oxygen, it can be argued that the chemical potential of oxygen in the melt, and hence the melt’s ferric/ferrous ratio, should be roughly fixed by external conditions rather than internal equilibria. Similarly, if the magma’s oxygen fugacity is largely controlled by internal buffers *which are exclusive of the “system” bulk composition*, then for calculational purposes the melt’s ferric/ferrous ratio can also be considered fixed by external conditions rather than internal equilibria. These concepts have been extensively developed in the literature on metasomatic processes and should be quite familiar to the meta-

⁸ Barron’s algorithm has proved more than adequate in the present application (see Part II) but is subject to “consolute drift” (L.M. Barron, personal communication) in that the computed solvus tie-line may migrate off the solvus isotherm near the consolute

morphic petrologist who has dealt with the notion of “perfectly mobile components” (Korzhinskii 1959; Thompson 1970). That the fugacity or chemical potential of oxygen in the melt is somehow fixed by the external conditions is *the* essential aspect of open system equilibrium calculations involving perfectly mobile components. In such systems the thermodynamic function which is minimized at equilibrium is not the Gibbs free energy, but the Korzhinskii potential, L (Thompson 1970; Shvarov, 1978). In the case of the magmatic system open to oxygen:

$$L = G - G_{O_2}. \quad (35)$$

Here G is defined by Eq. (3) and G_{O_2} is the Gibbs free energy of oxygen, given by:

$$G_{O_2} = n_{O_2} \mu_{O_2}. \quad (36)$$

In Eq. (36) n_{O_2} is taken as the “excess oxygen of the system” implied by the production of ferric from ferrous iron during the minimization of L at a given T and P . The chemical potential of oxygen, which is externally fixed, is given by

$$\mu_{O_2} = \mu_{O_2}^0 + RT \ln f_{O_2}$$

where $\mu_{O_2}^0$ is the chemical potential of oxygen in the standard state (see Appendix). The relationship between the fugacity of oxygen, melt composition and melt ferrous/ferric ratio has been provided by Kilinc et al. (1983).

If the μ_{O_2} of the melt is dictated by an externally fixed oxygen fugacity then the relationship of Kilinc et al. (1983) imposes an additional equality constraint on the system which involves the moles of the liquid components. This equality constraint replaces the one discarded by allowing the transformation of ferrous to ferric iron in the liquid. Recognizing this, we now have a new function to minimize (L) and a new set of equality constraints (C) and we could execute an algorithm like the one described above to minimize G except for the fact that the Kilinc et al. (1983) equality constraint is non-linear. It relates the logarithm of the ferrous/ferric ratio in the liquid to the mole fractions of the other liquid components.

Methods of minimizing non-linear functions subject to non-linear equality constraints have been discussed by Gill et al. (1981). These methods are complex enough to consider techniques of linearizing the Kilinc et al. (1983) equation. By evaluating the available experimental data (c.f. Kilinc et al. 1983; Ghiorso et al. 1983), it can be empirically shown that in a melt fractioning or crystallizing as temperature decreases along an f_{O_2} buffer like *QFM*, the ferric/total iron ratio, r , in the melt remains essentially constant. Thus, if the initial ferric/ferrous ratio in the melt is fixed using the Kilinc et al. (1983) equation at a known f_{O_2} , then preserving the ratio r in the melt as it crystallizes and cools is essentially equivalent to imposing the full Kilinc et al. (1983) non-linear constraint. In fact, what will happen (see Part II) is that the melt will crystallize along any f_{O_2} buffer which is initially fixed by the ratio. Note that this constant ferric/total iron ratio implies a *linear* equality constraint, for if (using Ghiorso et al. 1983, liquid components)

$$r = n_{Fe_{16/3}O_8}^{liquid} / (n_{Fe_{16/3}O_8}^{liquid} + \frac{3}{4} n_{Fe_4Si_2O_8}^{liquid}),$$

then

$$(1-r)n_{Fe_{16/3}O_8}^{liquid} - \frac{3}{4} r n_{Fe_4Si_2O_8}^{liquid} = 0. \quad (37)$$

By linearizing the Kilinc et al. (1983) expression according to Eq. (37) and using it as an equality constraint on the

chemical potential of oxygen, the potential L can be minimized using the algorithm discussed above.⁹ Phase equilibria can then be computed in magmatic systems open to oxygen.

