 Evaluating reaction stoichiometry in magmatic systems evolving under generalized thermodynamic constraints: Examples comparing isothermal and isenthalpic assimilation

MARK S. GHIORSO and PETER B. KELEMEN
Department of Geological Sciences, University of Washington, Seattle, WA 98195, U.S.A.

Abstract—Legendre transforms are utilized to construct thermodynamic potentials which are minimal in systems at thermodynamic equilibrium under conditions of fixed enthalpy, volume and chemical potential of oxygen. Numerical methods that facilitate the minimization of these potentials are described. These methods form the core of an algorithm for the calculation of reaction stoichiometry for irreversible processes in open magmatic systems proceeding under isenthalpic or isochoric constraints, or both.

As an example of the use of these methods, calculations of isothermal and isenthalpic assimilation in fractionating basaltic magma are presented. Isenthalpic calculations are most useful in considering the effects of solid–liquid reactions which are endothermic. In general, such reactions involve the assimilation of a less refractory phase in a high temperature magma, or assimilation of phases across a cotectic “valley” in the liquidus surface. The mass of crystals calculated to form during isenthalpic assimilation of pelitic rock in a magnesian MORB is six to ten times as great if the rock is assumed to be at 500°C than if the rock is at 1250°C. The examples illustrate the necessity of characterizing the temperature and phase assemblage, as well as the bulk composition, of the assimilate when considering the effect of solid–liquid reaction on the liquid line of descent.

INTRODUCTION

CHEMICAL MASS TRANSFER in magmatic systems has been simulated previously as a succession of steps in temperature, pressure or bulk composition, with each step characterized by heterogeneous equilibrium (GHIORSO, 1985; GHIORSO and CARMICHAEL, 1985). This approach has made possible the numerical simulation of magmatic processes such as equilibrium crystallization and crystal fractionation. This method has also proven useful in the investigation of the assimilation of solid phases (GHIORSO and CARMICHAEL, 1985; KELEMEN and GHIORSO, 1986). However, existing computational techniques are inadequate for calculation of reaction stoichiometry in thermodynamic systems evolving toward an equilibrium state under general system constraints. By general constraints we mean those other than temperature (T), pressure (P) and fixed bulk composition. There are two reasons for this inadequacy. Firstly, the Gibbs free energy, G, is not necessarily minimal in a thermodynamic system that is generally constrained. Thus, to calculate heterogeneous equilibrium at each step in a mass transfer calculation, proceeding under a specified set of generalized constraints, requires the generation of a thermodynamic potential which is minimal under these conditions. The second difficulty is computational. Constraints other than temperature, pressure or fixed bulk composition are usually non-linear functions of their independent variables, i.e., the enthalpy, H, is a non–linear function of temperature, pressure and the number of moles of system components. Therefore, after deduction of the appropriate potential, its minimum must be computed by finding those particular values of the independent variables of the system that satisfy the non–linear constraint(s). This is a formidable numerical problem, which in magmatic systems has only been attempted in an approximate fashion (GHIORSO, 1985).

In this paper we review the theory behind the construction of potentials which are minimal in systems subject to generalized thermodynamic constraints. This theory is rendered practical for computational purposes by a modification of the numerical algorithm utilized by GHIORSO (1985) along the lines suggested by GILL et al. (1981). These general procedures are applied to evaluate reaction stoichiometry in magmatic systems evolving under isenthalpic or isochoric constraints, or both. In addition, a more rigorous treatment of the calculation of equilibria in thermodynamic systems open to a perfectly mobile component (KORZHINSKII, 1959; THOMPSON, 1970) is given. Numerical examples that model assimilation in magmas under both isothermal and isenthalpic conditions are provided. These examples illustrate the utility of the technique in predicting the effects of assimilation on derivative liquids.
CONSTRUCTION OF THERMODYNAMIC POTENTIALS

In this section we utilize mathematical methods for defining thermodynamic potentials which have been described by CALLEN (1961) and THOMPSON (1970). Let \( \Psi \) be an unspecified thermodynamic potential which is minimal at equilibrium. This minimum is constrained by the specification of linear and possibly non-linear relationships among the independent variables of \( \Psi \). For example, if \( \Psi = G(T, P, n_1, n_2, \ldots, n_c) \), where \( n_1, n_2 \) to \( n_c \) are variables denoting the number of moles of each of the \( c \) system components in each phase, then \( G \) is minimal at equilibrium subject to constant temperature, pressure and fixed bulk composition. The latter constraint does not imply that \( n_1 \) through \( n_c \) must be held constant in the processes of minimizing \( G \), but rather that linear combinations of the \( n_1 \) through \( n_c \) must be constrained in order that the system bulk composition remain constant. There will always be more \( n_i \)'s than compositional variables in a multi-phase thermodynamic system. Mathematically, finding the minimum of \( G \) is simply a case of optimizing a non-linear function subject to linear equality constraints.

Let the independent variables of \( \Psi \) be denoted by \( x, y, n_1, n_2, \ldots, n_c \). For convenience, we will group the mol numbers of the various system components to form the elements of a vector denoted by \( n \) such that:

\[
\begin{bmatrix}
  n_1 \\
  n_2 \\
  \vdots \\
  n_c 
\end{bmatrix}
\]

Thus, we may write \( \Psi = \Psi(x, y, n) \). If a new thermodynamic potential, \( \Phi \), is to be defined such that \( \Phi = \Phi((\partial \Psi/\partial x)_{x,y,n}, y, n) \), then \( \Phi \) is given by the Legendre transform (CALLEN, 1961) of \( \Psi \):

\[
\Phi\left( \frac{\partial \Psi}{\partial x} \right)_{x,y,n} = \Psi(x, y, n) - x \left( \frac{\partial \Psi}{\partial x} \right)_{x,y,n}.
\] (2)

As an example, we might consider the case treated by THOMPSON (1970) and GHIORSO (1985) of a perfectly mobile component. Imagine a magmatic system whose boundaries are open to oxygen exchange such that the chemical potential of oxygen in the system is fixed by external constraints. By denoting this chemical potential \( \mu_{O_2} \), we seek a new potential, \( \Phi \), which is minimal at equilibrium in this partially open magmatic system at constant temperature and pressure. By recognizing that \( \mu_{O_2} \) is defined as \( (\partial G/\partial n_{O_2})_{T,P,n^\ast} \), where \( n^\ast \) denotes all mole numbers held constant except those of oxygen, the potential \( \Phi \) can be expressed as [Equation (2)]:

\[
\Phi = G - n_{O_2} \mu_{O_2}.
\] (3)

Potentials of the form of Equation (3), which are minimal in systems open to perfectly mobile components, are usually referred to as Korzhinskii potentials (THOMPSON, 1970).

We now utilize Equation (2) to construct a number of thermodynamic potentials which are useful in calculating reaction paths in magmatic systems.

Isenthalpic constraints

We seek the potential \( \Phi(H, P, n_1, n_2, \ldots, n_c) \). From the definition of the Gibbs free energy a new potential may be defined:

\[
G/T = H/T - S.
\] (4)

The total derivative of \( G/T \) may be deduced from Equation (4):

\[
da \left( \frac{G}{T} \right) = H \left( \frac{1}{T} \right) + \frac{1}{T} dH - dS,
\]

and given that

\[
dH = TdS + VdP + \sum_{i=1}^{c} \mu_i \, d\mu_i,
\]

we have:

\[
da \left( \frac{G}{T} \right) = H \left( \frac{1}{T} \right) + \left( \frac{V}{T} \right) dP + \left( \frac{1}{T} \right) \sum_{i=1}^{c} \mu_i \, d\mu_i.
\] (5)

Equation (5) demonstrates that

\[
\left( \frac{\partial G/T}{\partial 1/T} \right)_{P,n} = H,
\]

which allows us to write, by using Equation (2):

\[
\Phi(H, P, n) = \frac{G}{T} - \frac{1}{T} \left( \frac{\partial G/T}{\partial 1/T} \right)_{P,n} = \frac{G}{T} - \frac{1}{T} H
\]

\[
\Phi(H, P, n) = -S.
\] (6)

Equation (6) establishes that equilibrium in a closed system subject to constant enthalpy and pressure is given by a maximum in entropy.