An algorithm for calculating chemical mass transfer in magmatic systems

In the algorithms outlined above, methods are established for determining the identity and equilibrium proportions of phases in a magmatic system potentially open to a perfectly mobile component at a particular P and T . In order to model magmatic processes which involve changing T , P or even bulk composition (other than O_2), these algorithms must be extended to form the kernel of a calculational scheme describing chemical mass transfer. The essence of this calculational scheme will be that the evolution of a system undergoing any smoothly continuous change, such as gradually varying temperature, pressure or bulk composition with time, can be adequately approximated as a series of steps in T , P or system bulk composition, with each step characterized by thermodynamic equilibrium. The following procedure embodies this approximation. A FORTRAN 77 implementation has been used to numerically model crystallization and assimilation in magmatic systems (Part II).

Algorithm 3: The calculation of equilibrium crystallization, crystal fractionation, magma mixing or solid phase assimilation in magmatic systems

Step 1:

Choose an initial composition of the system and a set of characteristic intensive variables (T , P , initial f_{O_2}). The system is here assumed to consist entirely of a liquid phase (perhaps a metastable condition).

Step 2:

Evaluate standard state thermodynamic data at the temperature and pressure of interest (see appendix and Ghiorso et al. 1983).

Step 3:

Evaluate the extent of super- or under-saturation for all solid phases not in the system at this T , P , and liquid composition. For non-ideal solid solutions execute Algorithm (2) for each phase.

⁹ In the algorithm the vector \mathbf{g} must be replaced with $\mathbf{g} - \mathbf{g}_{O_2}$, where \mathbf{g}_{O_2} is a vector of length n and is defined by

$$\mathbf{g}_{O_2} \equiv (\partial G_{O_2} / \partial \mathbf{n})_{T,P}.$$

Recall that $G_{O_2} = n_{O_2} \mu_{O_2}$ and note that since the melt oxygen fugacity is a function of liquid composition, only the “mineral component” derivatives of μ_{O_2} are zero. In taking the above derivative the reader should recall that n_{O_2} is defined in terms of the excess oxygen in the system, that is, in terms of both liquid and solid components.

In addition, the matrix \mathbf{H} must be replaced by $\mathbf{H} - \mathbf{H}_{O_2}$, where

$$\mathbf{H}_{O_2} \equiv (\partial \mathbf{g}_{O_2} / \partial \mathbf{n})_{T,P},$$

and is symmetric and of dimension n . In general, \mathbf{H}_{O_2} is not of the simple block diagonal form of \mathbf{H} due to the non-zero liquid-solid component cross-derivatives of G_{O_2}

Step 4:

Add the most super-saturated phase determined in step 3 (largest Σ_ϕ) to the system (give it a trivial mass proportioned according to the expected mole fractions of its end-member components). If no solid is super-saturated proceed to step 5.

Step 5:

Construct bulk composition and/or oxygen buffer equality constraints appropriate to open or closed systems given this assemblage of liquid and solids.

Step 6:

Determine the equilibrium proportions and compositions of the solid and liquid phases by minimizing G or L according to Algorithm (1) described above. In the course of minimization if:

a) A solid phase is exhausted. Drop the phase from the system and go to Step 5.

b) The number of moles of a liquid component approaches "zero." Add an equality constraint and go to step 5.

c) The Lagrange multiplier for the equality constraint on a liquid component indicates the constraint is no longer necessary. Drop the constraint and go to Step 5.

d) The projected Hessian becomes singular, i.e. the system of Eq. (27) cannot be solved. This usually arises when the concentration of a solid or liquid component nears "zero". The situation can be remedied by taking action according to (a) or (b).

e) Convergence criteria cannot be met and the best quadratic approximation to G has been achieved. Stop in defeat.

Step 7:

Determine if additional solid phases should be included in the system. Evaluate the extent of super- or under-saturation for all solid phases not in the system at the T , P and new liquid composition. For non-ideal solid solutions execute algorithm (2) for each phase. Add the most super-saturated phase so determined to the system and go to Step 5. If no solid is super-saturated we have achieved the stable liquid/solid configuration. Proceed.

Step 8:

If modelling fractionation:

a) Adjust the masses of all solids in the system to trivial amounts and modify the bulk composition of the system accordingly.

b) Preserve the current mole fraction ratios in the residual solids.