Isochoric constraints

In this case we seek the function \( \Phi(T, V, n) \). The formalism of the Legendre transform is unnecessary
Evaluating reaction stoichiometry

in the case of isochoric constraints as the required function $\Phi$ is just the Helmholtz free energy, denoted by the symbol $A$:

$$\Phi(T, V, n) = A = G - PV.$$  \hspace{1cm} (7)

**Combined isenthalpic and isochoric constraints**

Under conditions of constant enthalpy and volume the potential $\Phi$ can be obtained from Equation (5) by recognizing that

$$\left(\frac{\partial G}{\partial P}\right)_{T,V,n} = \frac{V}{T}$$

from which the Legendre transform may be constructed as:

$$\Phi(H, V, n) = G - \frac{1}{T} H - \frac{P V}{T}$$

$$\Phi(H, V, n) = -S - \frac{VP}{T}. \hspace{1cm} (8)$$

Equation (8) establishes the potential which is minimal under conditions of constant enthalpy, volume and fixed bulk composition.

**THE MATHEMATICAL PROBLEM OF MINIMIZING $\Phi$**

In order to calculate heterogeneous equilibrium with the chemical mass transfer algorithm of GHIORSO (1985) we require a numerical method to minimize the newly defined functions, $\Phi$, subject to the appropriate constraints. To formulate correctly the problem we must recognize initially that the fixed bulk composition constraints are always linear functions of the system components. From GHIORSO (1985) we define the rectangular matrix $C$ such that

$$Cn - b = 0$$

and

$$\Delta x(n, T, P) = 0$$

From examination of Equation (10) it is clear that the calculation of heterogeneous equilibrium in generally constrained thermodynamic systems is essentially a problem in non-linear optimization subject to non-linear constraints. A numerical method for the solution of Equation (10) is provided in Appendix A.

**THE ADDITION OF PERFECTLY MOBILE COMPONENTS**

The necessity of modelling phase equilibria in magmatic systems open to oxygen exchange has been discussed by GHIORSO (1985), GHIORSO and CARMICHAEL (19850 and CARMICHAEL and GHIORSO (1986). This need arises out of a lack of knowledge regarding relevant oxidation-reduction couples which buffer the ferric/ferrous ratio in a crystallizing magma. For modelling purposes it is convenient to approximate the effect of these unknown homogeneous redox equilibria by specifying the chemical potential of oxygen in the system. GHIORSO (1985) formulated a solution to the minimization of the Korzhinskii potential for open system oxygen exchange by approximating the non-linear equality constraint corresponding to fixed chemical potential of oxygen in the system with an empirical linearized constraint. This formulation is adequate for many calculations, but is not an exact solution to the problem. With the algorithm discussed in Appendix A, it is possible to formulate the problem exactly.

A comprehensive expression for the chemical potential of oxygen in a magmatic liquid is provided by KILINC et al. (1983). Its value is a function of the fugacity of oxygen, temperature, pressure, the ferric/ferrous ratio in the melt and the number of moles of various liquid components. The Korzhinskii potential, which is minimized under equilibrium conditions in this open system, is given by (see above):

$$\Phi = G - n_{O_2}\mu_{O_2}. \hspace{1cm} (11)$$

We take $n_{O_2}$ to be the number of moles of oxygen produced or consumed in the course of crystallization; indexed by the relative increase or decrease in the ferric/ferrous ratio of the system necessary to maintain constant $\mu_{O_2}$. The minimum in $\Phi$ is
calculated subject to fixed $T$, $P$, $\mu_0$, and bulk composition with the provision of variable ferric/ferrous ratio. The optimal variables are the system components, $n$. Numerical methods suitable for minimizing the open system potential defined by Equation (11) are discussed in Appendix A. In Appendix B appropriate matrices and vectors needed for the minimization algorithm are derived and the results generalized to the case of the calculation of heterogeneous equilibrium in chemical systems open to oxygen and subject to isenthalpic and/or isochoric constraints.

**AN ALGORITHM FOR CHEMICAL MASS TRANSFER IN MAGMATIC SYSTEMS SUBJECT TO GENERALIZED CONSTRAINTS**

After having established the means of calculating heterogeneous equilibrium in arbitrarily constrained, open magmatic systems, we can now summarize a method for the calculation of chemical mass transfer in such systems. In isothermal, iso-baric open magmatic systems, the appropriate Korzhinskii potential is minimized at each step in reaction progress. This calculational scheme is identical to the free energy minimization method described by GHIORSO (1985). In systems subject to isochoric or isenthalpic constraints, the initial step in calculating the evolution of the system involves determining the heterogeneous phase assemblage by minimization of the Gibbs free energy or relevant Korzhinskii potential for the system. This establishes an initial "equilibrium" volume or enthalpy which can then be used to constrain the equilibrium "path" of all future steps in reaction progress. A typical calculation might involve determining the stable solid-liquid assemblage for a magma at a given temperature and pressure, and modelling isenthalpic assimilation by adding small increments of solid to the magma, keeping track of the attendant changes in system bulk composition and increase in total system enthalpy due to the added enthalpy of the solid. At each incremental step of solid addition a new equilibrium solid-liquid phase assemblage and temperature are calculated at the new system bulk composition and total enthalpy. By choosing small enough steps, the continuous irreversible process of isenthalpic assimilation can be modelled. By examination of the compositions and proportions of solid and liquid produced at each increment of reaction progress, the stoichiometry of the assimilation reaction can be determined.

Software has been designed to implement the non-linearly constrained optimization algorithm described in Appendix A in order to allow the modelling of isenthalpic, isochoric, isothermal and isobaric reactions in magmatic systems open to magmatic systems open to oxygen. This software constitutes version 2.0 of the program SILMIN (GHIORSO, 1985). Source code is available from the first author. Thermodynamic data essential for the numerical implementation of this algorithm are summarized by GHIORSO et al. (1983) and GHIORSO (1985). Some applications of these calculations in magmatic systems are presented below.

**APPLICATIONS**

Assimilation of wall rock into basaltic magma has been proposed to explain a range of chemical variation trends in igneous rock series. BOWEN (1922a) explained the basic principles for thermodynamic treatment of solid-liquid reaction in silicate systems. Few subsequent studies of interaction between magma and wall rock have taken this approach, probably due to the scarcity of data on the slope of the multi-component liquidus surface, heats of fusion of solid solutions, and heats of mixing in silicate liquids. Further investigation may also have been discouraged by BOWEN'S assertion that assimilation processes could not produce liquids fundamentally different from those produced by fractional crystallization alone. BOWEN (1922a) showed how, in the forsterite-anorthite-silaic system determined by ANDERSON (1915), assimilation of olivine in liquids could alter the crystal and liquid line of descent. However, he believed that all such phenomena were of secondary importance, because all liquids in the ternary still possess the theoretical capacity to fractionate toward the same eutectic composition. As emphasis in igneous petrology has changed from debate over the ultimate destination of liquid fractionation to explanation of the variation between different lines of descent, the potential effect of combined assimilation and crystallization has become a subject of increasing interest.

BOWEN (1922a) showed that, for the silicate systems which had been determined experimentally by 1922, heats of mixing were negligible by comparison with heats of fusion. This observation has generally been supported by recent work. Unlike the dissolution of salts in aqueous solution, which could evolve heat without consequent crystallization, the pure dissolution of silicate minerals in magma would be endothermic. Important exceptions include the heats of fusion of the silica poly-morphs $\beta$-quartz, tridymite and $\beta$-cristobalite. These enthalpies are relatively small, on the order of 30 cal/gm, in the range of estimated heats of mixing in natural silicate liquids (GHIORSO and CARMICHAEL, 1980).
In developing examples in the continuous and discontinuous reaction series (defined in Bowen, 1922b), Bowen (1922a,b) showed that the dissolution of refractory phases in liquids in equilibrium with less refractory phases in the same series, at constant temperature, causes crystallization of the phases with which the magma is saturated. This process maintains the composition of the magma on the liquidus surface; magma composition on the liquidus in a binary system is isothermally, isobarically invariant, whereas in a ternary system the composition may be univariant or invariant. In the examples given (Bowen, 1922a, pp. 523–537), the mass crystallized was calculated to be larger than the mass dissolved; Bowen (1922a) suggested that such reactions would generally be exothermic.