Step 9:

If changing T and P , increment to the next value (in the calculations which appear in Part II a step of 15° C is usually made).

Step 10:

If modelling the assimilation of a solid phase or the mixing of magmas, add a small increment of new material to the system by altering the bulk composition, assuming for the moment that any such material dissolves completely into the liquid phase. As the equilibrium solid/liquid propor-

tions will be subsequently determined this assumption is made only for computational convenience.

Step 11:

If only the bulk composition of the system has been changed (i.e. T , P remain constant) go to Step 3 to determine a new equilibrium configuration, otherwise go to Step 2 to recompute the standard state thermodynamic data.

By continuously monitoring the state of the system at Step 7, the evolution of the magmatic phase relations can be studied in a series of discrete intervals between some initial and final temperature, pressure and bulk composition. In practice, the method outlined above has been found to be quite satisfactory (see Part II). The most time-consuming aspect is the calculation of the saturation index (Σ_ϕ) for the various non-ideal solid solutions. However, this algorithm leads to very accurate solid phase selection for the equilibrium configuration. Convergence to a stable assemblage is usually achieved in four to five quadratic minimization attempts of the potential function. In addition, the solid phase deletion algorithm has proven adequate in dealing with a peritectic reaction relationship.

Summary

This paper describes an algorithmic framework within which chemical mass transfer calculations in magmatic systems can be performed. The main procedures in this algorithm are based upon the ability to describe the equilibrium state of a closed system by direct minimization of the Gibbs free energy. The minimization procedures incorporate non-linear mathematical programming (optimization) techniques which have not been extensively utilized by geochemists. The algorithm also contains procedures for identifying the heterogeneous phase assemblage stable at equilibrium and incorporates phase selection techniques which are more accurate than the empirical "rules" utilized by other workers (Wolery 1979; Saxena 1982). These techniques allow routine calculations with highly non-ideal solutions.

In Part II it will be demonstrated that incorporation of the concept of perfectly mobile components is essential in order to successfully model crystal fractionation in a magmatic system. Specifically, to obtain geologically acceptable results, the magma must be open to oxygen transfer with a fixed oxygen potential set by equilibria external to the system. The present algorithm easily accommodates this requirement through constrained minimization of the Korzhinskii potential and allows for the calculation of magmatic mass transfer in systems open to oxygen.

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Appendix: Revision of Thermodynamic Data and Solid-Solution Models

This appendix describes the pertinent revisions and additions that have been made to the thermodynamic database of Ghiorso et al. (1983, their appendices 1 and 2) in order to implement the algo-

Table A1. Additional sources of thermodynamic data

Phase	Solid-solution model	Component	Measured ΔH_f^0 (298 K, 1 bar) two standard errors	Adjusted ΔH_f^0 Ghiorso et al. 1983	Accepted ΔH_f^0
Olivine	c.f. Ghiorso et al. 1983	Forsterite	−518,731 317	−518,350	(same)
		Fayalite	−353,576 576	−352,365	(same)
Feldspar	Ghiorso (1984)	Albite	−937,916 870	−938,699	(same)
		Anorthite	−1,014,110 747	−1,013,656	(same)
		Sanidine	−946,358 805	−945,800	−943,919
Opx	Ideal Solution	Enstatite	−369,921 290	−369,640	−370,217
		Ferrosilite	−284,734 −	−283,920	−284,506
Cpx	Nicholls and Stout (1983)	Diopside	−767,390 2,180	−765,570	−766,099
		Hedenbergite	−678,496 −	−680,490	−681,487
		Enstatite	(−739,482) −	−	−735,222
		Ferrosilite	(−569,468) −	−	−564,732
Spinel	c.f. Ghiorso et al. 1983	Magnetite	−284,927 500	−284,630	−261,715 ^a
		Ulvöspinel	−356,758 −	−358,160	−357,661
Liquid		Fe _{16/3} O ₈	−518,224 800	−519,023	−563,990