Similarly, Bowen (1922a) developed examples of assimilation of less refractory phases in liquids saturated with higher-temperature phases. In the examples, it was shown that the energy required to dissolve the assimilate could not normally be provided by the heat capacity of the magma, because known heats of fusion, per gram, for silicates were two or three orders of magnitude larger than liquid heat capacities, which Bowen (1922a) estimated at 0.2 to 0.3 cal/gm°C. The result of dissolving a low-temperature melting member of the reaction series, he reasoned, is a drop in temperature, followed by crystallization of a smaller mass of the phase(s) with which the magma is saturated.

Schematic illustration of these relationships is given in Figure 1. Note that the assimilation of a refractory phase in liquid saturated in a less refractory phase in the same reaction series, at constant temperature, need not always be exothermic. Instead,

\[ \Delta H = Ma\Delta H_r - Mc\Delta H_f, \]  (12)

for \( Ma \) equal to the mass assimilated, \( Mc \) equal to the mass crystallized, and \( \Delta H_r \) and \( \Delta H_f \) equal to the apparent heats of fusion, per gram, of the assimilate and the resultant crystals, respectively. Apparent heats of fusion are the heats of fusion of the solids at some temperature, \( T' \), below the melting temperature of the pure solid. They are calculated as:

\[ \Delta H_f = \Delta H_F + \int_{T'_m}^{T'} C_{P,\text{solid}}dT - \int_{T'_m}^{T'} C_{P,\text{liquid}}dT, \]  (13)

where \( \Delta H_f \) is the apparent heat of fusion at \( T' \), \( \Delta H_F \) is the heat of fusion of the pure substance at its melting temperature, \( T_m \) is the melting temperature of the pure substance, and \( C_{P,\text{solid}} \) and \( C_{P,\text{liquid}} \) are the heat capacities of pure solid and liquid over the temperature range \( T_m - T' \). The magnitude and sign

![FIG. 1. (A) Schematic representation of assimilation of a refractory phase in liquid saturated with a less refractory member of the same reaction series. Resultant crystal and liquid products are shown for the cases of isothermal and isenthalpic assimilation. (B) Similar representation, for assimilation of a less refractory phase in a liquid saturated with a member of the same reaction series, or assimilation across a cotectic "valley".](image-url)
of $\Delta H$ in Equation (12) may vary depending on the ratios $Ma/Mc$ and $\Delta H_f^p/\Delta H_f^l$.

The $\Delta H$ for assimilation of a refractory phase in a magma saturated with a phase lower in the same reaction series will often be negative, but may be very close to zero. For example, take the assimilation of magnesian olivine in a liquid saturated with low-calcium pyroxene. In the Mg$_2$SiO$_4$–SiO$_2$ system, BOWEN (1922a,b) calculated $Ma/Mc$ approximately equal to 0.2 at 1550°C. Assuming $\Delta H_f^p = 238 \text{ cal/gm}$ and $\Delta H_f^l = 186 \text{ cal/gm}$ (data on $\Delta H_f$ and liquid and solid heat capacities from ROBIE et al., 1978, STEBBINS et al., 1984, and GHIORSO and CARMICHAEL, 1980), $Ma/Mc = 0.2$ corresponds to an enthalpy change of $-138 \text{ cal per gram clino-}
$

testanite crystallized at 1550°C. In natural basaltic to andesitic liquids, KELEMEN (1986) and KELEMEN and GHIORSO (1986) calculate a range of $Ma/Mc$ for the reaction olivine + liquid = orthopyroxene; a reasonable average might be 0.6. For this reaction stoichiometry, with $\Delta H_f^p \approx 185 \text{ cal/gm}$ and $\Delta H_f^l \approx 142 \text{ cal/gm}$ at $1200^\circ \text{C}$, the enthalpy change would be close to $-31 \text{ cal per gram orthopyroxene}$ produced.

During assimilation of a less refractory phase, or assimilation of material across a cotectic “valley”, $\Delta H$ will always be positive. For instance, assimilation of diopside in liquid saturated with forsterite in the system forsterite–diopside–anorthite (OSBORN and TAIT, 1952) must be endothermic at constant temperature. The process of dissolving diopside will move the liquid off the forsterite liquidus surface. There will be no limit to the enthalpy change produced by this reaction until the liquid is saturated in diopside. Until then, $\Delta H$ will be positive, increasing by 151 cal per gram diopside dissolved ($\Delta H_f^p$ at $1300^\circ \text{C}$ from ROBIE et al., 1978; GHIORSO and CARMICHAEL, 1980; STEBBINS et al., 1984). If a reservoir of forsterite is initially present in the system, dissolution of diopside at constant temperature will lead to dissolution of forsterite as well. Note that these effects are qualitatively similar to the effects of assimilation of forsterite in liquid saturated with diopside.

If, instead of constant temperature, the system were constrained to constant enthalpy, then the temperature would drop, such that;

$$\Delta T = [Ma\Delta H] - Mc\Delta H]/M^{\text{tot}} C_p, \quad (14)$$

where $M^{\text{tot}}$ is equal to the total mass of the system and $C_p$ is the heat capacity of the system (about $0.3 \text{ cal/gm } ^\circ \text{C}$, assuming the masses of the solid phases are negligible relative to the mass of liquid). For assimilation of a less refractory phase in the same reaction series, or assimilation across a cotectic, $\Delta T$ must be less than zero. In the particular case of diopside dissolving in liquid saturated in forsterite at $1300^\circ \text{C}$, this requires $Ma/Mc$ to be greater than about 1.3, and for assimilation of forsterite in diopside saturated liquid, $Ma/Mc$ must be greater than 0.75.

The foregoing discussion applies to dissolution and consequent crystallization where the assimilate is at magmatic temperature prior to reaction. Where this is not the case, the energy required to heat the assimilate to magmatic temperature must also be included in the calculation of mass and energy balance at constant temperature or constant enthalpy. Again, BOWEN (1922a) treated this problem. He noted that the heat of crystallization of saturated phases can supply the energy needed to heat inclusions or wall rock, or both. Because heats of fusion are orders of magnitude greater than heat capacities in silicate systems, per gram, crystallization of a mass of liquid can raise the temperature of an equal mass of solids tens, or even hundreds, of degrees.

All these relations apply in principle to reactions in natural systems. However, in practice, such calculations have been limited by lack of quantitative understanding of such important variables as the slope of the liquidus surface in pressure-temperature-composition space. Development of a solution model for silicate liquids (GHIORSO et al., 1983; GHIORSO, 1985; GHIORSO and CARMICHAEL, 1985), implemented in the computer program SILLIMIN, permits investigation of solid–liquid reaction stoichiometry in natural systems (e.g., GHIORSO, 1985; KELEMEN, 1986; KELEMEN and GHIORSO, 1986).

Constant temperature may be an unreasonable constraint for assimilation of low melting phases, or assimilation of phases across a cotectic. During such exothermic reactions, magmatic temperature cannot often be externally buffered at a constant value. It is easier to understand and apply the results of calculations constrained to constant enthalpy. Isenthalpic calculations may provide a close approach to some important natural phenomena.

To illustrate the relevance of such calculations, we present the following example. In Figure 2, we have shown liquid compositions in the system forsterite–diopside–anorthite (OSBORN and TAIT, 1952), which are saturated in forsterite, and will fractionate to the forsterite–diopside cotectic. Isothermal assimilation of anorthite, on the other hand, moves the magma composition off the liquidus towards the anorthite apex, first dissolving any reservoir of forsterite in the system, until it is saturated in anorthite. Schematic, isenthalpic assimilation paths are depicted as well; given a knowledge of the
Evaluating reaction stoichiometry

heats of fusion of anorthite and forsterite, and the heat capacity of the system, combined with the lever rule, such approximate paths are simple to determine. The liquid in the isenthalpic assimilation case fractionates to the anorthite field (case 1), or to the forsterite–anorthite cotectic (case 2), with decreasing temperature. At points C1 and C2 (Figure 2), the liquid will not dissolve further anorthite added to the system; its composition and temperature will remain constant.