^a New Accepted $S_{298,1\text{ bar}}^0 = 34.982\text{ cal/K}$; $C_p = 48.00\text{ cal/K}$ (Helgeson et al. 1978) consistent with $\Delta H_f^0 = -265,007\text{ cal}$

ritms outlined in this paper. In general these changes reflect the adoption of new models for the thermodynamic description of solid solutions. The necessity for these changes largely stems from the difficulty of using very general solid-solution models to back-calculate the composition of a mineral from the assumption of chemical equilibrium with a melt of known bulk composition. As an example consider pigeonite-melt equilibria. Ghiorso et al. (1983) outline a simple method, based upon ideal site mixing, to obtain an estimate of the activity of MgSiO₃ and FeSiO₃ in this pyroxene if its composition is known, and further demonstrate how these activities translate into a relationship between the activities of Si₄O₈, Mg₄Si₂O₈ and Fe₄Si₂O₈ in the liquid coexisting with this pyroxene. The ancillary data used by Ghiorso et al. (1983) to make this inference are the Gibbs free energy of fusion of enstatite and ferrosilite at the temperature and pressure of interest. Consider now the same equilibria and the calculation proposed in algorithm number two of this paper: from the composition of the liquid determine whether or not pigeonite is saturated in this liquid and if so estimate its composition. This calculation involves the determination of the activities of all the components in the pigeonite and requires that we know many more free energies of fusion. These activities must then be *translated back into mole fractions*. The available thermodynamic data are inadequate to the task and we must content ourselves with describing calculated pyroxene compositions involving manageable numbers of components.

Table A1 details the changes made to the activity/composition relations (Appendix 1) and thermodynamic data (Appendix 2) of Ghiorso et al. (1983). Specific corrections are discussed in detail below for each phase.

Feldspar

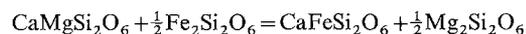
Ghiorso et al. (1983) modelled the plagioclase and alkali-feldspar binaries as ideal solutions specifically neglecting solid-solution within the ternary system NaAlSi₃O₈–CaAl₂Si₂O₈–KAlSi₃O₈. For the purposes of this paper the ternary feldspar model of Ghiorso (1984) has been adopted. This requires some readjustment of the enthalpy of formation of sanidine (Table A1) to bring the new solid activity formulation into accord with the liquid solution model of Ghiorso et al. (1983) and the experimentally determined plagioclase-liquid equilibria upon which this liquid model is based. The new feldspar activity/composition relations did not necessitate altering the previously adjusted enthalpy data for albite and anorthite. The rather large change in the enthalpy of formation of sanidine indicated in Table A1 suggests some problem with the K_{16/3}Si_{8/3}O₈ binary interaction coefficients in the liquid or the thermodynamic properties of molten potassium metasilicate adopted by Ghiorso et al. (1983). This suggestion is collaborated by the rather poor description of leucite-liquid equilibria provided by Ghiorso et al. (1983). It is further substantiated by preliminary calculations of the type described here, which indicate the need for further work before equilibrium relations involving K-silicates can be adequately modelled in liquids more potassic than tholeiites.

Pyroxene

Ghiorso et al. (1983) treated the Ca-poor pyroxenes using ideal site mixing theory. This approach is consistent with ideal mixing of MgSiO₃ and FeSiO₃ components if attention is restricted to

the enstatite-ferrosilite joins. Due to a lack of adequate thermodynamic data we have chosen to express the compositions of Ca-poor pyroxenes within this restricted binary system and have consequently treated the orthopyroxenes as ideal solutions.

The solution model suggested by Nicholls and Stout (1982) has been adopted to formulate activity/composition relations for calculations involving clinopyroxenes. Their model describes pyroxene compositions within the quadrilateral $\text{CaMgSi}_2\text{O}_6$ – $\text{CaFeSi}_2\text{O}_6$ – $\text{Mg}_2\text{Si}_2\text{O}_6$ – $\text{Fe}_2\text{Si}_2\text{O}_6$ and allows for the preferential site occupancy of Fe on the M2 site. The free energy for the solid exchange reaction



used in Nicholls and Stout's (1982) model has been made to conform to the data in Table A1 and that in Ghiorso et al. (1983).

The activities of $\text{CaMgSi}_2\text{O}_6$ and $\text{CaFeSi}_2\text{O}_6$ in clinopyroxenes were described using ideal site mixing theory by Ghiorso et al. (1983). For proper implementation of the back calculation scheme used in this paper, the ideal site mixing model has proved insufficient. Unfortunately, there are not adequate data to extend Nicholls and Stout's formulation to Al-, Na- or Ti-bearing clinopyroxenes. Therefore, the Ca-rich pyroxenes participating in the mass transfer calculations described in Part II have compositions restricted to the pyroxene quadrilateral.