Figure 3 and Table 1 illustrate some of the results of a similar calculation, by using a natural system: a magnesian MORB, FAMOUS 527-1-1 (BENDER et al., 1978) plus 2 weight percent H$_2$O at 1 kbar, constrained to react along the FMQ oxygen buffer. This wet basalt is calculated to crystallize olivine, beginning at about 1223°C, followed by clinopyroxene at about 1165°C, and plagioclase (An$_7$) at about 1095°C. Isenthalpic assimilation of anorthite ($T_{\text{solid}} = 1225$°C) in this basalt, beginning at 1225°C, leads to a decrease in temperature, accompanied by crystallization of olivine beginning at about 1208°C, and plagioclase (An$_{87}$) at 1162°C. The calculated temperature then rises, as continued assimilation of anorthite results in the precipitation of a larger mass of increasingly calcic plagioclase. The total mass of solids produced in the temperature interval 1225 to 1165°C is much greater in the equilibrium crystallization calculation than in the case of isenthalpic assimilation of anorthite.

In order to test the notion that isenthalpic assimilation of more refractory phases in crystallizing magma might be similar in its effect to isothermal assimilation, we compared the two paths for assimilation of magnesian olivine in FAMOUS 527-1-1, dry, at 3 kbar, evolving along the FMQ oxygen buffer. Results are summarized in Figure 4 and Table 2. Resultant crystal and liquid compositions are almost identical in the isothermal and isenthalpic cases. In both cases, dissolution of olivine (Fo$_{90}$) leads to crystallization of a slightly larger mass of more iron–rich olivine, accompanied by a small percentage of plagioclase in the isothermal case. Resultant liquid and solid compositions, phase proportions, and temperatures in the isenthalpic case, are calculated. Initial temperature of the liquid, and the temperature of the assimilate throughout the calculation, was set at 1225°C.
Table 1. Calculated total solid composition produced during the assimilation of anorthite in FAMOUS 527-1-1 + 2 weight percent H₂O, 1 kbar, on the FMQ oxygen buffer.

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Isothermal</th>
<th>Isenthalpic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Assimilated/100 gm initial liquid + crystals</td>
<td>0</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Initial Temperature of Anorthite</td>
<td>—</td>
<td>1225°C</td>
<td>1225°C</td>
</tr>
<tr>
<td>Total Mass Crystallized (gm)</td>
<td>0</td>
<td>0</td>
<td>10.72</td>
</tr>
<tr>
<td>Mass Olivine (gm)</td>
<td>0</td>
<td>0</td>
<td>2.11</td>
</tr>
<tr>
<td>Mol Fraction Fo</td>
<td>0</td>
<td>0</td>
<td>0.82</td>
</tr>
<tr>
<td>Mass Plagioclase</td>
<td>0</td>
<td>0</td>
<td>8.61</td>
</tr>
<tr>
<td>Mol Fraction An</td>
<td>0</td>
<td>0</td>
<td>0.88</td>
</tr>
<tr>
<td>Temperature of the System</td>
<td>1225°C</td>
<td>1225°C</td>
<td>1164°C†</td>
</tr>
</tbody>
</table>

* 0.27 gm Fo92 @ 1220°C.
† Minimum temperature @ 1162°C, 32 gm assimilated with 2.36 gm Fo92 and 0.43 gm An87 crystallized.

has an important effect on the liquid line of descent, because the conversion of Fo90 to Fo97 fractionates FeO from the magma, effectively buffering the magnesium number (Mg#) of the derivative liquid. Similar reactions between high temperature wall rock and fractionating basalt in the upper mantle are likely. Their effects are more fully discussed by KELEMEN (1986).

Initial temperature of the assimilate is the most important variable in considering the potential effects of assimilation of wall rock by magmas in the crust. Although the notion of assimilation of low melting pelitic or quartzo-feldspathic metasediments, or both, in high temperature, basaltic melts has an immediate, intuitive appeal, this process is strongly endothermic and cannot be viewed simply as bulk melting and mixing of a crustal component. To illustrate this point, already made on semi-quantitative grounds by BOWEN (1922a), we have made calculations modelling the assimilation of pure albite, and a composite pelitic composition, in a magnesian MORB.

The initial liquid composition used was FAMOUS 527-1-1, dry, at 3 kbar, constrained to react along the FMQ oxygen buffer, at an initial temperature of 1250°C. We first compare the predicted equilibrium crystallization path for this liquid to the experimental results of BENDER et al. (1978) on this composition. Results of calculations using SILMIN have olivine (Fo97) on the liquidus at 1290°C, followed by plagioclase (An85) at 1245°C, and clinopyroxene (Di85) at 1235°C. Comparable values from the experiments at 1 bar are olivine (Fo98.5) at 1268°C, and plagioclase (An89) at 1235°C. At 6 kbar, olivine (Fo87) appears at 1280°C, followed by plagioclase (An78) at 1240°C. Clinopyroxene first crystallized between 1135 and 1150°C, at 1 bar, and between 1240 and 1250°C, at 6 kbar. Low-calcium pyroxene was not observed in any experimental runs.

Three different reaction paths were modelled: (1) isothermal assimilation, with the solid assimilate at 1250°C (a metastable solid state, at least in the case of albite); (2) isenthalpic assimilation, with the assimilate at 1250°C; and (3) isenthalpic assimilation
Evaluating reaction stoichiometry

Table 2. Calculated total solid composition produced during the assimilation of olivine (Fo\textsubscript{90}) in FAMOUS 527-1-1, at 3 kbar, on the FMQ oxygen buffer.

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Isothermal</th>
<th>Isenthalpic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Assimilated/100 gm initial liquid + crystals</td>
<td>0</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Initial Temperature of Olivine</td>
<td>1250°C</td>
<td>1250°C</td>
<td>1250°C</td>
</tr>
<tr>
<td>Total Mass Crystallized (gm)</td>
<td>3.44</td>
<td>50.55</td>
<td>46.44</td>
</tr>
<tr>
<td>Mass Olivine (gm)</td>
<td>3.44</td>
<td>47.71</td>
<td>46.44</td>
</tr>
<tr>
<td>Mol Fraction Fo</td>
<td>0.867</td>
<td>0.863</td>
<td>0.866</td>
</tr>
<tr>
<td>Mass Plagioclase</td>
<td>0</td>
<td>2.84</td>
<td>0</td>
</tr>
<tr>
<td>Mol Fraction An</td>
<td>0.823</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of the System</td>
<td>1250°C</td>
<td>1250°C</td>
<td>1253.5°C</td>
</tr>
</tbody>
</table>

with the assimilate at 500°C. In modelling assimilation of pelitic rock, we used a bulk composition derived by averaging the group analyses for shale and slate reported by CLARKE (1924). This composition was recast as proportions of two mineral assemblages: assemblage A (quartz–K feldspar–ilmenite–orthopyroxene–spinel–plagioclase), representative of pelitic rocks in granulite and pyroxene hornfels facies; and assemblage B (quartz–muscovite–ilmenite–biotite–garnet–plagioclase), representative of pelitic rocks in amphibolite facies. Thermodynamic data for most of these solid phases are summarized by GHIORSO et al. (1983) and constitutes part of the SILMIN data base. Data for muscovite, phlogopite, annite, pyrope, and almandine are from HELGESON et al. (1978). Note that the phase assemblages are somewhat arbitrary. For instance, under most conditions, spinel + quartz break down to orthopyroxene + aluminosilicate. However, by use of spinel rather than sillimanite was more convenient for computational reasons. Similarly, all iron has been arbitrarily assumed to be ferrous iron. The bulk composition used and the proportions of mineral end-members are given in Table 3.

Some of the results of modelling assimilation of albite and pelitic rock are given in Figures 5, 6, and 7 and Tables 4 and 5. Figures 5 and 6 summarize

Table 3. Pelitic composition used in assimilation calculations. This composition was derived by averaging the group analyses for shale and slate reported by CLARKE (1924, pp. 552 and 631) H\textsubscript{2}O, CO\textsubscript{2}, SO\textsubscript{2}, C\textsubscript{1}, P\textsubscript{2}O\textsubscript{5} and trace components in the analyses were ignored; other oxides normalized to 100 weight percent.

<table>
<thead>
<tr>
<th>Bulk composition</th>
<th>Weight percent</th>
<th>Phase assemblage A</th>
<th>Mol percent</th>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>64.463</td>
<td>Hercynite</td>
<td>Hc\textsubscript{58}</td>
<td>4.94</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>0.731</td>
<td>Spinel</td>
<td>Sp\textsubscript{42}</td>
<td>2.93</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>17.107</td>
<td>Enstatite</td>
<td>En\textsubscript{46}</td>
<td>4.80</td>
</tr>
<tr>
<td>FeO*</td>
<td>6.691</td>
<td>Ferrosilite</td>
<td>Fs\textsubscript{54}</td>
<td>7.33</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>17.107</td>
<td>Sanidine</td>
<td>Sanidine</td>
<td>21.02</td>
</tr>
<tr>
<td>CaO</td>
<td>3.105</td>
<td>Albite</td>
<td>Al\textsubscript{b} \textsubscript{48}</td>
<td>13.48</td>
</tr>
<tr>
<td>MgO</td>
<td>2.754</td>
<td>Anorthite</td>
<td>An\textsubscript{52}</td>
<td>15.40</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>1.593</td>
<td>Ilmenite</td>
<td>Ilm</td>
<td>28.72</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>3.556</td>
<td>Phase assemblage B</td>
<td>Alm\textsubscript{61}</td>
<td>1.39</td>
</tr>
<tr>
<td>Phase assemblage B also includes 1.35 weight percent H\textsubscript{2}O in biotite and muscovite.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Phase assemblage B | |
|-------------------||
| Phase assemblage B | Almandine | Alm\textsubscript{61} | 3.66 |
| Pyrope | Py\textsubscript{39} | 1.92 |
| Phlogopite | Phl\textsubscript{47} | 7.20 |
| Annite | An\textsubscript{53} | 10.19 |
| Muscovite | Mus | 14.01 |
| Albite | Alb| 13.48 |
| Anorthite | An\textsubscript{52} | 15.40 |
| α-Quartz | α-Quartz | 32.75 |
| Ilmenite | Ilm | 1.39 |
FIG. 5. (A) Calculated total solid composition for isothermal and isenthalpic assimilation of albite in a magnesian MORB (FAMOUS 527-1-1), dry, at 3 kbar, on the FMQ oxygen buffer. Initial temperature of the liquid, and the temperature of the assimilate throughout the calculation, was set at 1250°C. Ma/Mc refers to the ratio of mass assimilated vs. mass crystallized. (B) Input parameters as in 5(A), but with the temperature of the assimilate set at 500°C throughout the calculation.

calculated solid compositions. Note that the vertical scale (cumulative mass crystallized) is ten times as large for reaction with the assimilate at 500°C than for reaction with the assimilate at 1250°C. Whereas isenthalpic assimilation of 40 grams of albite and pelitic rock at 1250°C have been calculated to produce less than 10 grams of olivine and plagioclase, isenthalpic dissolution of the same two phase assemblages at 500°C is predicted to result in crystallization of almost 100 grams of plagioclase and pyroxene. This difference results entirely from the energy requirements of heating the assimilate to magmatic temperatures. Dissolution of the high temperature solids leads to a decrease of 35 to 40°C in the temperature of the system. Dissolution of the 500°C solids leads to a decrease of 70 to 80°C.

It is also important to consider the differences between assimilation of pelitic phase assemblages A and B, both at 500°C. Phase assemblage A might be thought of as a granulite facies rock which cooled to 500°C after the peak of metamorphism. Phase assemblage B, characteristic of pelitic rocks in amphibolite facies, includes muscovite and biotite. Equilibrium dissolution of these hydrous minerals in fluid undersaturated magma saturated with olivine, pyroxenes, and plagioclase, can be thought of as a combination of three discrete steps: (1) dehydration reactions (such as biotite + 3 muscovite = 4 Kspar + 3 spinel + 4 H₂O); (2) melting of the dehydrated solid phases; and (3) solution of the new melt, plus H₂O, in the assimilating magma. Because dehydration reactions, like melting reactions, are endothermic at crustal pressures, the apparent enthalpy of fusion of a hydrous assemblage will generally be larger than the apparent enthalpy of fusion of an equivalent anhydrous assemblage.

We reasoned that isenthalpic assimilation of a phase assemblage including muscovite and biotite would result in a larger temperature drop, per gram assimilated, and thus (at the same bulk composition) more crystallization from the derivative liquid, compared to assimilation of an assemblage with Kspar and spinel replacing the hydrous phases. However, this hypothesis did not account for the actual difference in bulk compositions between phase assemblages A and B: assemblage B contains 1.35 weight percent H₂O. Addition of H₂O to the magma has the general effect of suppressing crystallization. Our calculations illustrate this effect. Although assimilation of the hydrous assemblage B results in a larger temperature drop, per gram assimilated, it produces a smaller mass of crystals than assimilation of the anhydrous assemblage A.

This observation is not a general one. If the initial magma composition prior to assimilation includes a few weight percent H₂O, solution of a small amount of H₂O in the assimilate does not affect the course of reaction very much. Under these circum-
Fig. 6. Calculated total solid composition for isothermal and isenthalpic assimilation of pelitic rock in a magnesian MORB (FAMOUS 527-1-1), dry, at 3 kbar, on the FMQ oxygen buffer. Composition and phase assemblages of the pelitic assimilate are given in Table 3. Phase assemblages A and B have identical bulk composition (except that B includes 1.35 weight percent H₂O), but A is composed of Qtz-Ilm-Kspar-Opx-Spinel-Plag, whereas B is composed of Qtz-Ilm-Musc-Bio-Garnet-Plag. Figure 6(A). Initial

Fig. 7. Calculated liquid composition for isothermal and isenthalpic assimilation of pelitic rock in a magnesian MORB. Input parameters as for Figure 6(A) and (B).

stances, assimilation of a hydrous assemblage will result in a lower final temperature and a larger mass of crystals than assimilation of the same mass of an equivalent anhydrous assemblage.

The different reaction paths for assimilation of pelitic rock result in markedly different liquid compositions, as illustrated in Figure 7 and Table 6. Liquids produced by isenthalpic assimilation of temperature of the liquid, and the temperature of the assimilate throughout the calculation, was set at 1250°C. Ma/Mc refers to the ratio of mass assimilated vs. mass crystallized. Figure 6(B). Input parameters as in 6(A), but with the temperature of the assimilate set at 500°C throughout the calculation.
pelitic rock at an initial temperature of 500°C diverge from those produced by assimilation of the same composition at 1250°C early in their fractionation history, becoming strongly iron–enriched and alkaline. Whereas the other two cases show continuously increasing silica contents in derivative liquids, the assimilation of “cold” pelitic rock undergoes a decrease in silica content beginning with the appearance of orthopyroxene on the liquidus, as a result of the reaction olivine + SiO$_2$(liq) = orthopyroxene. Note that this reaction, which is discontinuous in the Mg$_2$SiO$_4$–SiO$_2$ system, is a continuous reaction occurring over a finite temperature interval in iron–bearing systems. An increase in SiO$_2$ concentration in the liquid resumes with the disappearance of olivine from the system.

These calculations have been done in equilibrium mode; that is, the total solid composition is in equilibrium with the liquid at every step. If the calculations were performed in fractional crystallization mode, the discontinuous reaction would be limited to a single step (in this case, defined by the addition
Evaluating reaction stoichiometry

Table 6. Calculations of crystal fractionation, assimilation of pelitic rock at 500°C, and assimilation of albite at 500°C, in FAMOUS 527-1-1, at 3 kbar, on the FMQ oxygen buffer. Composition and phase assemblages for pelitic assimilate are given in Table 3.

<table>
<thead>
<tr>
<th>Crystal fractionation</th>
<th>Isenthalpic assimilation (assimilate at 500°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pelitic</td>
</tr>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Weight percent SiO₂</td>
<td>48.0</td>
</tr>
<tr>
<td>Weight percent MgO/(MgO + FeO*) FeO* = total Fe as FeO</td>
<td>0.30</td>
</tr>
<tr>
<td>Na₂O + K₂O weight percent</td>
<td>2.41</td>
</tr>
<tr>
<td>Gm Assimilated</td>
<td>0</td>
</tr>
<tr>
<td>Gm Crystallized</td>
<td>77</td>
</tr>
<tr>
<td>Temp °C</td>
<td>1190</td>
</tr>
<tr>
<td>Gm Assimilated/°C</td>
<td>0</td>
</tr>
<tr>
<td>Mass Liquid/Initial Mass Liquid</td>
<td>0.21</td>
</tr>
</tbody>
</table>

of 2 grams of pelitic rock, and the calculated silica content of the liquid would not decrease over a long interval of assimilation. However, derivative liquids would still be far more iron-enriched and alkaline than those produced by reaction with a wall rock already at magmatic temperature.