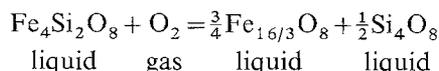
The revised enthalpies listed in Table A1 reflect adjustment to make the liquid solution model and pyroxene-liquid database of Ghiorso et al. (1983) conform to the new solid-solution model for the pyroxenes.

Spinel

The activity/composition relations for spinels adopted by Ghiorso et al. (1983) express compositions within the 5-space: FeAl_2O_4 – MgAl_2O_4 – FeCr_2O_4 – Fe_2TiO_4 – Fe_3O_4 . Because activity/composition relations involving Cr in the liquid have not been properly calibrated and because in the absence of the chromite component most low pressure igneous spinels can be essentially treated as ulvöspinel-magnetite solid solutions, we have limited spinel solid-solution in Part II to the Fe_2TiO_4 – Fe_3O_4 join. The relevant solution properties appropriate to this binary have been retained and the enthalpies of formation (Table A1) adjusted to fit the magnetite-liquid and ulvöspinel-liquid data of Ghiorso et al. (1983) exclusive of the other spinel components. The correction for magnetite reflects an additional adjustment to the accepted entropy and heat capacity of the mineral (a preference for the heat capacity of Helgeson et al., 1978, over that of Robie et al., 1978, see Table A1) and a change in the accepted enthalpy of formation of the liquid component $\text{Fe}_{1.6/3}\text{O}_8$ (see below).

Other Phases

The data reported in Kilinc et al. (1983) can be used to evaluate the redox equilibria:



in a wide variety of natural silicate liquids above their one-bar liquidus. These data were not used to explicitly constrain ferric iron interactions in the solution model of Ghiorso et al. (1983) but the $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratios determined in liquids equilibrated along the QFM buffer have been used here to adjust the enthalpy of formation of $\text{Fe}_{1.6/3}\text{O}_8$. Such an adjustment makes the Ghiorso et al. (1983) model consistent with the Kilinc et al. (1983) database at QFM without recalibrating all the regular solution liquid-interaction terms. It appears in retrospect that these interaction parameters were not adequately fixed by the solid-liquid equilibria considered in Ghiorso et al. (1983). The indicated adjustment of the enthalpy of formation, as opposed to the entropy or enthalpy of fusion, of $\text{Fe}_{1.6/3}\text{O}_8$ is quite arbitrary but reflects an acknowledged uncertainty in the thermochemical properties of this liquid component. A more satisfactory approach would be the complete recal-

ibration of the solution model of Ghiorso et al. (1983) incorporating the constraints provided by the entire Kilinc et al. (1983) database. This recalibration is under investigation.

The thermodynamic properties of oxygen gas are taken from Helgeson et al. (1978). Values of the fugacity of oxygen corresponding to a particular oxygen buffer as a function of T (at 1 bar) were obtained from Myers and Eugster (1983). The pressure dependence of the oxygen buffers have been computed from thermodynamic data reported by Robie et al. (1978).

The solid phases leucite and the rhombohedral oxides (hematite-ilmenite-geikielite solid solutions) were not considered in the mass transfer calculations described in this paper and reported in Part II. In the case of the former, the activity/composition relations involving $\text{K}_{1.6/3}\text{Si}_{8/3}\text{O}_8$ in the liquid (e.g., Ghiorso et al., 1983) are deemed inadequate for highly potassic liquids and for consistency, the phase was not allowed to form during calculations on any liquid composition. Careful examination of the rhombohedral oxide data utilized by Ghiorso et al. (1983) suggests that these phases crystallized metastably. The evidence includes their rather high-temperature appearance on the liquidus ($\sim 100^\circ$ above their expected appearance) and their excessively high Mg-contents (~ 7 wt. % MgO). When the mass transfer calculations described in Part II were first performed, rather high-temperature Mg-rich rhombohedral oxides were crystallized under P – T conditions obviously outside their natural stability range. For this reason the phase was suppressed from forming entirely in all the calculations reported in Part II.

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