Table 6 allows further comparison of the liquid compositions produced by assimilation of wall rock at 500°C. This comparison makes it abundantly clear that calculation of the effect of assimilation on derivative liquids demands accurate characterization of the bulk composition and the phase assemblage of the assimilate, as well as the temperature of both wall rock and magma. It is also instructive to compare the calculated liquid and solid lines of descent for isenthalpic assimilation with those calculated for equilibrium or fractional crystallization alone. Whereas some of the liquids produced by assimilation have almost the same Mg# as the liquids produced by crystal fractionation alone, all the liquids derived by assimilation are relatively rich in silica and alkalies.

Neither the equilibrium nor fractional crystallization of FAMOUS 527-1-1 were calculated to produce orthopyroxene at 1190°C. The total solid composition resulting from equilibrium crystallization at this temperature is 22 weight percent olivine (Fo73), 23 weight percent clinopyroxene (Di83), and 55 weight percent plagioclase (An65). The assimilation of pelitic assemblage A leads to a predicted solid composition with 29 weight percent orthopyroxene (En78), 16 weight percent clinopyroxene (Di83), and 55 weight percent plagioclase (An65) at 1190°C. Similar phase proportions were calculated for assimilation of pelitic assemblage B. This is in partial accord with Bowen's prediction (1922a, pp. 549–558) that the assimilation of aluminous sediment in basaltic magma would increase the modal proportion of orthopyroxene and plagioclase, and decrease the proportion of clinopyroxene, produced during crystallization.

CONCLUSIONS

Assimilation of wall rock in fractionating magma may fundamentally alter the solid and liquid line of descent, producing various distinctive magma series, all derived from a common parental liquid. Thermodynamic modelling of such processes is essential in predicting solid–liquid reaction stoichiometry, and thus the compositional effects of such reactions on derivative liquids and solids. Constant temperature assimilation of refractory solids in liquids saturated in less refractory members of the same “reaction series” will often be exothermic. Assimilation of less refractory phases in the same reaction series, and assimilation of phases across a cotectic “valley”, will always be endothermic at constant temperature. Particularly for endothermic reactions, modelling of isenthalpic, rather than isothermal, conditions may yield results more generally applicable to natural phenomena. Also useful, though not explicitly presented here, are calculations based on externally controlled conditions of decreasing temperature.

The sample calculations presented here reemphasize the point made by Bowen (1922a) that the most important variable in the energy balance of reaction between magma and wall rock, besides bulk composition, is the temperature difference between the two. Assimilation of solids with the same composition, but different initial temperatures, is cal-
Acknowledgements—We would like to acknowledge material support from NSF and the termination of the phase proportions, phase com-
appendix; . . . more matter with less . . .

The ability to model isenthalpic crystallization in magmatic systems may also prove useful in the numerical simulation of the cooling history of magma bodies. In the past, substantial difficulty has been encountered in modelling the thermal history of “real” magmatic systems due, in part, to the ne-
cessity of knowing the temporal and spatial depen-
dence of the enthalpy of fusion of the magma in order to calculate the evolving temperature field. These enthalpies of fusion are dependent upon the extent of crystallization and consequently, the tem-
perature of the magma. Thus magma chamber cooling models must be solved iteratively if they involve realistic parameterizations of the enthalpies of fusion of the solid phases. With the ability to determine heterogeneous equilibrium under isenthalpic constraints, an alternative method of calculation exists. If temperature and phase proportions can be calculated given a fixed enthalpy content of the magma at any given time or point in space, then knowledge of the heat flux and the geo-
metry of the chamber will allow simultaneous de-
termination of the phase proportions, phase com-
positions and temperature field in the cooling magma body. Such calculations need not be per-
formed recursively and are amenable to inclusion in more traditional fluid dynamical models of magma dynamics.

REFERENCES

ANDERSON O. (1915) The system anorthite–forsterite–sil-


CARMICHAEL I. S. E. and GHIORSO M. S. (1986) Oxida-
tion–reduction relations in basic magma: a case for ho-

geneous equilibria. Earth Planet. Sci. Lett. 78, 200–


GHIORSO M. S. (1985) Chemical mass transfer in magmatic processes I. Thermodynamic relations and nu-


GHIORSO M. S. and CARMICHAEL I. S. E. (1980) A regular solution model for mea-aluminous silicate liquids: Ap-


GHIORSO M. S., CARMICHAEL I. S. E., RIVERS M. L. and SACK R. O. (1983) The Gibbs Free Energy of natural silicate liquids; an expanded regular solution approxi-
mation for the calculation of magmatic intensive vari-


HELGESON H. C., DELANY J. M., NESBITT H. W. and BIRD D. K. (1978) Summary and critique of the ther-


KELEMEN P. B. and GHIORSO M. S. (1986) Assimilation of peridotite in zoned calc-alkaline plutonic complexes: evidence from the Big Jim Complex, Washington Cas-


KORZHINSKII D. S. (1959) Physiochemical Basis of the Analysis of the Paragenesis of Minerals. 142 pp. Con-

sultants Bureau.


APPENDIX A NUMERICAL METHODS FOR MINIMIZING $\Phi$

We seek solutions (optimal values of $n$ and possibly temperature $(T)$ and pressure $(P)$) to the following problem in non-linear optimization:

\[
\text{minimize} \quad \Phi(x, y, n) \\
\text{such that} \\
Cn - b = 0 \\
\Delta x(n, T, P) = 0 \\
\text{and} \\
\Delta y(n, T, P) = 0. \\
\tag{A1}
\]

We will let the vector $z$ denote all the variables being optimized in the minimization of $\Phi$. $z$ may contain the elements of $n$ as well as $T$ and $P$. The last two equality constraints ($\Delta x = 0$, $\Delta y = 0$) are non-linear, so the usual minimization method of projecting with the constraint matrix and solving the unconstrained quadratic sub-problem (GHORSO, 1985) fails. Instead, the suggestion of GILL et al. (1981) will be followed and the unconstrained related Lagrange function corresponding to Equation (A1) will be optimized. We denote the Lagrangian of $\Phi$ by $Z$ and define it such that

\[
Z(x, y, n, \lambda_n, \lambda_x, \lambda_y) = \Phi - \lambda_n(Cn - b) - \lambda_x\Delta x - \lambda_y\Delta y. \\
\tag{A2}
\]

The new variables $\lambda_n$, $\lambda_x$, and $\lambda_y$ are generally referred to as Lagrange multipliers. The minimum of $Z$ is obtained iteratively by seeking steps, $s$, away from an initial non-optimal, but feasible guess to the solution vector of Equation (A1), which we will denote $z_o$, and stepping along this direction while continuously maintaining the feasibility of the solution parameters. In this problem, feasible parameters refer to the set of solutions that satisfy the constraints. To define the search direction $s$ we construct a vector $c$ such that

\[
c = \begin{bmatrix} 
Cn - b \\
\Delta x(n, T, P) \\
\Delta y(n, T, P)
\end{bmatrix}
\]

and define a matrix, $A$, which represents the derivative of this vector of equality constraints with respect to the optimal variables. $A$ is commonly referred to as the Jacobian of the system of non-linear constraints and should be evaluated at the initial feasible point, $z_o$. Thus,

\[
A = \left( \frac{dc}{dz} \right)_{z_o} = \begin{bmatrix} C^T \\
\frac{\partial x}{\partial z} \bigg|_{z_o} \\
\frac{\partial y}{\partial z} \bigg|_{z_o}
\end{bmatrix}.
\]

A matrix, $Z$, can be computed from the orthogonal decomposition of $A$ (GILL et al., 1981), which projects the optimal parameters of $\Phi$ into the null-space of the quality constraints. Unlike linearly constrained optimization, this null-space projection operator is only reliable "close" to the initial feasible guess $z_o$. An approximation, $Z_p$, to the feasible search direction, $s$, is computed by solving the quadratic (second order) Newton approximation to the minimum of the Lagrangian:

\[
Z^T W Z p = -Z^T g. \\
\tag{A3}
\]

The vector, $g$, is defined as the gradient of the original potential function [Equation (A1)] with respect to the optimal variables, $z$, evaluated at the initial feasible point, and the matrix $W$ is defined as the second derivative matrix of the Lagrangian [Equation (A2)] with respect to the optimal variables and evaluated at the initial feasible point. This matrix is often referred to as the Hessian matrix of the Lagrangian function, $Z$. The Lagrange multipliers which are needed to compute the matrix, $W$, are estimated by solving the system of linear equations:

\[
g = A^T \begin{bmatrix} \lambda_n \\
\lambda_x \\
\lambda_y
\end{bmatrix}.
\]

The descent direction, $Zp$, obtained from Equation (A3), may not be feasible because of the non-linearity of the quality constraints. Thus the new feasible guess to the solution of Equation (A1), which we will denote $z_o + s$, is found by determining the value of the steplength parameter, $\gamma$, which minimizes the potential, $\Phi$, along the search direction, $s$, subject to maintaining the feasibility of the non-linear constraints; the linear constraints are implicitly maintained by the null-space operator, $Z$. This feasibility is guaranteed by solving, for every proposed value of $\gamma$, the system of non-linear equations

\[
\Delta x(z_o + \gamma Zp + Yp) = 0,
\]
and
\[ \Delta y(z_0 + \gamma Zp + Yp_i) = 0, \]  
(Eq. A4)
for the elements of the vector, \( p_i \). The search direction, \( s \), is defined as \( \gamma Zp + Yp_i \), where \( Y \) is a matrix which spans the range-space of \( A \) and \( p_i \) is a vector whose length is equal to the total number of equality constraints. \( Y \) may be taken to be \( A^T \) (GILL et al., 1981) which emphasizes that the range-space describes the space of feasible solutions to Equation (A1). The \( p_i \) obtained from the solution of Equation (A4) have no particular physical significance except insofar as their non-zero values indicate the sensitivity of the system of equality constraints to the optimal solution parameters about the initial feasible point.

The minimum of the potential function, \( \Phi \), is determined by solving successive quadratic approximations to the Lagrangian [Equations (A3) and (A4)] until the computed norm of the feasible step direction, \( s \), is smaller than machine precision. This minimum is verified by examining the sufficient conditions to insure convergence. These are (1) The equality constraints are satisfied; (2) The norm of the projected gradient is approximately zero \( (Z^T g \approx 0) \); and (3) The projected Hessian of the Lagrangian function \( (Z^T W Z) \) is positive definite.

For the convenience of the reader appropriate expressions are provided below for the quantities, \( g \) and \( W \) in the three explicit cases of the potential, \( \Phi \), discussed in the text.

The isenthalpic case \( (\Phi = -S) \)
In this case the optimal variables are the system components, \( n \) and the temperature, \( T \). The first derivative of \( \Phi \) is given by the partitioned vector:
\[ g = \begin{bmatrix} \frac{\partial S}{\partial n} \bigg|_{T,P} \\ \frac{\partial H}{\partial n} \bigg|_{T,P} \\ -\frac{C_P}{T} \end{bmatrix} \]  
(Eq. A5)
evaluated at \( n_0 \) and \( T_0 \). The Jacobian of the system of equality constraints may be written:
\[ A = \begin{bmatrix} C^T & 0 \\ \left( \frac{\partial H}{\partial n} \right)_{T,P} & C_P \end{bmatrix}. \]  
(Eq. A6)
The elements of this matrix should be evaluated at \( n_0 \) and and \( T_0 \). The second derivative of the associated Lagrangian is provided by the partitioned symmetrix matrix:
\[ W = \begin{bmatrix} \frac{\partial^2 S}{\partial n^2} \bigg|_{T,P} & -\lambda \left( \frac{\partial^2 H}{\partial n^2} \right)_{T,P} & \left( \frac{1}{T + \lambda} \right) \left( \frac{\partial C_P}{\partial n} \right)_{T,P} \\ -\lambda \left( \frac{\partial^2 H}{\partial n^2} \right)_{T,P} & \frac{1}{T + \lambda} \left( \frac{\partial C_P}{\partial n} \right)_{n,P} + \frac{C_P}{T^2} \\ \frac{1}{T + \lambda} \left( \frac{\partial C_P}{\partial T} \right)_{n,P} + \frac{C_P}{T^2} \end{bmatrix}. \]  
(Eq. A7)
The elements of this matrix should be evaluated at \( n_0 \) and \( T_0 \).

The isochoric case \( (\Phi = A) \)
For the case of constant volume, the optimal variables are the system components, \( n \) and the pressure, \( P \). The gradient of \( \Phi \) is given by the partitioned vector:
\[ g = \begin{bmatrix} \frac{\partial G}{\partial n} \bigg|_{T,P} - P \left( \frac{\partial V}{\partial n} \right)_{T,P} \\ -P \left( \frac{\partial V}{\partial P} \right)_{T,n} \end{bmatrix} \]  
(Eq. A8)
evaluated at \( n_0 \) and \( P_0 \). The derivative matrix of the equality constraints is provided by:
\[ A = \begin{bmatrix} C^T & 0 \\ \left( \frac{\partial V}{\partial n} \right)_{T,P} & \left( \frac{\partial V}{\partial P} \right)_{T,n} \end{bmatrix}. \]  
(Eq. A9)
This matrix should be evaluated at \( n_0 \) and \( P_0 \). The Hessian matrix of the Lagrangian is given by the symmetric partitioned matrix:
Evaluating reaction stoichiometry

\[
W = \begin{bmatrix}
\left( \frac{\partial^2 G}{\partial n^2} \right)_{T,P} - (P + \lambda) \left( \frac{\partial^2 V}{\partial n^2} \right)_{T,P} & \frac{\partial V}{\partial n} \frac{\partial P}{\partial n} \\
\frac{\partial V}{\partial T} & -\left( \frac{\partial V}{\partial P} \right)_{n,T}
\end{bmatrix}
\]

(A10)

This matrix should be evaluated at \( n_0 \) and \( P_0 \).

The isenthalpic and isochoric case (\( \Phi = -S - PV/T \))

In this most complicated example, the optimal variables are the system components, \( n \), the temperature, \( T \) and the pressure, \( P \). The gradient of \( \Phi \) is given by the partitioned vector:

\[
g = \begin{bmatrix}
-\left( \frac{\partial S}{\partial n} \right)_{T,P} - P \left( \frac{\partial V}{\partial n} \right)_{T,P} \\
-\frac{C_p}{T} + \frac{VP}{T^2} - \frac{P}{T} \left( \frac{\partial V}{\partial T} \right)_{n,P} \\
\end{bmatrix}
\]

(A11)

evaluated at the initial point \( n_0 \), \( T_0 \) and \( P_0 \). The derivative matrix of equality constraints is provided by:

\[
A = \begin{bmatrix}
C_P & V - T \left( \frac{\partial V}{\partial T} \right)_{P,n} \\
\left( \frac{\partial H}{\partial n} \right)_{T,P} & C_P \\
\left( \frac{\partial V}{\partial T} \right)_{T,P} & \left( \frac{\partial V}{\partial n} \right)_{T,P}
\end{bmatrix}
\]

(A12)

This matrix should be evaluated at \( n_0 \), \( T_0 \) and \( P_0 \). The symmetric second derivative matrix of the Lagrangian is given by:

\[
W = \begin{bmatrix}
W_{n,n} & W_{n,T} & W_{n,P} \\
W_{T,n} & W_{T,T} & W_{T,P} \\
W_{P,n} & W_{P,T} & W_{P,P}
\end{bmatrix}
\]

(A13)

where

\[
W_{n,n} = \left( \frac{\partial^2 S}{\partial n^2} \right)_{T,P} - \lambda_T \left( \frac{\partial^2 H}{\partial n^2} \right)_{T,P} - \left( \frac{P}{T} + \lambda_T \right) \left( \frac{\partial^2 V}{\partial n^2} \right)_{T,P}
\]

(A14)

\[
W_{n,T} = -\left( \frac{1}{T} + \lambda_T \right) \left( \frac{\partial C_p}{\partial n} \right)_{T,P} + \frac{P}{T} \left( \frac{\partial V}{\partial n} \right)_{T,P} - \left( \frac{P}{T} + \lambda_T \right) \left( \frac{\partial^2 V}{\partial n^2} \right)_{T,P}
\]

(A15)

\[
W_{n,P} = -\left( \frac{1}{T} + \lambda_T \right) \left( \frac{\partial V}{\partial n} \right)_{T,P} (1 + \lambda_T) \left( \frac{\partial^2 V}{\partial n \partial T} \right)_{n,P} - \left( \frac{P}{T} + \lambda_T \right) \left( \frac{\partial^2 V}{\partial n \partial P} \right)_{n,P}
\]

(A16)

\[
W_{T,P} = \frac{C_p}{T^2} - \frac{2VP}{T^2} + \frac{P}{T^2} \left( \frac{\partial V}{\partial T} \right)_{n,P} - \left( \frac{1}{T} + \lambda_T \right) \left( \frac{\partial C_p}{\partial T} \right)_{n,P} - \left( \frac{P}{T} + \lambda_T \right) \left( \frac{\partial^2 V}{\partial T^2} \right)_{n,P}
\]

(A17)

\[
W_{T,T} = \left( 1 + \lambda_T \right) \left( \frac{\partial^2 V}{\partial T^2} \right)_{n,P} - \frac{V}{T^2} + \left( \lambda_T + \frac{1}{T} \right) \left( \frac{\partial V}{\partial T} \right)_{n,P} + \left( \frac{P}{T^2} \left( \frac{\partial V}{\partial P} \right)_{n,T} - \left( \frac{P}{T} + \lambda_T \right) \left( \frac{\partial^2 V}{\partial T \partial P} \right)_{n,P}
\]

(A18)

and

\[
W_{P,P} = \left( 1 + \lambda_T \right) \left( \frac{\partial^2 V}{\partial P^2} \right)_{n,T} - \lambda_T \left( \frac{\partial V}{\partial T} \right)_{n,T} - \left( \frac{P}{T} + \lambda_T \right) \left( \frac{\partial^2 V}{\partial T^2} \right)_{n,T}
\]

(A19)

Equations (A14)–(A19) should be evaluated at the point \( n_0 \), \( T_0 \) and \( P_0 \).
APPENDIX B HETEROGENEOUS EQUILIBRIUM IN OPEN SYSTEMS SUBJECT TO GENERALIZED THERMODYNAMIC CONSTRAINTS

The gradient necessary for the minimization of the potential $\Phi$ given by Equation (11) is:

$$g = \left( \frac{\partial G}{\partial n} \right)_{T,P} - \left( \frac{\partial n_0}{\partial n} \right)_{T,P} \mu_0 - \left( \frac{\partial \mu_0}{\partial n} \right)_{T,P} .$$

(B1)

The derivative of the constraint matrix is provided by:

$$A = \begin{bmatrix} C^* T \\ \frac{\partial \mu_0}{\partial n} \\ \frac{\partial \mu_0}{\partial T} \\ \frac{\partial \mu_0}{\partial P} \end{bmatrix}_{T,P}$$

(B2)

where $C^*$ represents a linear bulk composition constraint matrix modified for constancy of total iron and variable ferric/ferrous ratio. The Hessian matrix of Equation (11) may be written:

$$W = \left( \frac{\partial G}{\partial n^2} \right)_{T,P} - 2 \left( \frac{\partial G}{\partial n} \right)_{T,P} \left( \frac{\partial \mu_0}{\partial n} \right)_{T,P} - \left( n_0 + \lambda_0 \left( \frac{\partial^2 \mu_0}{\partial n^2} \right) \right)_{T,P} .$$

(B3)

Equations (B1) through (B3) should be evaluated at the initial feasible point $n_0, T_0, P_0$. The potentials defined by Equations (6), (7) and (8) can be transformed to allow for the modelling of isenthalpic and isochoric processes in magmatic systems open to oxygen. We will illustrate the most complicated case. The “isenthalpic/isochoric” potential defined by Equation (8) can be modified for open systems by recognizing that:

$$\left( \frac{\partial G}{\partial \mu_0} \right)_{T} = \mu_0$$

from which a new open system potential, $\Phi$, can be defined as:

$$\Phi(H,V,n) = \frac{G}{T} - \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_{P,n} - \frac{P}{T} \left( \frac{\partial G}{\partial P} \right)_{T,n} - \frac{n_0}{T} \left( \frac{\partial G}{\partial n_0} \right)_{T,P,n} - \frac{\mu_0}{T} \left( \frac{\partial G}{\partial \mu_0} \right)_{T,P,n}$$

$$= \frac{G}{T} - \frac{1}{T} H - \frac{V}{T} \frac{n_0}{T} \mu_0$$

$$\Phi(H,V,n) = -S - \frac{VP}{T} - \frac{n_0 \mu_0}{T} .$$

(B4)

The optimal variables of this new potential $\Phi$ are $n, T$ and $P$; the oxygen chemical potential constraint does not introduce new optimal variables and only modifies the relationships among the elements of $n$. If $g$ and $W$ denote the gradient and Hessian defined by Equations (A11) and (A13), then the gradient of Equation (B4) is defined by:

$$g_{(B4)} = g + \begin{bmatrix} \frac{\partial G_0}{\partial T} \\ \frac{\partial G_0}{\partial n} \end{bmatrix}$$

(B5)

where, given that $G_0 = n_0 \mu_0$, we have;

$$g_T = \frac{G_0}{T^2},$$

(B6)

$$g_n = \frac{G_0}{n_0} \frac{n_0}{T},$$

(B7)

This gradient must be evaluated at the initial feasible point $n_0, T_0, P_0$. The Hessian matrix corresponding to the associated Lagrangian of $\Phi$ is given by:

$$W_{(B4)} = W + \begin{bmatrix} W_{n,n} \Phi_0 & W_{n,T} \Phi_0 & W_{n,P} \Phi_0 \\ W_{T,n} \Phi_0 & W_{T,T} \Phi_0 & W_{T,P} \Phi_0 \\ W_{P,n} \Phi_0 & W_{P,T} \Phi_0 & W_{P,P} \Phi_0 \end{bmatrix} ,$$

(B9)

where,

$$W_{n,n} \Phi_0 = -\left( \frac{\partial G_0}{\partial n^2} \right)_{T,P} - \lambda_0 \left( \frac{\partial^2 \mu_0}{\partial n^2} \right)_{T,P} .$$

(B10)

$$W_{n,T} \Phi_0 = \frac{1}{T} \left( \frac{\partial G_0}{\partial T} \right)_{T,P} + \frac{1}{T} \left( \frac{\partial S_0}{\partial T} \right)_{T,P} + \lambda_0 \left( \frac{\partial \mu_0}{\partial n} \right)_{T,P} .$$

(B11)

$$W_{n,P} \Phi_0 = -\frac{1}{T} \left( \frac{\partial V_0}{\partial n} \right)_{T,P} - \lambda_0 \left( \frac{\partial \mu_0}{\partial n} \right)_{T,P} .$$

(B12)

$$W_{T,T} \Phi_0 = -\frac{2}{T^3} G_0 - \frac{2}{T^2} S_0 + \frac{1}{T} C_{T} P_0 + \lambda_0 \left( \frac{T}{T} \right) \cdot C_{T} P_0 ,$$

(B13)

$$W_{T,P} \Phi_0 = \frac{V_0}{T^2} - \frac{1}{T} \left( \frac{\partial V_0}{\partial T} \right)_{T,P} - \lambda_0 \left( \frac{\partial \mu_0}{\partial n} \right)_{T,P} ,$$

(B14)

and,

$$W_{P,P} \Phi_0 = -\frac{1}{T} \left( \frac{\partial V_0}{\partial P} \right)_{T,P} - \lambda_0 \left( \frac{\partial \mu_0}{\partial n} \right)_{T,P} .$$

(B15)

For use in the algorithm described in Appendix A the matrix defined in Equation (B9) must be evaluated at the initial feasible point.